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Unexpected Photochemical Reactivity of Ruthenium(II) Polypyridine Complexes Induced by a Bis(bidentate) Phosphine

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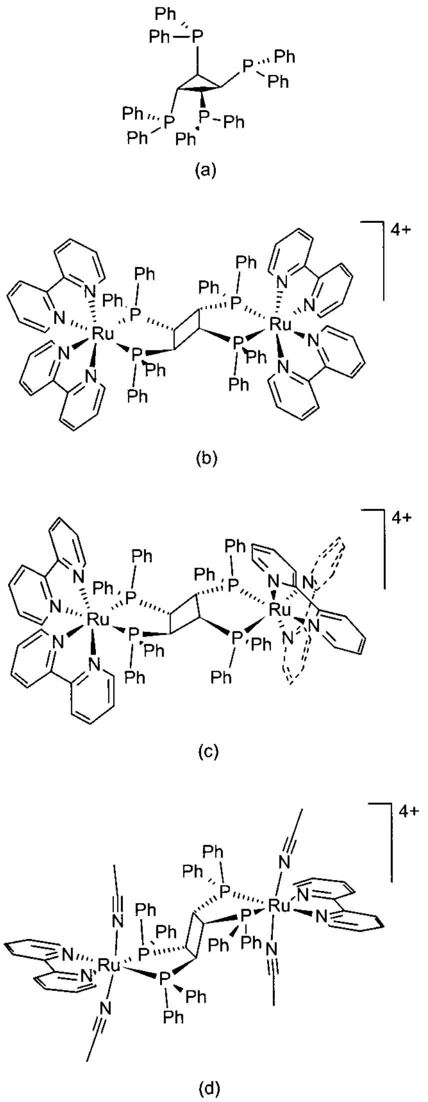
Introduction

Ruthenium(II) polypyridine complexes represent interesting possibilities as components in photochemical and electrochemical devices and potential chemotherapeutics.[1] In this connection, dinuclear Ru(II) complexes bridged by bis(bidentate) ligands have received much attention.[2] In the case of polyphosphine ligands, the large stereochemical control of the ligand and the added electron density on the metal atom contribute to electron rich coordination sites.[3] In this work, we report that the bis(bidentate) phosphine *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane (dppcb)[4] (see Chart 1) prepared in our laboratory only recently and designed as a spacer having two bidentate sets of coordination sites to incorporate molecular components such as $[\mathrm{Ru(bipy)_2}]^{2+}$,[5] where bipy is 2,2′-bipyridine, leads to a completely unexpected photochemical reactivity of the resulting homobimetallic complexes $[\mathrm{Ru_2(dppcb)(bipy)_4}]^{4+}$. To the best of our knowledge, no other phosphine combined with the building block $[\mathrm{M(bipy)_2}]^{2+}$ (M = Ru, Os) shows this reactivity.[6−15] Both diastereoisomerically pure forms of $[\mathrm{Ru_2(dppcb)(bipy)_4}]^{4+}$ undergo a photochemical ligand exchange reaction, where in the presence of acetonitrile $[\mathrm{Ru_2(dppcb)(bipy)_2(MeCN)_4}]^{4+}$ is produced (see Chart 1), and all three complexes have been fully characterized by X-ray diffraction methods. Hitherto, this type of reaction has been mainly restricted to carbonyl complexes of Ru(II),[16−18] $[\mathrm{Ru(bipy)_3}]^{2+}$,[19] Ru(II)−arene systems,[20] and Ru(II) compounds containing Schiff base ligands.[21]

Chart 1. Structure Types: (a) Dppcb, (b) Cation of **1**, (c) Cation of **2**, (d) Cation of **3**



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Experimental Section

Materials. Dppcb was prepared as described earlier.[4] *cis*-[RuCl$_2$(bipy)$_2$]·2H$_2$O and all other reagents were obtained commercially and used without purification. Solvents used for NMR measurements and crystallization purposes were of purissimum grade quality. A Schlenk apparatus and oxygen-free, dry Ar were used in the syntheses of all complexes. Solvents were degassed by several freeze−pump−thaw cycles prior to use.

Physical Measurements. Fourier-mode ^{31}P{^{1}H} and ^{1}H NMR spectra were obtained using Bruker DPX-300 (internal deuterium lock) and Varian Unity Plus 500 (external deuterium lock) spectrometers. Positive chemical shifts are downfield from the standards: 85% H$_3$PO$_4$ for the ^{31}P{^{1}H} resonances and TMS for the ^{1}H resonances.

Syntheses of the Pure Diastereoisomers *meso*-(ΔΛ/ΛΔ)-[Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ (1) or *rac*-(ΔΔ/ΛΛ)-[Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ (2). *cis*-[RuCl$_2$(bipy)$_2$]·2H$_2$O (0.260 g, 0.50 mmol) was suspended in 10 mL of ethylene glycol. Then, dppcb (0.198 g, 0.25 mmol) was added with vigorous stirring. The reaction mixture was stirred at 90 °C for 72 h. To the cooled intense red solution was added NaPF$_6$ (0.840 g, 5.0 mmol) dissolved in 6 mL of H$_2$O. An orange precipitate immediately formed. The resulting mixture was stirred at 90 °C for 48 h. The cooled slurry was filtered. The orange residue was washed with H$_2$O and dried in vacuo. The orange powder was suspended in 10 mL of CH$_2$Cl$_2$, and the mixture was stirred at ambient temperature for 1 h. The slurry was filtered, and the yellow residue was washed with CH$_2$Cl$_2$ and dried in vacuo. A yellow powder was obtained. Yield: 0.248 g (45%). Mp: 313−317 °C. FAB mass spectrum: *m/z* 2054.5 [Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_3^+$, 1909.5 [Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_2^+$. Anal. Calcd for C$_{92}$H$_{76}$F$_{24}$N$_8$P$_8$Ru$_2$: C, 50.2; H, 3.48; N, 5.09. Found: C, 50.0; H, 3.59; N, 4.93.

Compounds **1** and **2** were separated by partial crystallization. The formation of pure single crystals containing only **1** is the thermodynamic driving force. The 10:7 mixture of diastereoisomers (**1**:**2**; this ratio was determined by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy leading to the same result) of [Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ obtained from the preceding description (0.160 g, 0.073 mmol) was dissolved in 8 mL of MeCN, and the solution was filtered. The volume of the solvent was reduced to 4 mL. Gas-phase diffusion of CH$_2$Cl$_2$ into this solution at −20 °C yielded a yellow precipitate containing a 10:3 mixture of diastereoisomers (**1**:**2**; this ratio was again determined by NMR spectroscopy). This procedure was repeated several times, producing a sample of yellow crystals of the pure diastereoisomer **1**. For **2**, all filtrates, which are already enriched with **2**, have been collected. Because crystals from this solution still contain more **1** than **2**, after subsequent recrystallizations, a pure solution containing only **2** was obtained, and out of it, a sample of yellow crystals of the pure diastereomer **2** was crystallized. **1**. Mp: 328−329 °C. ^{31}P{^{1}H} NMR (MeCN): δ 81.2 (d), 75.3 (d), ^{2}J(P,P) 8 Hz, −103.3 (m, PF$_6^-$). ^{1}H NMR (DMF-*d*$_7$): δ (bipy) 9.42 (d, ^{3}J(H,H) = 7.7 Hz, 4H), 8.82 (d, ^{3}J(H,H) = 8.0 Hz, 4H), 8.70 (d, ^{3}J(H,H) = 8.5 Hz, 4H), 8.59 (t, ^{3}J(H,H) = 7.3 Hz, 4H), 8.33 (d, ^{3}J(H,H) = 8.5 Hz, 4H), 8.24 (d, ^{3}J(H,H) = 8.5 Hz, 4H), 8.14 (t, ^{3}J(H,H) = 8.0 Hz, 4H), 8.04 (t, ^{3}J(H,H) = 7.5 Hz, 4H); 6.0−8.1 (m, 40H, Ph); 4.73 (br s, 4H, CH). UV−vis absorption: $\lambda_{\max} = 406$ nm (4×10^{-3} M in MeCN, $\epsilon = 7900$ M^{-1} cm^{-1}). **2**. Mp: 325−327 °C. ^{31}P{^{1}H} NMR (MeCN): δ 77.7 (s), 76.6 (s), −103.9 (m, PF$_6^-$). ^{1}H NMR (DMF-*d*$_7$): δ (bipy) 9.09 (d, ^{3}J(H,H) = 6.0 Hz, 4H), 8.73 (d, ^{3}J(H,H) = 8.5 Hz, 4H), 8.68 (d, ^{3}J(H,H) = 8.0 Hz, 4H), 8.41 (d, ^{3}J(H,H) = 8.0 Hz, 4H), 8.40 (t, ^{3}J(H,H) = 6.0 Hz, 4H), 8.34 (d, ^{3}J(H,H) = 7.5 Hz, 4H), 8.15 (t, ^{3}J(H,H) = 8.0 Hz, 4H), 8.14 (d, ^{3}J(H,H) = 8.0 Hz, 4H); 6.0−8.1 (m, 40H, Ph); 4.56 (br s, 2H, axial CH), 4.26 (br s, 2H, equatorial CH). Because of the folded cyclobutane ring in **2**, in contrast to **1** and **3**, the difference between the absolute values of 111.6(8) and 124.2(7)° of the torsion angles (P(2)−C(2)−C(4)−P(4) and P(1)−C(1)−C(3)−P(3), respectively, see Figure 2b) along the *trans* axes of the cyclobutane ring produces one pair of “axial” hydrogen atoms along C(2)−C(4) and one pair of “equatorial” hydrogen atoms along C(1)−C(3). UV−vis absorption: $\lambda_{\max} = 439$ nm (4×10^{-3} M in MeCN, $\epsilon = 7930$ M^{-1} cm^{-1}).

Single crystals suitable for X-ray structure analyses with the compositions **1**·4.3CH$_2$Cl$_2$ and **2**·2CH$_2$Cl$_2$ were also obtained by this method.

Synthesis of [Ru$_2$(dppcb)(bipy)$_2$(MeCN)$_4$](PF$_6$)$_4$ (3). The 10:7 mixture of diastereoisomers (**1**:**2**) of [Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ obtained as described (0.080 g, 0.036 mmol) was dissolved in 6 mL of MeCN. This solution was irradiated with an unfocused 700 W high-pressure Hg lamp with vigorous stirring for 48 h. The solvent was completely removed, and the orange residue was suspended in 10 mL of CH$_2$Cl$_2$. The slurry was filtered, and the yellow residue was washed with CH$_2$Cl$_2$ and dried in vacuo. A yellow powder was recrystallized from CH$_2$Cl$_2$/MeCN (5:1). Yield: 0.044 g (52% referring to C$_{80}$H$_{72}$F$_{24}$N$_8$P$_8$Ru$_2$·3.4CH$_2$Cl$_2$). Mp: 135 °C dec. IR (KBr, cm^{-1}) ν (CN): 1605 (s). FAB mass spectrum: *m/z* 1906.4 [Ru$_2$(dppcb)(bipy)$_2$(MeCN)$_4$](PF$_6$)$_3^+$, 1679.3 [Ru$_2$(dppcb)(bipy)$_2$(MeCN)$_2$](PF$_6$)$_2^+$. ^{31}P{^{1}H} NMR (MeCN): δ 79.0 (s), −104.0 (m, PF$_6^-$). ^{1}H NMR (MeCN-*d*$_3$): δ (bipy) 8.57 (d, ^{3}J(H,H) = 6.9 Hz, 4H), 8.24 (d, ^{3}J(H,H) = 5.3 Hz, 4H), 7.59 (t, ^{3}J(H,H) = 6.3 Hz, 4H), 7.45 (d, ^{3}J(H,H) = 7.6 Hz, 4H); 5.8−8.0 (m, 40H, Ph); 4.39 (br s, 4H, CH); 2.93 (s, 6H, CH$_3$), 0.96 (s, 6H, CH$_3$). UV−vis absorption: $\lambda_{\max} = 432$ nm (4×10^{-3} M in MeCN, $\epsilon = 6800$ M^{-1} cm^{-1}). Anal. Calcd for C$_{80}$H$_{72}$F$_{24}$N$_8$P$_8$Ru$_2$·3.4CH$_2$Cl$_2$: C, 42.8; H, 3.39; N, 4.79. Found: C, 42.5; H, 3.59; N, 4.75.

Single crystals suitable for an X-ray structure analysis with the composition **3**·3.4CH$_2$Cl$_2$ were obtained by gas-phase diffusion of CH$_2$Cl$_2$ into a solution of **3** in MeCN at −20 °C. The analytical and crystallographic samples are identical. This has been confirmed by several lattice determinations using the diffractometer and by ^{31}P{^{1}H} NMR and FAB mass spectra.

Electrochemical measurements were made with an EG&G PAR model 264A voltameter. Cyclic voltammetry was carried out with a 2-mm platinum-disk working electrode, a platinum-wire counter electrode, and a Ag/AgCl pseudoreference electrode. A solution of 0.05 M Me$_4$NClO$_4$ was used as the electrolyte. Potentials are quoted relative to an SSCE at a scan rate of 100 mV s^{-1} and in degassed MeCN (4×10^{-3} M) of purissimum grade quality at room temperature. The $E_{1/2}$ values for **1** or **2** are identical: Ru$^{\mathrm{II/III}}$ +1.11 V, 1st bipy$^{0/-}$ −1.31 V, 2nd bipy$^{0/-}$ −1.54 V. **3**: Ru$^{\mathrm{II/III}}$ +1.09 V, bipy$^{0/-}$ −1.35 V. The Ru$^{\mathrm{II/III}}$ redox couples for **1**−**3** correspond to two completely overlapping one-electron redox waves.

X-ray Crystallography. Details of the crystals and data collections are summarized in Table 1. In the cases of **1** and **3**, all data were collected on a Siemens P4 diffractometer using ω-scans. Cell refinement and data reduction were done by the software of the Siemens P4 diffractometer, and the empirical absorption corrections were based on ψ-scans of nine reflections, respectively ($\chi = 78$−102°, 360° scans in 10° steps in ψ).[22] In the case of **2**, the data collection was performed on a Nonius Kappa CCD diffractometer using combined ϕ−ω-scans. Cell refinement, data reduction, and the empirical absorption correction were done by Denzo and Scalepack programs.[23]

All structure determination calculations were carried out using SHELXTL NT 5.10 including SHELXS-97[24] and SHELXL-97.[25] Final refinements on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms except for the phenyl rings of **2** and a disordered CH$_2$Cl$_2$ solvent molecule in the case of **2**. The occupancy factors of the CH$_2$Cl$_2$ molecules in **1** and **3** have been refined. Hydrogen atoms were included using a riding model with isotropic U values depending on the U_{eq} of the adjacent carbon atoms. Table 2 contains selected bond distances and bond angles of **1**, **2**, and **3**.

Results and Discussion

Synthesis and Chemical Properties. The syntheses of the pure diastereoisomers *meso*-(ΔΛ/ΛΔ)-[Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ (**1**) and *rac*-(ΔΔ/ΛΛ)-[Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ (**2**) are further examples that, more and more frequently, diastereoisomerically

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Table 1. Crystallographic Data for *meso*-(ΔΛ/ΛΔ)-$[Ru_2(dppcb)(bipy)_4](PF_6)_4$ (**1**), *rac*-(ΔΔ/ΛΛ)-$[Ru_2(dppcb)(bipy)_4](PF_6)_4$ (**2**), and $[Ru_2(dppcb)(bipy)_2(MeCN)_4](PF_6)_4$ (**3**)

	1	**2**	**3**
formula	$C_{92}H_{76}F_{24}N_8P_8Ru_2 \cdot 4.3CH_2Cl_2$	$C_{92}H_{76}F_{24}N_8P_8Ru_2 \cdot 2CH_2Cl_2$	$C_{80}H_{72}F_{24}N_8P_8Ru_2 \cdot 3.4CH_2Cl_2$
fw	2566.40	2369.36	2340.11
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	12.463(2)	13.0220(6)	12.965(4)
b, Å	13.271(2)	14.4990(6)	13.044(4)
c, Å	17.795(2)	27.283(1)	16.528(4)
α, deg	95.48(1)	76.251(3)	68.71(1)
β, deg	92.19(1)	86.730(2)	79.91(1)
γ, deg	115.06(1)	77.422(2)	71.95(1)
V, Å^3	2643.9(7)	4883.4(4)	2470.0(12)
Z	1	2	1
D(calc), Mg m^{-3}	1.612	1.611	1.573
temp, K	293	213	213
$R(F)^a$	0.0477	0.0586	0.0492
$R(wF^2)^a$	0.1096	0.1419	0.1283
GOF	0.982	1.038	1.048

[a] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o,0)]/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *meso*-(ΔΛ/ΛΔ)-$[Ru_2(dppcb)(bipy)_4](PF_6)_4$ (**1**), *rac*-(ΔΔ/ΛΛ)-$[Ru_2(dppcb)(bipy)_4](PF_6)_4$ (**2**), and $[Ru_2(dppcb)(bipy)_2(MeCN)_4](PF_6)_4$ (**3**)

Compound **1**	
Ru(1)−P(1)	2.3406(11)
Ru(1)−P(2)	2.3154(11)
Ru(1)−N(1)	2.100(4)
Ru(1)−N(2)	2.121(4)
Ru(1)−N(3)	2.127(4)
Ru(1)−N(4)	2.097(4)
P(1)−Ru(1)−P(2)	86.50(4)
N(1)−Ru(1)−N(2)	77.67(15)
N(3)−Ru(1)−N(4)	77.54(15)
Compound **2**	
Ru(1)−P(1)	2.321(3)
Ru(1)−P(2)	2.355(3)
Ru(2)−P(3)	2.324(3)
Ru(2)−P(4)	2.348(3)
Ru(1)−N(1)	2.086(8)
Ru(1)−N(2)	2.125(8)
Ru(1)−N(3)	2.112(9)
Ru(1)−N(4)	2.128(9)
Ru(2)−N(5)	2.111(8)
Ru(2)−N(6)	2.112(9)
Ru(2)−N(7)	2.120(10)
Ru(2)−N(8)	2.092(9)
P(1)−Ru(1)−P(2)	86.50(10)
P(3)−Ru(2)−P(4)	86.57(10)
N(1)−Ru(1)−N(2)	76.8(3)
N(3)−Ru(1)−N(4)	77.8(4)
N(5)−Ru(2)−N(6)	77.7(4)
N(7)−Ru(2)−N(8)	76.4(4)
Compound **3**	
Ru(1)−P(1)	2.3434(10)
Ru(1)−P(2)	2.3285(9)
Ru(1)−N(1)	2.169(3)
Ru(1)−N(2)	2.171(3)
Ru(1)−N(1A)	2.033(3)
Ru(1)−N(1B)	2.037(3)
P(1)−Ru(1)−P(2)	82.82(3)
N(1)−Ru(1)−N(2)	76.87(10)
N(1A)−Ru(1)−N(1B)	171.00(10)

pure complexes are prepared in order to study the effect of multiple chiral centers.[1] Because of the interest that octahedral Ru(II) complexes have generated as a consequence of their potential as molecular electronics components, the development of a new, easily applicable synthesis of such compounds is a desirable challenge.[26] In this respect, the facile synthesis of $[Ru_2(dppcb)(bipy)_2(MeCN)_4](PF_6)_4$ (**3**) in good quantum yield, eq 1, represents the unique possibility of the preparation of

$$\textit{meso-}\text{ or }\textit{rac-}[Ru_2(dppcb)(bipy)_4](PF_6)_4 \xrightarrow{h\nu,\ MeCN} [Ru_2(dppcb)(bipy)_2(MeCN)_4](PF_6)_4 + 2bipy \quad (1)$$

highly functionalized Ru(II) complexes containing a polyphosphine. After a "dark control" of the reaction leading from **1** or **2** to **3**, we have not found any trace of **3**, and thus, this reaction only proceeds photochemically. For purposes of comparison, the known compound $[Ru(cis\text{-}dppen)(bipy)_2](PF_6)_2$[14] was prepared, where *cis*-dppen is *cis*-1,2-bis(diphenylphosphino)ethene. Because of its rigid backbone, *cis*-dppen resembles one-half of dppcb. A solution of this complex in MeCN was irradiated under the same conditions as **1** or **2**. After 14 days, the $^{31}P\{^1H\}$ NMR signal at 67.7 corresponding to $[Ru(cis\text{-}dppen)(bipy)_2](PF_6)_2$ is still present as the main component (>90%). Furthermore, the $^{31}P\{^1H\}$ NMR peaks belonging to the main products of this irradiation are located in the region 20−30, typical of phosphine oxides. Thus, no photochemical reaction comparable to the formation of **3** from **1** or **2** is observed for $[Ru(cis\text{-}dppen)(bipy)_2](PF_6)_2$.

Compared with diphosphines, the bis(bidentate) ligand dppcb exerts a steric and not an electronic effect on the $[Ru(bipy)_2]^{2+}$ fragment. This is confirmed by a study of $\nu(C{\equiv}N)$ in the infrared spectra of a series of complexes of the type $[Pd(CN)_2(L{-}L)]$, where L−L is a diphosphine, and of $[Pd_2(CN)_4(dppcb)]$.[33] Though $\nu(C{\equiv}N)$ is very sensitive to electronic effects, the influence of different diphosphines including *cis*-dppen or of dppcb on a variation of $\nu(C{\equiv}N)$ is negligible. This means that the first occurrence of a well-behaved photochemical reaction

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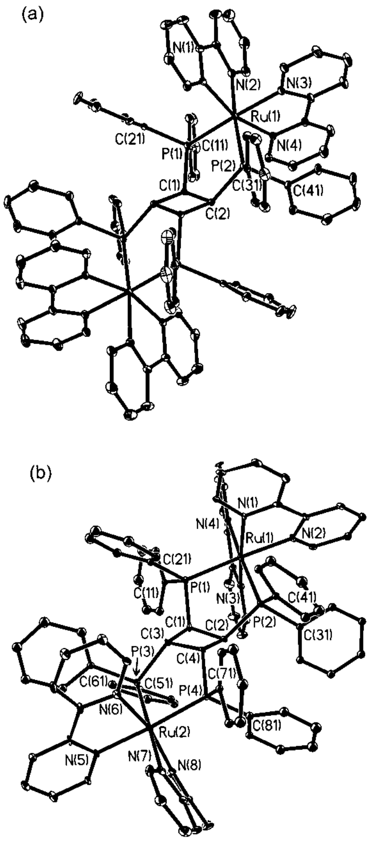

Figure 1. (a) View of the cation of *meso*-[Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ (**1**). (b) View of the cation of *rac*-[Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ (**2**). The atom labeling schemes are shown. Hydrogen atoms are omitted for clarity.

for the combination of a phosphine with the building block $[Ru(bipy)_2]^{2+}$ is due to the steric nature of dppcb.

Comparable to *cis*-$[Ru(bipy')(bipy'')(MeCN)_2]^{2+}$, where bipy′ and bipy″ are different bipy derivatives,[26] **3** is a highly versatile intermediate containing four easily replaceable MeCN ligands. Interestingly, both diastereoisomeric forms **1** and **2** show the same reactivity, producing **3** when irradiated in MeCN, because during the growth of the $^{31}P\{^1H\}$ NMR peak characteristic of **3** the ratio of 10:7 for **1**:**2** is maintained. Furthermore, also the pure diastereomers **1** or **2** react in the same way under the same reaction conditions.

Structures of *meso*-(ΔΛ/ΛΔ)-[Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ (1) and *rac*-(ΔΔ/ΛΛ)-[Ru$_2$(dppcb)(bipy)$_4$](PF$_6$)$_4$ (2). X-ray structure analyses of two diastereoisomeric forms of dinuclear Ru(II) or Os(II) complexes containing polypyridyl ligands are rare,[5] where in this work the first crystallographic characterization of two diastereoisomeric forms of a dinuclear Ru(II) complex containing polypyridyl ligands and phosphines is presented. *meso*-(ΔΛ/ΛΔ)-$[Ru_2(dppcb)(bipy)_4]^{4+}$ is located on a center of symmetry leading to two identical coordination environments, whereas *rac*-(ΔΔ/ΛΛ)-$[Ru_2(dppcb)(bipy)_4]^{4+}$ shows two slightly different Ru(II) centers (Figure 1). Comparable to the case of Ru(II) compounds having 2-phenyl substituted phenanthroline ligands,[27] the phenyl rings of the two forms of $[Ru_2(dppcb)(bipy)_4]^{4+}$ show π-stacking interactions with adjacent coordinated 2,2′-bipyridyl ligands representing the intriguing opportunity for interligand communication. In **1**, a π-stacking alignment of the bipy ligand containing N(4) and the phenyl ring with C(41) as the first atom can clearly be seen. This leads to the shortest interaction between these groups N(4)···C(41) of 2.940 Å. This steric crowding produces van der Waals contacts between the two coordination environments of **1**: the shortest distances between the phenyl rings attached to the two different phosphorus atoms along the *trans* axis of the cyclobutane ring are 3.010 and 3.102 Å. In **2**, π-stacking alignments of the bipy ligand containing N(4) and the phenyl ring with C(11) as the first atom and between the analogous groups containing N(5) and C(61) are clearly present (Figure 1). Both alignments lead to comparable shortest van der Waals contacts of 2.768 and 2.781 Å, respectively. As in the case of **1**, this "steric pressure"[3] produces interactions between the two coordination environments of **2**: the shortest distances between phenyl rings attached to P(1) or P(3) along the corresponding *trans* axis of the cyclobutane ring are 2.850 and 2.929 Å. All these intramolecular contact distances in **1** and **2** are much shorter than the van der Waals distance between two aromatic rings of about 3.5 Å.[27] Via the process of mechanical coupling,[28] where this effect refers to the energy terms associated with bond stretches, bond angle bends, torsional deformations, van der Waals interactions, and electrostatic interactions, these π-stacking interactions lead to conformational changes such as differences in cyclobutane ring folding between the diastereoisomers of $[Ru_2(dppcb)(bipy)_4]^{4+}$. Also, in the case of [Ru(binicotinic acid)(bipy)$_2$](PF$_6$), an allosteric manipulation has been observed that alters the geometry of the binicotinic acid ligand in such a way as to affect its electronics.[29] As a consequence, several bipy ligands in **1** and **2** are twisted or bowed (Figure 1), which are the two categories of bipy distortions.[30,31] The twist angles are typical of the usual range 0−31° found for a survey of comparable structures.[32] Because of the disappearance of steric stress, the twist angle of bipy in **3** is 0.

Figure 2 shows that the strain of the five-membered rings produced by chelating dppcb is partly released by "envelope"-folding. These "envelope"-foldings are present in the solid state as well as in solution at least on the NMR time scale. The corresponding folding angles are 174.1° for **1** and 160.9 and 162.2° for **2**, respectively. For **1**, this folding angle is the dihedral angle between the least-squares planes through the atoms P(1)−C(1)−C(2)−P(2) and P(1)−Ru(1)−P(2), respectively (see Figure 2a). The corresponding angles for **2** and **3** are defined in an analogous manner (see Figures 2b and 3b). However, in both cases **1** and **2**, the direction of the folding is away from the cyclobutane rings, which is in contrast to the homobimetallic complexes of dppcb with Pd(II), Pt(II), and Hg(II).[4,33−36] Because of crystallographic constraints produced by the center of symmetry, the cyclobutane ring is completely planar in **1**, whereas the folding angle of the cyclobutane ring in **2** is 169.7° (Figure 2). In **1** and **2**, the Ru−N bond lengths and N−Ru−N chelate angles are located within the usual ranges (Table 2).[27,31,37] Within statistical significance, the P−Ru−P chelate angles are identical in **1** and **2** and typical of the range for chelating phosphines.[4,33,34,36,38−42]

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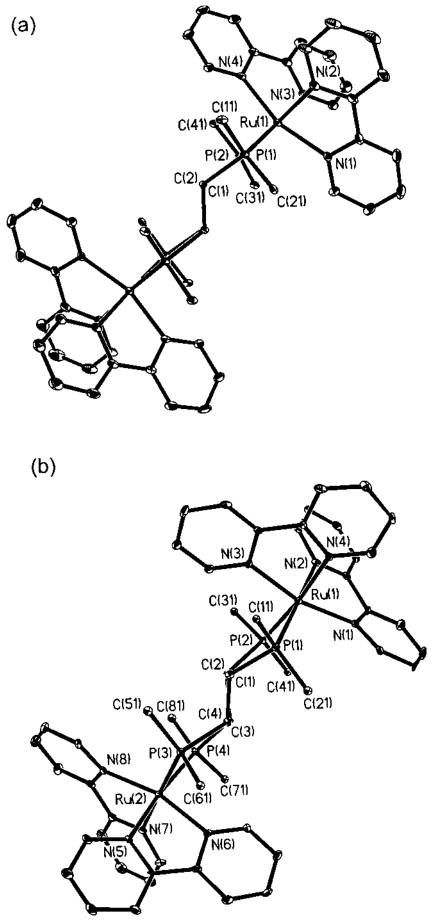

Figure 2. (a) View of the cation of *meso*-$[Ru_2(dppcb)(bipy)_4](PF_6)_4$ (**1**) with the cyclobutane plane perpendicular to the projection plane. (b) View of the cation of *rac*-$[Ru_2(dppcb)(bipy)_4](PF_6)_4$ (**2**) with the cyclobutane plane perpendicular to the projection plane. For clarity, only the first atoms of the phenyl rings and no hydrogen atoms are shown.

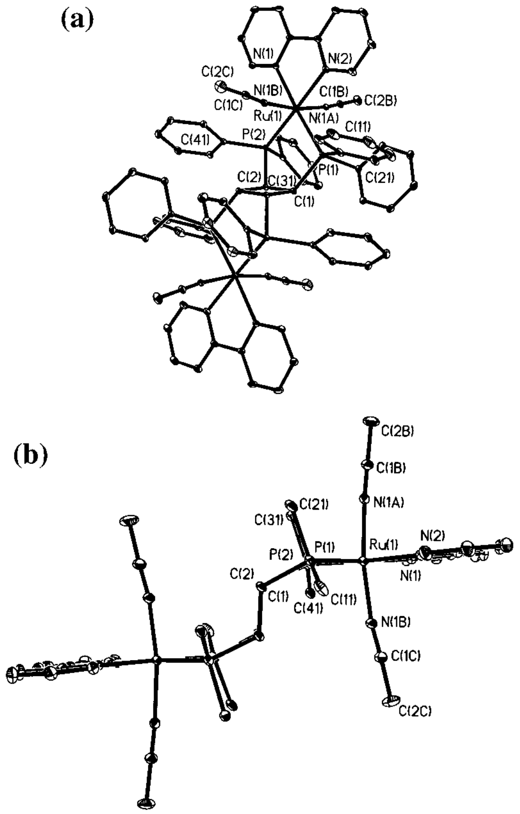

Figure 3. (a) View of the cation of $[Ru_2(dppcb)(bipy)_2(MeCN)_4](PF_6)_4$ (**3**) showing the atom labeling scheme. Hydrogen atoms are omitted for clarity. (b) View of the cation of $[Ru_2(dppcb)(bipy)_2(MeCN)_4](PF_6)_4$ (**3**) with the cyclobutane plane perpendicular to the projection plane. For clarity, only the first atoms of the phenyl rings and no hydrogen atoms are shown.

Structure of $[Ru_2(dppcb)(bipy)_2(MeCN)_4](PF_6)_4$ (3). $[Ru_2(dppcb)(bipy)_2(MeCN)_4]^{4+}$ is located on a center of symmetry producing two identical coordination environments (Figure 3). Because of the release of steric strain as a consequence of the loss of two bipy ligands in **3** compared with **1** or **2**, no short intramolecular contacts are present in **3**. Furthermore, it can clearly be seen that the strain of the five-membered rings produced by chelating dppcb is again diminished by "envelope"-folding. The corresponding folding angle is 155.0°. However, in contrast to **1** and **2**, the direction of the folding is toward the cyclobutane ring in **3**. The cyclobutane ring is completely planar in **3** because of the center of symmetry. The Ru−N bond lengths for coordinated bipy in **3** are significantly larger than in **1** and **2**, because in **3** both N atoms of bipy are located in *trans* positions with respect to the P atoms, which exert high *trans* influences (Table 2). The N−Ru−N and P−Ru−P chelate angles in **3** are again within the usual ranges.[4,27,31,33,34,36−42] The octahedral coordination in **3** is distorted, where the MeCN ligand containing N(1B) is tilted away from the cyclobutane ring (Figure 3b).

Origin of the Unexpected Photochemical Reactivity of $[Ru_2(dppcb)(bipy)_4]^{4+}$. In the crystal structures of **1**−**3**, no significant intermolecular contacts below 3.5 Å have been observed. This means that as a first approximation the forces on the molecule in solution are of the same order as those in the solid.[43] Indeed, the diastereoisomeric forms **1** and **2** show two different pairs of $^{31}P\{^1H\}$ NMR signals in solution. This twinning of the NMR peaks stems from the fact that the process of mechanical coupling[28] is also present in solution, leading to one type of Ru(II) coordination environment in **1** and another type in **2**. To the best of our knowledge, **1** and **2** are the first examples, where a polyphosphine induces the process of mechanical coupling in the solid state as well as in solution.

Because of the folding of the cyclobutane ring in the "free" ligand dppcb,[4] the difference in $^{31}P\{^1H\}$ chemical shifts is 14 ppm between the axial and equatorial diphenylphosphino groups, respectively. This produces a $^3J(P,P)_{cis}$ coupling of 99 Hz. Because of diastereotopicity, the differences in $^{31}P\{^1H\}$ chemical shifts are 5.9 ppm in **1** and 1.1 ppm in **2**, where the corresponding $^3J(P,P)_{cis}$ couplings are 8 Hz in **1** and 0 Hz in **2**. Obviously, the magnitudes of the $^3J(P,P)_{cis}$ couplings dramatically increase with increasing differences in $^{31}P\{^1H\}$ chemical shifts.

The photochemical induction of eq 1 is well established: after irradiation, conversion from the initially populated ^{3}MLCT state to the substitutionally labile ^{3}LF state occurs.[13,16,17,19,27,44] The directions of the "envelope"-foldings of all five-membered rings containing four atoms of chelating dppcb and Ru(II), respectively, are reversed during the photochemical reaction leading

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from **1** or **2** to **3** (Figures 2, 3b). As a consequence, all three subunits of the cations of **1** or **2** consisting of dppcb and two metal centers, respectively, are turned around like a switch when **3** is formed. Because shifting of subunits relative to each other is a very common mechanism for allostery, this effect could be tentatively assigned to an allosteric interaction.

The labile *trans* axial MeCN sites in **3** are suitable for subsequent linear chain construction.[45,46] A replacement of the four MeCN ligands by different groups could lead to asymmetrical ligand environments, which have been found to be important for photoinduced electron and energy transfer.[47] The introduction of appropriate donor and acceptor units on the Ru(II) center can improve the lifetime of the excited state, resulting in a much longer and more efficient storage of energy.[48] Further work on this is in progress.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for *meso*-(ΔΛ/ΛΔ)-[$\mathrm{Ru_2(dppcb)(bipy)_4](PF_6)_4$ (**1**), *rac*-(ΔΔ/ΛΛ)-[$\mathrm{Ru_2(dppcb)(bipy)_4](PF_6)_4$ (**2**), and [$\mathrm{Ru_2(dppcb)(bipy)_2(MeCN)_4](PF_6)_4$ (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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