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Pairing of Propellers: Dimerization of Octahedral Ruthenium(II) and Osmium(II) Complexes of Eilatin via $\pi-\pi$ Stacking Featuring Heterochiral Recognition

Dalia Gut, Amira Rudi, Jacob Kopilov, Israel Goldberg, and Moshe Kol*

Contribution from The School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel

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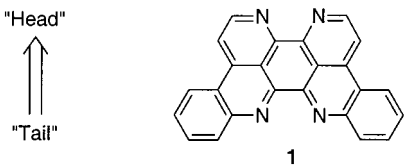
Abstract: Five octahedral eilatin complexes of the type $[M(L-L)_2(eilatin)]^{2+}$ (M = Ru, Os; L−L = bipyridyl-type ligands) were synthesized, and their dimerization via $\pi-\pi$ stacking was studied by crystallography and ^{1}H NMR techniques. The X-ray structures of these racemic complexes were solved and revealed that the eilatin complexes are organized as discrete dimers in which the eilatin residues of each complex are stacked in centrosymmetric packing. Chemical shift dependence on concentration in the ^{1}H NMR spectra support fast dimer−monomer equilibrium, and the structures of the dimers in acetonitrile solution are proposed to be analogous to their solid-state structures. Dimerization constants in acetonitrile were measured for the five racemic eilatin complexes that exhibit different structural parameters, as well as for the two enantiomeric forms of one of these complexes. They were found to be independent of the metal (Ru vs Os), strongly dependent on the steric effects introduced by the L−L ligands (2,2′-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, and 2,2′-biquinoline), and dependent on the optical purity of the complexes. A clear preference for heterochiral over homochiral dimer formation was demonstrated. This is the first report of chiral recognition in solution, exhibited by simple chemical systems held solely by π-stacking interactions.

Introduction

The role of attractive interactions between aromatic units in the assembling of supramolecular architectures has been drawing considerable attention.[1] These interactions have been thoroughly investigated in relation to diverse topics in biological and chemical systems, including the stabilizing interaction between base pairs in the double helical DNA,[2] crystal engineering,[3] the stacking of porphyrin units,[1a,4] and the intercalation of metal complexes into DNA.[5] Recently, several reports described the aggregation or discrete dimer formation due to stacking interactions of simple chemical systems in solution.[6] However, crystallographic data that may shed more light on the geometrical arrangement of such aggregates is limited.



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Eilatin (**1**), a planar heptacyclic aromatic alkaloid that was isolated from the Red Sea purple tunicate *Eudistoma sp*[7] and found to exhibit a strong anticancer reactivity,[8] is currently prepared according to a biomimetic synthesis.[9] It has two distinct potential binding sites for metals: a bipyridyl-type "head" and a biquinolyl-type "tail". We have recently shown[10] that eilatin selectively binds through its less hindered binding site in a "sterically demanding" octahedral environment, in the synthesis of two mononuclear ruthenium(II) complexes: $[Ru(bpy)_2(eilatin)][PF_6]_2$ (**2**) (bpy = 2,2′-bipyridine) and $[Ru(phen)_2$-

* Corresponding author. E-mail: moshekol@post.tau.ac.il.

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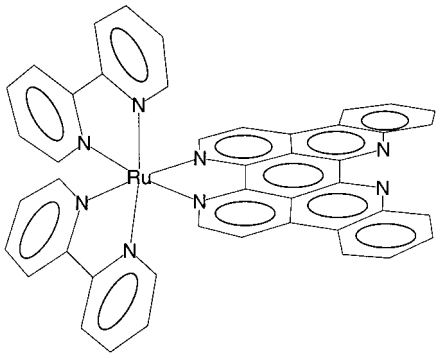
(eilatin)][PF_6]$_2$ (**3**) (phen = 1,10-phenanthroline).



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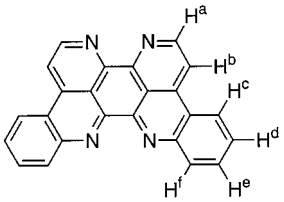
These complexes tend to aggregate in solution via stacking interaction, which seems to involve only the extended π-surfaces of the eilatin moieties, as evident from preliminary ^{1}H NMR studies.[10] In the current work, we set out to determine the factors that affect the directionality and magnitude of the stacking interactions in octahedral eilatin complexes, which may be employed in the construction of supramolecular arrays. The effects of the metal, the steric hindrance about the metal center, and most intriguingly, the homo-/heterochirality of these C_2-symmetrical complexes were studied. Although both π-stacking interactions and chiral recognition have significant roles in biological systems, this is the first attempt, to our knowledge, to demonstrate chiral recognition based solely on a π-stacking interaction in simple chemical systems.

Results and Discussion

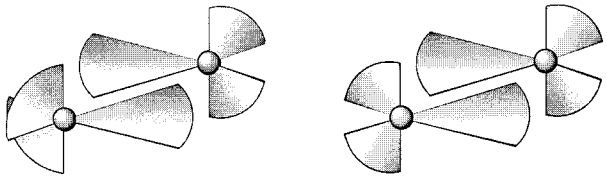
Initial ^{1}H NMR characterization of the two eilatin complexes, **2** and **3**, exhibited a strong dependence of the chemical shifts of several protons on concentration and temperature. For example, upon warming a solution of **3** in CD_3CN a strong downfield shift of all the eilatin protons, excluding the "head" H^a-protons, was observed, whereas the protons of the phen units were hardly affected (Table 1).[11] A similar behavior was observed for complex **2**. These findings suggest that in solution, an aggregation of the complexes via π-stacking interactions between the eilatin moieties takes place, while the smaller L−L ligands are not involved. The aggregates are in fast equilibrium with the monomers on the NMR time scale. As the temperature is lowered or the total complex concentration raised, the ratio of aggregate to monomer increases hence the variation in the chemical shifts.

We propose the following illustrative model for the description of the π-stacking interactions between the eilatin complexes. These octahedral complexes have a C_2 symmetry, and may be envisioned as a three-bladed propeller, where one blade (the eilatin fragment) is significantly larger than the others (the L−L ligands, Figure 1). The π-stacking interaction takes place by the overlapping of two large blades, from two propeller units (complexes). The two smaller blades of each propeller play an important role in directing the formation of well-defined arrays: (a) they direct a face-to-face overlap via the tail ends as well as restricting its extent by serving as barriers, (b) they encourage the formation of well-defined dimers rather than amorphous aggregates by blocking the space above and below the large blades, and most interestingly, (c) due to the C_2 symmetry of these propellers, the small blades may direct the formation of either homo- ($\Delta-\Delta$ or $\Lambda-\Lambda$) or heterochiral ($\Delta-\Lambda$) dimers.

Table 1. Temperature Effect on the ^{1}H NMR of **3** in CD_3CN, and Proton Assignments



eilatin proton	chemical shift [ppm] 298 K	330 K	Phen proton	chemical shift [ppm] 298 K	330 K
H^a	8.05	8.07	H^2	8.70	8.55
H^b	7.94	8.23	H^3	7.84	7.80
H^c	8.25	8.48	H^4	8.69	8.68
H^d	7.81	7.89	H^5	8.34	8.33
H^e	7.70	7.89	H^6	8.34	8.33
H^f	7.35	7.89	H^7	8.72	8.71
			H^8	7.76	7.76
			H^9	8.10	8.11



Δ,Δ Λ,Δ

Figure 1. Schematic representation of interactions between two propeller units: (left) homochiral dimer and (right) heterochiral dimer.

To gain better insight on the solid-state structure and packing arrangement, single crystals of these complexes were grown. Crystals of **2** were grown by the slow diffusion of diethyl ether into an acetonitrile solution of racemic **2**, and crystals of **3** were grown by the slow evaporation of acetonitrile from a solution of racemic **3**. **3** crystallized as a racemate in a triclinic unit cell with a centrosymmetric $P\bar{1}$ space group. As was deduced from the NMR measurements of the complex,[10] **3** is a C_2-symmetrical complex in which the eilatin is bound "head-on" to the Ru(II) center and its "tail" end is uncoordinated. The bond lengths of 2.06 Å between the eilatin nitrogens and the Ru(II) center are typical of a bipyridyl-type ligand.[12] Both the phenanthroline units and the eilatin are not distorted substantially from planarity, indicating that the complex is unstrained. A stereoview of the crystal packing of **3** is shown in Figure 2.

Each centrosymmetric unit cell contains two molecules of the complex with the eilatin moieties stacked face-to-face via the tail ends. The average interplanar separation in the dimer is 3.4 Å, a typical distance for systems held by stacking interactions.[1a] The separation between the eilatin units in adjacent unit cells is large, and may be attributed to the

(11) In a presumed π-stacked dimer, the head H^a-protons of each of the eilatin residues are remote from the π-surface of the other eilatin residue. Therefore, they do not experience any ring current effects from that residue, and their chemical shift is almost unaffected by temperature or concentration. We attribute the 0.15 ppm upfield shift of the H^2 proton of the phenanthroline unit to interactions with one of the "tail" nitrogen atoms of the eilatin unit. In the X-ray structure of **3** the $CH^2\cdots N$ separation in the dimer was found to be 2.55 Å (vide infra).

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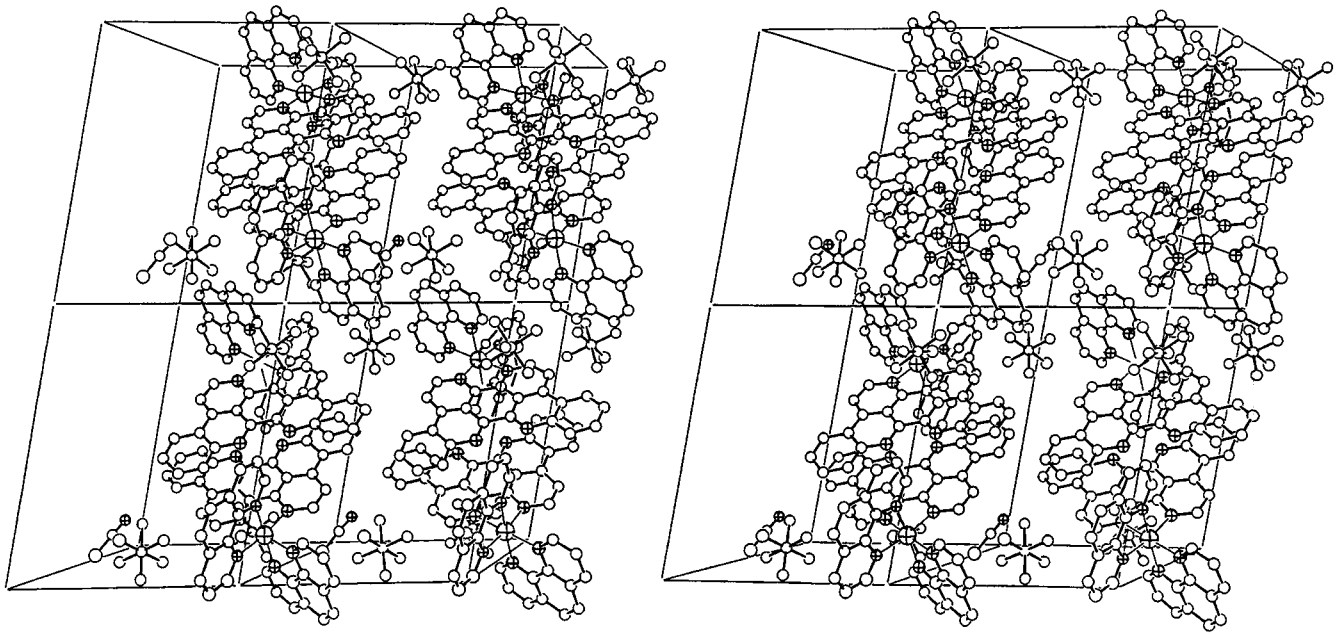

Figure 2. Stereoview of the crystal packing of **3**.

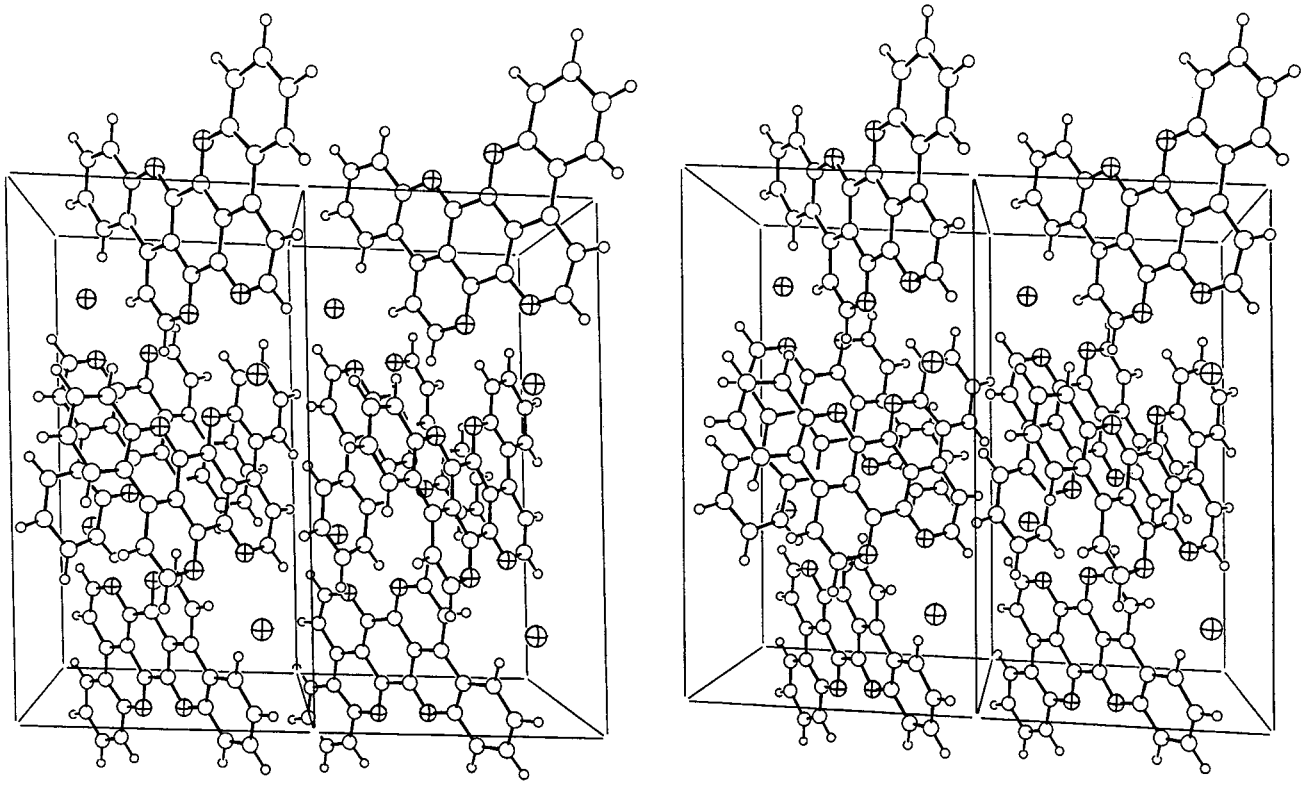

Figure 3. Stereoview of the crystal packing of eilatin.

perpendicular phenanthroline units, which block the space around the eilatin dimers. The X-ray structure of **2** closely resembles that of **3**. In contrast, in the X-ray structure of eilatin, two types of stacking interactions that lead to infinite stacks of dimers were observed (Figure 3).[7] Based on the solid-state structures of **2** and **3** and on the model introduced above, we propose that a very similar aggregation of these complexes, namely, discrete dimer formation, takes place in solution as well.

To assess the factors governing the stacking phenomenon, we measured its magnitude in solution, as a function of the following parameters: (a) the nature of the metal (Ru(II) vs Os(II)); (b) the steric hindrance about the metal center (by varying the size of the "small blades"); and (c) the optical purity of the complex (enantiomerically pure vs racemic). Thus, in addition to **2** and **3**, the following complexes were synthesized: $[Os(bpy)_2(eilatin)][PF_6]_2$ (**4**), $[Ru(neoc)_2(eilatin)][PF_6]_2$ (neoc = 2,9-dimethyl-1,10-phenanthroline) (**5**), $[Ru(biq)_2(eilatin)][PF_6]_2$ (biq = 2,2′-biquinoline) (**6**), and Δ- and Λ-$[Ru(bpy)_2(eilatin)][PF_6]_2$ (Δ-**2** and Λ-**2**, respectively). For the additional racemic complexes (**4**, **5**, and **6**) single crystals

Table 2. Mean Dimerization Constants[14] Measured in CD_3CN at 295 K

compd	K_D [M^{-1}][a]
2	260
3	325
4	310
5	25
6	< 1[b]
Δ-**2**	68
Λ-**2**	71

[a] The mean dimerization constants are an average of the two values calculated independently from proton *b* and proton *c* of the eilatin ligand. See Supporting Information. [b] The chemical shifts of the eilatin protons in **6** exhibited only a slight change over a large concentration range.

suitable for X-ray analysis were obtained, and their structures were solved.

The dimerization constants for the self-association of the eilatin complexes in acetonitrile solutions were determined by utilizing the curve-fitting method described by Horman and Dreux,[13] which relies on the gradual variation in the ^1H NMR chemical shifts as a function of concentration at a constant temperature. This method involves an iterative estimation of the dimerization constant, K_D, by plotting the observed chemical shift (δ_i) of each proton versus the mole fraction of dimer (x_i) present at each concentration (where x_i is calculated from the estimated value of K_D). The most accurate value of K_D is defined as that which yields the best linear relationship between δ_i and x_i.[14] Monomer−dimer equilibrium was assumed as the predominant process in the concentration range in which the measurements were preformed (1−10 mM). At higher concentrations, higher order aggregation could be significant (possibly by interaction between the "smaller blades"). It is important to note that this method was developed for a simple self-association process, and is therefore suitable for determining dimerization constants of the optically pure complexes. However, for the racemic mixtures, both homo- and heterochiral dimerization processes may take place, thus the values obtained are "mean" dimerization constants, defined by:

$$K_{D(mean)} = \frac{[D]}{[M]^2} \quad (1)$$

wherein [D] is the total dimer concentration (homo- *and* heterochiral), and [M] is the total monomer concentration. For the specific case of a racemic mixture (see the Appendix for the derivation of this expression) the mean dimerization constant is a weighted average of the hetero- and homochiral dimerization constants as described by the following equation:

$$K_{D(mean)} = \frac{K_{D(hetero)} + 2K_{D(homo)}}{4} \quad (2)$$

The mean dimerization constants of the eilatin complexes, presented in Table 2, span a wide range of values (from ∼0 to 325 M^{-1}).

The Effect of the Metal on K_D. Complexes **2** and **4**, having an identical ligand environment but a different metal (Ru and Os, respectively), exhibit similar dimerization constants in solution within the accuracy limitations. Assuming that the $\pi-\pi$ stacking interactions between the eilatin moieties depend on the steric effects introduced by the "barrier" bpy units, as well as on the electron density of the eilatin, this similarity is not unexpected, since (a) the similar covalent radii of Ru and Os bring about a similar effect of the "barrier" ligands and (b) although Os is somewhat softer than Ru, this is not expected to have a major effect on the charge distribution of eilatin. Hence, the similarity in the binding constants.

The Effect of the Bulk of the "Small-Blade" Ligands on K_D. The extent of the "large-blades" overlap should be governed by the steric hindrance around the metal center introduced by the L−L ligands ("small blades"): the bulkier the L−L ligand, the lesser the extent of the eilatin overlap, and accordingly, the smaller the dimerization constant. Thus, although phen and bpy differ in their rigidity, it is expected that the dimerization constant of their complexes (**2** and **3**, respectively) will be of the same magnitude, since they both introduce similar steric hindrance about the metal center. This notion is confirmed by the results listed in Table 2: both complexes have a mean dimerization constant of ca. 300 M^{-1}. On the other hand, the introduction of substituents to the 2 and 9 positions of phenanthroline (or 6 and 6′ positions of bipyridine) promotes large steric hindrance about the metal center. Thus, the magnitude of the mean dimerization constant of the neocuproine complex (**5**) is significantly lower than that of **3**, and that of biquinoline (**6**) is very low. The crystal structures of the racemic complexes supported these results. All complexes crystallized as centrosymmetric racemates. In all structures a well-defined discrete dimer is observed, in which the eilatin surfaces of two enantiomers are ca. 3.4 Å apart, consistent with a strong stacking interaction. A crude estimate of the effective overlap between the eilatin planes may be obtained from the distance between the two metal atoms in the unit cell. Interestingly, the intermetallic distances in **2** (11.05 Å), **3** (10.65 Å), and **4** (10.26 Å), which exhibit similar dimerization constants, are quite different. This broad range of distances may be ascribed to different packing arrangements, e.g., different location of the counterions and number and kind of solvent molecules. The intermetallic distances in the two complexes that exhibited lower dimerization constants, i.e., **5** and **6**, were, as expected, longer (11.46 and 11.66 Å, respectively). A comparative view of the packing of the dimers in the crystal is shown in Figure 4.

The Effect of the Homo-/Heterochirality of the Complex on K_D. The complexes considered thus far were racemic mixtures which crystallized as heterochiral dimers. Of course, in solution, both hetero- and homochiral dimers may form. To determine the possible preference for the formation of either a hetero- or a homochiral dimer in solution, we measured the homochiral dimerization constant of **2**, namely, that obtained for an optically pure complex. The two enantiomers of **2** were prepared by the reaction of eilatin with the appropriate optically active building block Δ-/Λ-$[Ru(bpy)_2(py)_2]^{2+}$, with full retention of configuration.[15] The resultant complexes, Δ-**2** and Λ-**2**, respectively, were characterized by circular dichroism measurements, which indicated that these enantiomeric complexes are of identical optical purity (Figure 5).

(13) Horman, I.; Dreux, B. *Helv. Chim. Acta* **1984**, *67*, 754.
(14) An accurate determination of K_D is difficult, since a good linear fit is obtained for a relatively broad range of values. For example, the measurements for proton *b* of eilatin in **2** yielded a dimerization constant of $K_D = 275$ M^{-1} for the best linear fit ($R^2 = 0.9999$). However, a good linear fit ($R^2 > 0.999$) is obtained for the range $160 < K_D < 400$.
(15) Hua, X.; von Zelewsky, A. *Inorg. Chem.* **1995**, *34*, 5791.

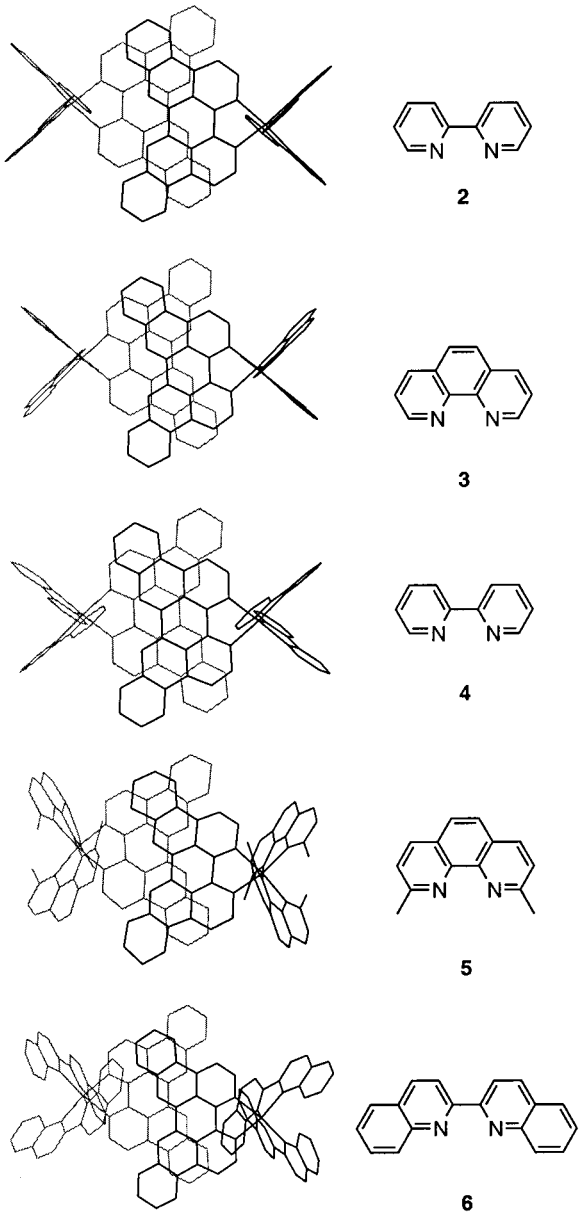

Figure 4. Top view of the dimers formed by compounds **2**, **3**, **4**, **5**, and **6** (top to bottom, respectively) extracted from the X-ray structures, and formulas of the "small blades".

The dimerization constants of Δ-**2** and Λ-**2** in CD_3CN were measured and found to be identical and significantly lower than the dimerization constant measured for racemic **2**. This is demonstrated in the graph of ^1H NMR chemical shifts (of proton *c*) vs concentration for these complexes (Figure 6). According to the Horman and Dreux method, the value of the dimerization constant for the enantiomerically pure complexes was ca. 70 M^{-1}. To obtain a more accurate evaluation of the heterochiral dimerization preference, we imposed an additional condition, namely, that the chemical shifts of a pure monomer should be identical for the racemic and enantiomerically pure complexes (identical δ_0). This resulted in $K_{D(mean)} = 200\ M^{-1}$ and $K_{D(homo)} = 100\ M^{-1}$. To substantiate this ratio the following experiment was conducted: equally concentrated ($(3.40 \pm 0.05) \times 10^{-3}$ M)[16] solutions of Δ-**2** and Λ-**2** in CD_3CN were prepared, and their ^1H NMR spectra were recorded. As expected, the NMR spectra of the enantiomeric complexes overlapped. However,

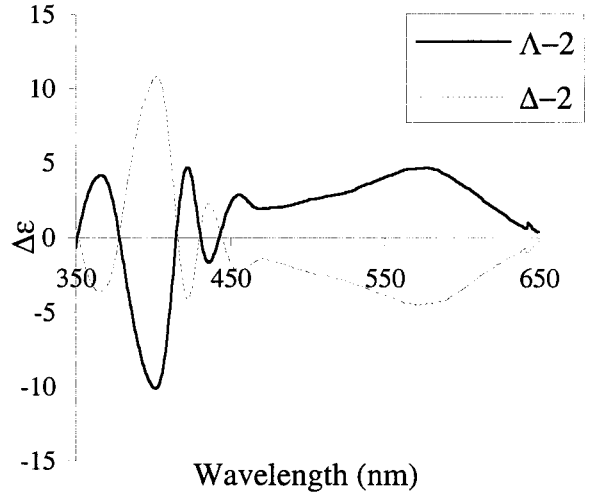

Figure 5. CD spectrum of Δ-**2** and Λ-**2**.

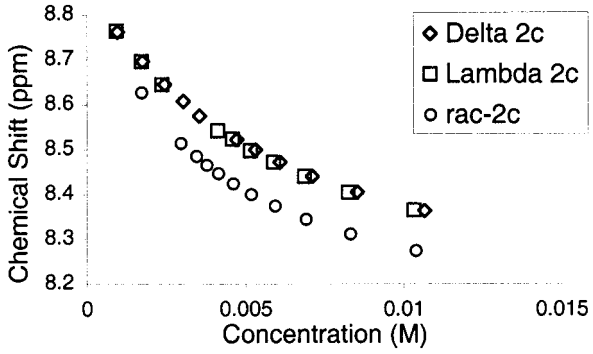

Figure 6. The concentration dependence of ^1H NMR chemical shifts of proton *c* in *rac*-**2**, Δ-**2**, and Λ-**2**.

these spectra were different from the spectrum of racemic **2** of the same concentration, and almost superimposable on a spectrum of racemic **2** at a concentration of $(1.58 \pm 0.05) \times 10^{-3}$ M, thus supporting a lower dimer-to-monomer ratio. Then, 0.50 mL of Λ-**2** was added to the NMR tube containing 0.50 mL of Δ-**2**, and the spectrum of the consequent solution was recorded. The resultant spectrum was equivalent to a spectrum obtained for the racemic complex of a similar concentration. Namely, *upon racemization of 2, without changing the total complex concentration, the dimer-to-monomer ratio increases*. These results indicate that although homochiral dimers do form in solution, there is a clear tendency to form heterochiral dimers in racemic mixtures of **2**. Complexes **3** and **4**, having similar "small blades", are expected to exhibit a similar behavior.

The dimerization constants appearing in Table 2 for the racemic complexes are mean dimerization constants, which include contributions from both homochiral and heterochiral dimers. From these values and from the value of the dimerization constant of the homochiral complexes it is possible to calculate the heterochiral dimerization constant. Assuming that the limiting chemical shifts for the homochiral and the heterochiral dimers are similar, then for a racemate it follows that $K_{D(hetero)} = 4K_{D(mean)} - 2K_{D(homo)}$ (for further details see the Appendix). It then follows that $K_{D(hetero)}$ of **2** is 600 M^{-1}, namely 6 times

(16) The specified concentrations of the solutions of Δ-**2** and Λ-**2** ($3.40 \pm 0.05 \times 10^{-3}$ M each) were confirmed by diluting 0.5 mL of each solution to 10.0 mL and measuring their UV/vis spectra. The concentration of the complexes calculated from the UV/vis spectra indicated that both solutions are of the correct concentration within the specified range of error.

higher than $K_{D(homo)}$. Therefore, in solution, the concentration of the heterochiral dimer is about 3 times higher than the concentration of the sum of the $\Delta\Delta$ and the $\Lambda\Lambda$ homochiral dimers. The ratio of ca. 3:1 in favor of a heterochiral dimer is substantial, when taking into account the nondirectional nature of stacking interactions and the "peripheral" site of the C_2 center.[17] To the best of our knowledge, this is the first description of chiral-recognition in dimerization reactions in solution based solely on π-stacking interactions.

Conclusions

We have shown that the octahedral mono-eilatin complexes tend to form discrete dimers held by stacking interactions in the solid state and in solution. The formation of these dimers is mainly controlled by the steric hindrance introduced by the L−L ligands. In racemic solutions, a heterochiral dimer was found to be strongly favored over a homochiral dimer. We are currently investigating the application of these stacking interactions in the construction of more elaborate supramolecular architectures.

Experimental Section

Materials. Eilatin,[9] *cis*-$[Ru(phen)_2Cl_2]$,[18] *cis*-$[Ru(neoc)_2Cl_2]$,[18] *cis*-$[Ru(biq)_2Cl_2]$,[18] and *cis*-$[Os(bpy)_2Cl_2]$[19] were synthesized according to literature procedures. The enantiomers of $[Ru(bpy)_2(py)_2][Cl_2]$ were synthesized[20] and resolved[15] into the Δ- and Λ-optical isomers according to literature procedures. All other chemicals and solvents used were of reagent grade and used without further purification. All the reactions were perfomed under an argon atmosphere. The syntheses of the optically active complexes were carried out in the dark.

Instrumentation. The initial characterization of the complexes, including assignments of all the atoms, by 1D and 2D ^{1}H and ^{13}C NMR techniques was achieved with a Bruker ARX-500 spectrometer, using the residual protons of the solvent (DMSO-d_6) as an internal standard at δ 2.5 ppm. The ^{1}H NMR dimerization experiments were performed with a Bruker AMX-360 spectrometer, and with a Bruker Avance 400 spectrometer, using the residual protons of the solvent (CD_3CN) as an internal standard at δ 1.93 ppm. UV/vis absorption spectra in acetonitrile were measured with a Kontron UVIKON 931 UV/vis spectrometer. FABMS were obtained on a VG-AutoSpec M250 mass spectrometer, in a *m*-nitrobenzyl alcohol matrix. CD spectra in acetonitrile were measured on an Aviv model 202 circular dichroism spectrometer.

NMR Dimerization Experiments. Typical concentrated stock solutions of the complexes (0.010−0.015 M) were prepared by accurately weighing out known amounts of the dried complexes (15.0−20.0 mg) and dissolving them in an accurately measured volume of CD_3CN (1.00−1.50 mL). The concentration dependence of the chemical shifts of all complexes was studied at 295.5(±0.5) K. In a typical experiment, 50 μL aliquots of the stock solution were added to a NMR tube initially containing 0.50 mL of CD_3CN, and 100 μL aliquots of CD_3CN were added to a NMR tube initially containing 0.40 mL of the concentrated stock solution to obtain a wide concentration range. The NMR spectrum was recorded after a 5 min thermal equilibration time, following each addition. The NMR experiments of all the racemic complexes and those of Δ-**2** were performed on a 360 MHz spectrometer. These results were substantiated by repeating the NMR experiments of racemic-**2** and Δ-**2** and performing the NMR experiments of Λ-**2** employing a 400 MHz spectrometer.

Synthesis. $[Ru(bpy)_2(eilatin)][PF_6]_2$ (2): *rac*,*cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (30 mg, 0.058 mmol) and eilatin (23 mg, 0.065 mmol) were dissolved in 10 mL of a 4:1 methanol−water solution and refluxed for 5 h. The resultant green reaction mixture was cooled and the solvent was evaporated. The crude solid was washed several times with 3 mL of chloroform to remove excess ligand. The green complex was then dissolved in a minimal amount of methanol and was precipitated by the addition of a saturated aqueous solution of KPF_6. The mixture was filtered, and the complex was washed twice with 5 mL of H_2O. The complex was purified by recrystallization from acetonitrile/ether. Typical yield: 95%. ^{1}H NMR ($(CD_3)_2SO$, 298 K) δ 8.94 (d, J = 8.2 Hz, 1H, H^3), 8.88 (d, J = 8.1 Hz, 1H, H$^{3'}$), 8.77 (d, J = 7.9 Hz, 1H, H^c), 8.74 (d, J = 6.0 Hz, 1H, H^b), 8.29 (t, J = 7.9 Hz, 1H, H^4), 8.17 (m, 2H, H^f, H$^{4'}$), 8.14 (d, J = 6.1 Hz, 1H, H^a), 8.07 (t, J = 7.7 Hz, 1H, H^e), 7.99 (m, 2H, H^d, H$^{6'}$), 7.88 (d, J = 5.5 Hz, 1H, H^6), 7.69 (t, J = 6.9 Hz, 1H, H^5), 7.43 (t, J = 6.7 Hz, 1H, H$^{5'}$); ^{13}C NMR δ 150.0 (*C*-H$^{6'}$), 148.1 (*C*-H^6), 146.0 (*C*-H^a), 135.2 (*C*-H$^{4'}$), 135.2 (*C*-H^4), 129.8 (*C*-H^e), 128.3 (*C*-H^f), 127.0 (*C*-H^d), 125.0 (*C*-H^5), 124.0 (*C*-H$^{5'}$), 121.5 (*C*-H^3), 121.3 (*C*-H^c), 121.2 (*C*-H$^{3'}$), 118.3 (*C*-H^b); UV−vis [λ_{max}, nm ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1})] 241 (6.8), 286 (7.3), 341 (2.2), 405 sh, 424 (3.3), 460 sh, 583 (1.0); FABMS, 771 [M − 2PF$_6$ + H]$^+$.

Δ-$[Ru(bpy)_2(eilatin)][PF_6]_2$ (Δ-2): Δ-$[Ru(bpy)_2(py)_2][(+)$-*O*,*O*′-dibenzoyl-D-tartrate$]\cdot 12H_2O$ (13 mg, 0.011 mmol) and eilatin (6 mg, 0.017 mmol) were added to 3 mL of a 4:1 ethylene glycol−water solution and heated to 120 °C for 7 h. The resultant green reaction mixture was cooled, diluted with 10 mL of H_2O, and filtered. A saturated aqueous solution of KPF_6 was then added to the filtrate until no more precipitate formed. The mixture was filtered and the crude solid was washed once with H_2O and several times with 3 mL of chloroform to remove excess ligand. The complex was purified by recrystallization from acetonitrile/ether. Typical yield: 80%. Anal. Calcd (found) for $C_{44}H_{28}F_{12}P_2Ru\cdot H_2O$: C, 49.03 (48.70); H, 2.81 (3.07); N, 10.40 (9.91). CD [λ_{max}, nm ($\Delta\epsilon$, cm^{-1}M^{-1})] 232(8.80), 252 (−11.9), 267 (53.6), 290(−110), 366(−3.58), 402(10.9), 422(−4.10), 436(2.25), 455(−2.27), 572(−4.48).

Λ-$[Ru(bpy)_2(eilatin)][PF_6]_2$ (Λ-2): The complex was prepared by the same method described for the Δ-form, using the chiral building block Λ-$[Ru(bpy)_2(py)_2][(-)$-*O*,*O*′-dibenzoyl-L-tartrate$]\cdot 12H_2O$. CD [λ_{max}, nm ($\Delta\epsilon$, cm^{-1} M^{-1})] 232 (−7.74), 252 (12.9), 267 (−55.0), 290 (111), 366 (4.14), 402 (−10.1), 422 (4.69), 436 (−1.72), 456 (2.87), 571 (4.62).

$[Ru(phen)_2(eilatin)][PF_6]_2$ (3): The complex was prepared and purified by the same method described for the bpy analogue, utilizing *rac*,*cis*-$[Ru(phen)_2Cl_2]$ (16 mg, 0.030 mmol) and eilatin (12 mg, 0.037 mmol). The product, a dark green complex, was obtained in 93% yield. Anal. Calcd (found) for $C_{48}H_{28}F_{12}N_8P_2Ru$: C, 52.04 (51.79); H, 2.55 (2.71); N, 10.12 (9.88). ^{1}H NMR ($(CD_3)_2SO-CD_3CN$, 302 K) δ 8.74 (d, J = 8.3 Hz, 1H, H^4), 8.70 (d, J = 8.2 Hz, 1H, H^7), 8.68 (d, J = 8.3 Hz, 1H, H^c), 8.51 (d, J = 6.2 Hz, 1H, H^b), 8.42 (d, J = 5.0 Hz, 1H, H^9), 8.34 (m, 2H, H,^{5} H^6), 8.18 (d, J = 8.3 Hz, 1H, H^f), 8.07 (d, J = 6.1 Hz, 2H, H^a, H^2), 7.98 (t, J = 7.7 Hz, 1H, H^e), 7.91 (t, J = 7.6 Hz, 1H, H^d), 7.75 (t, J = 5.3 Hz, 1H, H^8), 7.74 (t, J = 5.2 Hz, 1H, H^3); ^{13}C NMR δ 150 (*C*-H^2), 150 (*C*-H^9), 147.0 (*C*-H^a), 132 (*C*-H^7), 132(*C*-H^4), 128 (*C*-H^e), 127 (*C*-H^f), 125 (*C*-H^d), 123 (*C*-H^6), 122 (*C*-H^5), 121 (*C*-H^3), 121 (*C*-H^8), 118 (*C*-H^c), 117 (*C*-H^b); UV−vis [λ_{max}, nm ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1})] 224 (5.4), 263 (6.3), 292 (2.9), 341 (1.2), 405 sh, 423 (2.3), 460 sh, 581 (0.7); FABMS, 819 [M − 2PF$_6$ + H]$^+$, 963 [M − PF$_6$]$^+$.

$[Os(bpy)_2(eilatin)][PF_6]_2$ (4): *rac*,*cis*-$[Os(bpy)_2Cl_2]$ (25 mg, 0.043 mmol) and eilatin (17 mg, 0.048 mmol) were dissolved in 3 mL of ethylene glycol and heated to 140 °C for 5 h. The green reaction mixture was cooled, and a saturated solution of KPF_6 was added. The mixture

(17) A possible explanation for the preferred formation of a heterochiral dimer is a reduced steric repulsion in comparison to the homochiral dimer. Interestingly, a homochiral preference was observed for the interactions of the propeller-shaped TRISPHAT anion with $[Ru(bpy)_3]^{2+}$ type complexes. In contrast to the eilatin complexes that interact via π-stacking of the eilatin residues, the TRISPHAT anion is proposed to interact through ion-pairing along its C_3-axis. See: (a) Lacour, J.; Ginglinger, C.; Favarger, F.; Torche-Haldimann, S. *Chem. Commun.* **1997**, 2285. (b) Lacour, J.; Goujon-Ginglinger, C.; Torche-Haldimann, S.; Jordy, J. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3695. (c) Maury, O.; Lacour, J.; Le Bozec, H. *Eur. J. Inorg. Chem.* **2001**, 201.

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was filtered, and the crude green solid was washed first with water and then several times with chloroform to remove excess ligand. The complex was purified by recrystallization from acetonitrile/ether. Typical yield: 80%. Anal. Calcd (found) for $C_{44}H_{28}F_{12}N_8OsP_2$: C, 46.00 (46.30); H, 2.46 (2.70); N, 9.75 (9.48). ^{1}H NMR ($(CD_3)_2SO$, 322 K) δ 8.90 (d, $J = 8.2$ Hz, 1H, H^3), 8.86 (d, $J = 8.3$ Hz, 1H, H^c), 8.79 (d, $J = 8.1$ Hz, 1H, H$^{3'}$), 8.60 (d, $J = 6.5$ Hz, 1H, H^b), 8.47 (d, $J = 8.1$ Hz, 1H, H^f), 8.18(d, $J = 6.5$ Hz, 1H, H^a), 8.09 (t, $J = 7.5$ Hz, 2H, H^e, H^4), 8.00 (t, $J = 7.7$ Hz, 1H, H^d), 7.97 (t, $J = 7.6$ Hz, 1H, H$^{4'}$), 7.77 (d, $J = 5.6$ Hz, 1H, H^6), 7.75(d, $J = 6.0$ Hz, 1H, H$^{6'}$), 7.64 (t, $J = 6.7$ Hz, 1H, H^5), 7.28 (t, $J = 6.6$ Hz, 1H, H$^{5'}$); ^{13}C NMR δ 153.0 (*C*-H$^{6'}$), 151.0 (*C*-H^6), 148.5 (*C*-H^a), 138.5 (*C*-H$^{4'}$), 134.1 (*C*-H,^{4} *C*-H^e), 132.0 (*C*-H^f), 130.1 (*C*-H^d), 129.0 (*C*-H^5), 129.0 (*C*-H$^{5'}$), 125.2 (*C*-H^3), 125.0 (*C*-H^c), 125.0 (*C*-H$^{3'}$), 123.3 (*C*-H^b); UV−vis [λ_{max}, nm ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1})] 242 (5.6), 289 (6.4), 355 (1.9), 418 (2.3), 450 sh, 612 (0.9); FABMS, 860 $[M - 2PF_6 + H]^+$.

[Ru(neoc)$_2$(eilatin)][PF$_6$]$_2$ (5): The complex was prepared and purified by the same method described for the bpy analogue, utilizing *rac,cis*-[Ru(neoc)$_2$Cl$_2$] (12 mg, 0.020 mmol) and eilatin (10 mg, 0.028 mmol). The product, a dark green complex, was obtained in 95% yield. Anal. Calcd (found) for $C_{52}H_{36}F_{12}N_8P_2Ru$: C, 53.66 (53.38); H, 3.12 (3.42); N, 9.63 (9.47). ^{1}H NMR ($(CD_3)_2SO$, 298 K) δ 8.98 (d, $J = 8.4$ Hz, 1H, H^4), 8.76 (d, $J = 8.3$ Hz, 1H, H^c), 8.58 (d, $J = 6.6$ Hz, 1H, H^b), 8.51 (d, $J = 8.1$ Hz, 1H, H^f), 8.47 (d, $J = 8.3$ Hz, 1H, H^5), 8.45 (d, $J = 7.8$ Hz, 1H, H^7), 8.28 (d, $J = 8.8$ Hz, 1H, H^6), 8.09 (t, $J = 7.5$ Hz, 1H, H^e), 8.04 (d, $J = 8.4$ Hz, 1H, H^3), 7.94 (t, $J = 7.6$ Hz, 1H, H^d), 7.41 (d, $J = 8.3$ Hz, 1H, H^8), 7.38 (d, $J = 4.1$ Hz, 1H, H^a), 1.96 (s, 6H, CH_3); ^{13}C NMR δ 146.0 (*C*-H^a), 135.0 (*C*-H^4), 134.0 (*C*-H^7), 130.0 (*C*-H^e), 128.6 (*C*-H^f), 126.6 (*C*-H^d), 124.3 (*C*-H^3), 124.3 (*C*-H^5), 124.0 (*C*-H^8), 123.7 (*C*-H^6), 121.7 (*C*-H^c), 117.1 (*C*-H^b), 21.0 (*C*-H$_3$); UV−vis [λ_{max}, nm ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1})] 226 (8.03), 268 (7.6), 294 (4.7), 334 (1.8), 405 sh, 426 (2.7), 460 sh, 599 (0.7); FABMS, 874 $[M - 2PF_6 + H]^+$, 1019 $[M - PF_6]^+$.

[Ru(biq)$_2$(eilatin)][PF$_6$]$_2$ (6): *rac,cis*-[Ru(biq)$_2$Cl$_2$] (20 mg, 0.029 mmol) and eilatin (14 mg, 0.039 mmol) were dissolved in 3 mL of ethylene glycol and heated to 100 °C for 15 h. The resultant brown-green reaction mixture was cooled, and a saturated solution of KPF_6 was added. The mixture was filtered, and the crude green-brown solid was purified by partial dissolution in 3 mL of chloroform and precipitation by diethyl ether. The brown complex was recrystallized by the slow diffusion of ether into an acetonitrile solution of the complex. Typical yield: 54%. Anal. Calcd (found) for $C_{60}H_{36}F_{12}N_8P_2Ru{\cdot}H_2O$: C, 56.39 (56.13); H, 3.00 (3.14); N, 8.77 (8.52). ^{1}H NMR (CD_3CN, 320 K) δ 9.12 (d, $J = 8.8$ Hz, 1H, H$^{3'}$), 9.06 (d, $J = 8.8$ Hz, 1H, H$^{4'}$), 8.86 (d, $J = 8.9$ Hz, 1H, H^3), 8.72 (d, $J = 8.1$ Hz, 1H, H^c), 8.71 (d, $J = 6.6$ Hz, 1H, H^b), 8.40 (d, 8.8 Hz, 1H, H^4), 8.36 (d, $J = 8.0$ Hz, 1H, H^f), 8.28 (d, $J = 6.6$ Hz, 1H, H^a), 8.19 (d, 8.8 Hz, 1H, H$^{5'}$), 8.06 (t, $J = 7.9$ Hz, 1H, H^e), 7.96 (t, $J = 8.0$ Hz, 1H, H^d), 7.65 (d, $J = 8.0$ Hz, 1H, H^5), 7.55 (t, $J = 7.3$ Hz, 1H, H$^{6'}$), 7.39 (d, $J = 8.9$ Hz, 1H, H$^{8'}$), 7.21 (d, $J = 8.9$ Hz, 1H, H^8), 7.15 (t, $J = 7.7$ Hz, 1H, H^6), 7.09 (t, $J = 7.4$ Hz, 1H, H$^{7'}$), 6.87 (t, $J = 8.4$ Hz, 1H, H^7); ^{13}C NMR δ 148.3 (*C*-H^a), 140.1 (*C*-H$^{4'}$), 139.0 (*C*-H^4), 133.3 (*C*-H^e), 132.4 (*C*-H$^{7'}$), 131.5 (*C*-H^f), 130.5 (*C*-H^7), 130.1 (*C*-H^d), 129.5 (*C*-H$^{5'}$), 129.1 (*C*-H$^{6'}$), 128.8 (*C*-H^5), 128.5 (*C*-H^6), 125.1 (*C*-H^8), 125.0 (*C*-H$^{8'}$), 123.6 (*C*-H^c), 122.1 (*C*-H$^{3'}$), 121.2 (*C*-H^3), 121.0 (*C*-H^b); UV−vis [λ_{max}, nm ($\epsilon \times 10^{-4}$ M^{-1} cm^{-1})] 244 (7.0), 267 (9.8), 307 (5.0), 333 (5.3), 360 (3.9), 382 (3.9), 430 (1.6), 466 (1.3), 544 (1.0), 599 sh; FABMS, 970 $[M - 2PF_6 + H]^+$, 1115 $[M - PF_6]^+$.

X-ray Structure Determinations. The X-ray diffraction measurements were carried out at ca. 115 K on a Nonius Kappa CCD diffractometer, using Mo Kα (L = 0.7107 Å) radiation. Single crystals of these compounds could be grown only as acetonitrile, water, and/or diethyl ether solvates. To avoid deterioration, the analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to 115 K.

Crystal data for 2: $C_{44}H_{28}F_{12}N_8P_2Ru{\cdot}2(CH_3CN)$, formula weight 1141.86, triclinic, space group $P\bar{1}$, $a = 12.707(1)$ Å, $b = 12.940(1)$ Å, $c = 15.748(1)$ Å, $\alpha = 81.85(1)°$, $\beta = 87.60(1)°$, $\gamma = 63.89(1)°$, $V = 2301.1$ Å^3, $Z = 2$, $D_{calc} = 1.648$ g·cm^{-3}, $F(000) = 1148$, μ(Mo Kα) = 5.08 cm^{-1}, crystal size $0.40 \times 0.25 \times 0.10$ mm^3, $2\theta_{max} = 55.8°$, 10188 unique reflections. $R1 = 0.068$ and $wR2 = 0.150$ for 5689 reflections with $F_o > 4\sigma(F_o)$, and $R1 = 0.145$ ($wR2 = 0.182$) for all unique data. The asymmetric unit contains two PF_6 ions as well as two molecules of acetonitrile solvent, which were found to be partly disordered.

Data for 3: $C_{48}H_{28}F_{12}N_8P_2Ru{\cdot}CH_3CN{\cdot}H_2O$, formula weight 1166.86, triclinic, space group $P\bar{1}$, $a = 12.645(1)$ Å, $b = 13.399(1)$ Å, $c = 15.324(1)$ Å, $\alpha = 85.67(1)°$, $\beta = 79.80(1)°$, $\gamma = 63.82(1)°$, $V = 2293.1$ Å^3, $Z = 2$, $D_{calc} = 1.690$ g·cm^{-3}, $F(000) = 1172$, μ(Mo Kα) = 5.13 cm^{-1}, crystal size $0.25 \times 0.10 \times 0.10$ mm^3, $2\theta_{max} = 55.7°$, 9415 unique reflections. $R1 = 0.048$ and $wR2 = 0.117$ for 7733 reflections with $F_o > 4\sigma(F_o)$, and $R1 = 0.064$ ($wR2 = 0.126$) for all unique data.

Data for 4: $C_{44}H_{28}F_{12}N_8P_2Os$ (excluding solvent), formula weight 1148.88, triclinic, space group $P\bar{1}$, $a = 11.442(1)$ Å, $b = 13.447(1)$ Å, $c = 16.397(1)$ Å, $\alpha = 77.29(1)°$, $\beta = 78.44(1)°$, $\gamma = 81.71(1)°$, $V = 2397.9$ Å^3, $Z = 2$, $D_{calc} = 1.591$ g·cm^{-3}, $F(000) = 1124$, μ(Mo Kα) = 28.12 cm^{-1}, crystal size $0.20 \times 0.05 \times 0.05$ mm^3, $2\theta_{max} = 60.3°$, 10420 unique reflections. $R1 = 0.069$ for 8240 reflections with $F_o > 4\sigma(F_o)$, and $R1 = 0.092$ for all data, without accounting for the contribution of the heavily disordered diethyl ether solvent (its content could not be reliably determined). After subtracting the contribution of the disordered solvent to the diffraction pattern from the observed data,[21] final $R1 = 0.048$ and $wR2 = 0.111$ for 8240 observations above the intensity threshold, and $R1 = 0.068$ ($wR2 = 0.117$) for all unique data. The two PF_6 counterions located near the solvent area in the lattice were also found to be partly (mainly rotationally) disordered.

Data for 5: $C_{52}H_{36}F_{12}N_8P_2Ru$ (excluding solvent), monoclinic, space group Pn, $a = 12.316(1)$ Å, $b = 19.636(1)$ Å, $c = 21.883(1)$ Å, $\beta = 99.52(1)°$, $V = 5219.3$ Å^3, $Z = 4$, $D_{calc} = 1.481$ g·cm^{-3}, $F(000) = 2344$, μ(Mo Kα) = 4.50 cm^{-1}, crystal size $0.15 \times 0.10 \times 0.10$ mm^3, $2\theta_{max} = 56.0°$, 20195 unique reflections. The crystals diffracted poorly due to loose crystal packing, and heavy disorder of the PF_6 anions and of the crystallization solvent. The latter could not be located reliably from the diffraction pattern. After subtracting their contribution from the observed data,[21] a preliminary refinement of an isotropic model (except for an anisotropic Ru) of the partial structure converged at $R1 = 0.091$ for 7112 observations above the intensity treshold of $F_o > 4\sigma(F_o)$. This confirms the overall correctness of the [Ru(neoc)$_2$(eilatin)]$^{2+}$ complex, but further studies are required to determine its structure with a satisfactory precision.

Data for 6: $C_{60}H_{36}F_{12}N_8P_2Ru{\cdot}2(CH_3CN){\cdot}(C_4H_{10}O)$, formula weight 1416.21, triclinic, space group $P\bar{1}$, $a = 12.975(1)$ Å, $b = 13.448(1)$ Å, $c = 18.390(1)$ Å, $\alpha = 74.30(1)°$, $\beta = 85.45(1)°$, $\gamma = 76.89(1)°$, $V = 3008.1$ Å^3, $Z = 2$, $D_{calc} = 1.564$ g·cm^{-3}, $F(000) = 1440$, μ(Mo Kα) = 4.07 cm^{-1}, crystal size $0.30 \times 0.25 \times 0.10$ mm^3, $2\theta_{max} = 55.0°$, 12600 unique reflections. $R1 = 0.069$ and $wR2 = 0.189$ for 7733 reflections with $F_o > 4\sigma(F_o)$, and $R1 = 0.088$ ($wR2 = 0.208$) for all unique data. One of the PF_6 ions and the crystallization solvent (two molecules of acetonitrile and one molecule of diethyl ether) were found to be partly disordered.

Appendix

For a dimerization process of a chiral entity, the following equilibria take place:

$$\Delta + \Delta \overset{K_{\Delta 2}}{\rightleftharpoons} \Delta_2 \quad (K_{\Delta 2} = [\Delta_2]/[\Delta]^2)$$

$$\Lambda + \Lambda \overset{K_{\Lambda 2}}{\rightleftharpoons} \Lambda_2 \quad (K_{\Lambda 2} = [\Lambda_2]/[\Lambda]^2)$$

$$\Delta + \Lambda \overset{K_{\Delta\Lambda}}{\rightleftharpoons} \Delta\Lambda \quad (K_{\Delta\Lambda} = [\Delta\Lambda]/[\Delta][\Lambda])$$

We define the following:

$$K_{D(homo)} \equiv K_{\Delta 2} = K_{\Lambda 2}$$

$$K_{D(hetero)} \equiv K_{\Delta\Lambda}$$

The total dimer concentration is given by:

$$[D] = [\Delta_2] + [\Lambda_2] + [\Delta\Lambda] = K_{D(homo)}[\Delta]^2 + K_{D(homo)}[\Lambda]^2 + K_{D(hetero)}[\Delta][\Lambda]$$

The total monomer concentration is defined as [M]. For a racemic solution, it follows that:

$$[\Delta] = [\Lambda] = 0.5[M]$$

Thus,

$$[D] = K_{D(homo)}(0.5[M])^2 + K_{D(homo)}(0.5[M])^2 + K_{D(hetero)}(0.5[M])^2 = [M]^2\frac{K_{D(hetero)} + 2K_{D(homo)}}{4}$$

Therefore,

$$K_{D(mean)} \equiv \frac{[D]}{[M]^2} = \frac{K_{D(hetero)} + 2K_{D(homo)}}{4}$$

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Supporting Information Available: ^{1}H NMR data for all the dimerization experiments (PDF) and X-ray crystallographic files for the structure determinations of complexes **2**, **3**, **4**, **5**, and **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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