In summary, the ortho ester Claisen rearrangement has occurred in this system predominantly (9–13:1) from the top face of the double bond, while the Claisen rearrangement has taken place exclusively from the bottom face of the olefinic system. Since the Claisen rearrangement has presumably occurred via a chair transition state[10] (Figure 2a), this work provides strong evidence that the ortho ester rearrangement must have occurred predominantly through boat transition states (see Figure 3a,b). Evidently attack from the α-face via the chair transition state (Figure 2a) is favored in the Claisen rearrangement, while the analogous transition state (Figure 2b) for the ortho ester Claisen rearrangement is not. Moreover, substitution of the smaller N_b-methyl group for the N_b-benzyl function had virtually no effect on the product ratios in either of the rearrangements. This suggests that the interaction between the enol ether group (OCH_3) and the proton located 1,3 to it in the ortho ester rearrangement may play a role in destabilizing this transition state (Figures 2b and 4a) relative to that of the Claisen rearrangement (Figure 2a) rather than the N_b-substituent.

These represent the first cases in a rigid system wherein the Claisen rearrangement has proceeded via a chair transition state while the corresponding ortho ester Claisen rearrangement, under similar stereochemical constraints, has proceeded principally by the boat transition state. Alkenic esters **3a–c** have recently been converted into suaveoline,[6] while work is currently in progress to convert the 1,3-dicarbonyl compound **8** into alstonerine.[3] Further work (computational and chemical) is currently under way to fully understand the reasons for the reversal in stereofacial selectivity in the Claisen and the ortho ester Claisen rearrangements.

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Supplementary Material Available: Details of the structure determination, crystal data, and lists of fractional coordinates and anisotropic temperature factors for **3a** (4 pages). Ordering information is given on any current masthead page.

Controlled One-Dimensional Energy Migration in the Crystals of Binuclear Platinum(II) Diphosphite Complexes[1]

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Energy migration among chromophores of identical nature is one of the simplest but most fundamental photophysical processes in particular in molecular aggregate systems. Nevertheless, its quantitative rate analysis has not been reported until very recently.[2] The energy transfer process involving either the singlet or triplet state is highly relevant to material science (e.g., photodegradation of polymers[3]), photoreactions (energy harvesting and sensitization[4]), and expected photonic devices.[5] In the last case, the controlled one-dimensional flow of energy and/or electrons is a key process, which has hardly been surveyed. To test the possibility, we chose $X_4[Pt_2(P_2O_5H_2)_4]$ ($X = Na^+, K^+, Et_4N^+$, and $(n\text{-}Bu)_4N^+$) crystals and measured the laser-induced phosphorescence.[6,7] Judging from its crystal structure[8b] and preceding discussion on the nature of orbital interactions,[8c] the possible path for the triplet energy migration is exclusively along the Pt–Pt direction (i.e., along the z axis). In the well-grown crystals, the phosphorescence decay profile is nonsingle exponential and dependent on the excitation density. The lower the excitation density, the better the decay profile analysis by a single exponential function. This indicates explicitly the participation of T–T annihilation even at room temperature under atmospheric pressure.[9] It should be noted that *the phenomenon is observed only for well-grown crystals but not for amorphous samples* which have random arrangement of the Pt_2 unit.[10] This supports the interpretation of anisotropic energy migration via overlapped $5d_{z^2}$ orbitals directing to the z axis in the crystals.

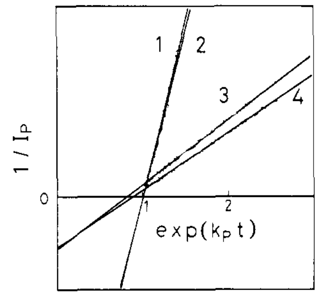

Figure 1. Plots expressing the participation of a bimolecular decay path according to eq 2 for $X_4[Pt_2(P_2O_5H_2)_4]$; X = Na^+ (1), K^+ (2), Et_4N^+ (3), and $(n\text{-}Bu)_4N^+$ (4). $1/k_P$ was taken as 4.6 μs.[18] Phosphorescence decays were measured by the combination of a pulsed Nd:YAG laser (Spectron, SL803, 355 nm, pulse width ~ 13 ns), a photomultiplier (R-928, Hamamatsu Photonics), and a storage oscilloscope (TS-8123). The data were averaged over 30 measurements.

When T–T annihilation is involved, the kinetic expression of triplet state decay is given by eq 1 and 2, where n_T, k_P, and k_{TT}

$$-dn_T/dt = k_P n_T + k_{TT} n_T^2 \qquad (1)$$

$$1/n_T(t) = (1/n_T(0) + k_{TT}/k_P)\exp(k_P t) - k_{TT}/k_P \qquad (2)$$

are the population of T_1, the reciprocal of the normal triplet lifetime, and the T–T annihilation rate constant, respectively. The data of phosphorescence decay is plotted in the form of eq 2 in Figure 1, the negative intercept giving the T–T annihilation rate constant.[9,11]

Aiming at control of the energy migration probability from one site to the nearest neighbor, we modulate the distance between the Pt_2 units by changing the countercation from K^+ to Na^+, Et_4N^+, and $(n\text{-}Bu)_4N^+$.[12] The phosphorescence decay curves are similarly analyzed by eq 2, and the results are presented in Figure 1 as well. As we expect, the larger the size of the countercations,

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† Deceased on July 11, 1989.

[1] The major part of this paper was reported at the 58th Annual Meeting of Chemical Society of Japan, Kyoto, April 1989; preprints 2ID12.

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[12] Although crystallographic data are not available except for $K_4[Pt_2(P_2O_5H_2)_4]$, a similar crystal structure with different lattice parameters has been suggested for the $(n\text{-}Bu)_4N^+$ salt.[8a]

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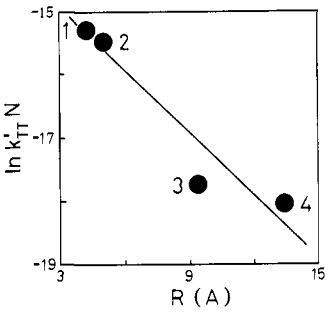

Figure 2. Correlation between intermolecular Pt–Pt distance between two Pt_2 units and k_{TT}' for $X_4[Pt_2(P_2O_5H_2)_4]$; X = Na^+ (1), K^+ (2), Et_4N^+ (3), and $(n\text{-}Bu)_4N^+$ (4). The magnitude of N was estimated from the known value of the K^+ salt.[8b] The increment or decrement of the ion radius depending on the countercation was adjusted on the intermolecular Pt–Pt distance.

the smaller the k_{TT} value. We believe that this is a reflection of interatomic distance between two Pt_2 units.

To gain further insight into the mechanism, we apply the Dexter mechanism to the present systems.[13] The hopping rate constant from molecule 1 to one of the nearest neighbors (W_1) is given by eq 3, where R, L, H_0, and $\int f(\nu)\epsilon(\nu)\,d\nu$ are the intermolecular Pt–Pt distance between two Pt_2 units along the z axis, the effective average Bohr radius of orbitals related to energy transfer, the preexponential factor, and the spectrum overlap integral between the phosphorescence and the singlet–triplet absorption, respectively.

$$W_1 = \frac{4\pi^2(H_0)^2 \exp(-2R/L)}{h} \frac{\int f(\nu)\epsilon(\nu)\,d\nu}{\int f(\nu)\,d\nu \int \epsilon(\nu)\,d\nu} \qquad (3)$$

The exponential part in eq 3 is proportional to the exchange integral between initial and final states. On the assumption that the exchange integral is calculated according to the Wolfsberg–Helmholz formula,[14] the relevant orbitals are confined to $5d_{z^2}$ and $6p_z$, which are related to the lowest excited state. Consequently, a meaningful value of W_1 is conceivable only for the interaction among Pt_2 units along the z axis. The resident time of a triplet exciton on molecule 1 (τ_1) is given by eq 4, since there are two nearest neighbors in these systems. In the case of one-dimensional energy migration over evenly distributed molecules (N molecules per unit length), the proportional relationship is concluded to be eq 5, where the number of nearest neighbors is 2.[15] Since only R and N are affected by the countercation, eq 6 is derived from eq 3–5, expressing the effect of the countercation on the relative T–T annihilation constant k_{TT}'. Using the values of R and N estimated by the CPK model,[16] we obtained a reasonable linear plot as shown in Figure 2. The slope gives L = 6 Å. This large value in comparison with those in the usual organic systems[17a] is attributed to a much larger spatial distribution of $6p_z$ and $5d_{z^2}$ orbitals relative to $2p\pi$ orbitals. Furthermore, the present Pt–Pt interaction is a σ-type interaction and stronger than a π-type interaction in organic compounds.[17b]

$$\tau_1^{-1} = 2W_1 \qquad (4)$$

$$k_{TT} \propto 2/\tau_1 N \qquad (5)$$

$$\ln k_{TT}'N = \text{constant} - 2R/L \qquad (6)$$

We have demonstrated that the probability of oriented triplet energy migration can be controlled by simple chemical modification. For the design of well-oriented energy migration, the use of triplet-state interaction requiring orbital overlap would be more suitable than singlet energy migration governed by long-range electrostatic interaction.

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Novel Strategy of Using a C_2 Symmetric Chiral Diether in the Enantioselective Conjugate Addition of an Organolithium to an α,β-Unsaturated Aldimine[†]

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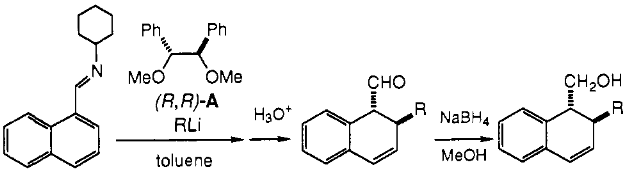
Enantioselective conjugate addition of organometallics to α,β-unsaturated carbonyl compounds has been a challenge in synthetic organic chemistry.[1,2] It is most important, at the present time, to propose a rational strategy for designing a chiral ligand. We report herein a prototype of enantioselective conjugate addition of an organolithium to an achiral α,β-unsaturated aldimine based on the novel strategy of using a C_2 symmetric chiral diether as a stereocontrol catalyst. The procedure is exemplified by the reaction of butyllithium with 1-naphthaldehyde cyclohexylimine **1** in the presence of (*R*,*R*)-1,2-diphenylethane-1,2-diol dimethyl ether A.



1 **2** (1*R*,2*S*)-**3**

A solution of butyllithium (1.3 equiv) in hexane was added to a mixture of aldimine **1**[3] and (*R*,*R*)-A[4] (1.4 equiv) in toluene at −78 °C, and the whole was stirred at −78 °C for 6 h and then treated with acetate buffer (pH 4.5) for 12 h. The usual workup afforded 2-butyl-1,2-dihydronaphthalene-1-carbaldehyde **2**, which was then reduced with $NaBH_4$ in MeOH to afford, after silica gel column chromatography (hexane–AcOEt, 10:1), the corresponding 1*R*,2*S* alcohol **3** (R = Bu) of 91% ee ($[\alpha]^{22}_D$ +406° (*c* 1.14, $CHCl_3$))[5] in 80% overall yield.[6] The absolute configuration and % ee were determined by optical rotation[5] and by HPLC analysis using a chiral column (Waters Opti-Pak TA, XC, or PC, hexane–*i*-PrOH, 9:1). The diether A was recovered quantitatively for reuse without any loss of optical purity. It is important to note

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[†] We dedicate this paper to the memory of the late Professor John K. Stille.

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