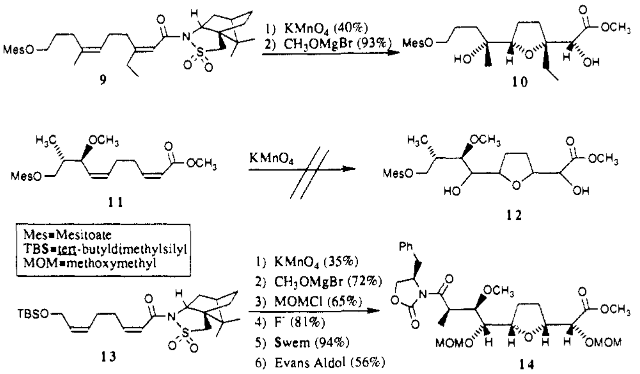
Scheme II. Oxidative Cyclization of Unsymmetrical Dienoates and Enantioselective Synthesis of an Ionophore Fragment



The problems of low face selectivity and difficulty in removal of the chiral auxiliary are solved with Oppolzer's bornane-10,2-sultam system.[13] Thus, oxidation of dienoate **8**,[5,6a,b] functionalized with (2*S*)-bornane-10,2-sultam, gave a >9:1 mixture of diastereomers,[7] from which the major diastereomer[6a,b] could be readily isolated by flash chromatography in 38% yield. Treatment of this THF diol with CH_3OMgBr then gave a sample of nonracemic THF diol **4a** (55%), shown to possess the 2*R* absolute configuration by correlation with the Mosher ester (**4b**) from authentic diol **4a** prepared from enantiomerically enriched dienoate **1**.[14]

Thus, the major diastereomer in oxidation of the bornane-10,2-sultam derived dienoate **8** results from attack on the *Re* face of the conjugated double bond. As expected, this is the same facial bias observed by Oppolzer in the osmylation of sultam-functionalized enoates.[15] It must be pointed out, however, that the mechanism of the oxidative cyclization reaction is not known, the mass balance is never quantitative, and α-ketol byproducts are always produced, most likely from the same intermediate that leads to THF diol. Thus, the ratio of THF diol diastereomers is not necessarily a reflection of the face selectivity in the attack of permanganate on thee unsaturated system. Nevertheless, diastereofacial bias in initial attack of permanganate on the conjugated double bond to give a Mn(V) diester, followed by oxidative cyclization by the Sharpless-type mechanism previously suggested by us in the literature.[1c,16] is certainly an attractive explanation of the observed results.

In order to further explore the scope of the asymmetric oxidative cyclization, we have studied the cyclization of dienoates **9**,[6a,b17] **11**[6a,18] and **13**,[6a,18] as shown in Scheme II. Cyclization of the dienoate **9** proceeded similarly to that of dienoate **8**, to give the expected 9:1 ratio of diastereomeric THF diols.[7] The major diastereomer, assigned the structure resulting from *Re*-face attack by analogy with the results presented above, was easily purified by flash chromatography and isolated in 40% yield.[6a,b] Treatment of this material with CH_3OMgBr then gave enantiomerically pure THF diol **10** in good yield.[6a,b] Compound **10** has the substitution pattern of the C ring of monensin, but of opposite absolute configuration.

Interestingly, oxidation of dienoate **11** with permanganate under our standard conditions gave no trace of THF diol **12**. Apparently, the substitution at the allylic carbon remote from the dienoate carbonyl effectively shuts down oxidative cyclization in favor of other pathways (the only products isolated from this reaction, in 79% combined yield, were identified as diastereomeric mixtures of the two regioisomeric α-ketols resulting from attack of permanganate at the conjugated double bond). A product possessing the substitution pattern present in THF diol **12**, however, could easily be obtained by diastereoselective oxidative cyclization of dienoate **13**, followed by straightforward elaboration as shown in Scheme II to give THF diol derivative **14**.[6a,19]

Acknowledgment. We thank the National Science Foundation (Grant No. CHE80-11391) and the National Institutes of Health (Grant No. GM31215 and GM31051) for financial support of this work, and we especially thank the A. P. Sloan Foundation, the Camille and Henry Dreyfus Foundation, Inc., Monsanto Agricultural Products Co., and Displaytech, Inc., for gifts of unrestricted money which made this work possible.

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[13] Oppolzer, W.; Chapuis, C.; Bernardinelli, G. *Helv. Chim. Acta* **1984**, *67*, 1397-1401.

[14] The esters **4b** and **5b** were easily prepared regioselectively from diols **4a** and **5a**, respectively, by treatment of the diols with (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid in the presence of 1,3-dicyclohexylcarbodiimide and (dimethylamino)pyridine. The ^1H NMR spectra of these esters proved nicely diagnostic of their structure. Thus, for example, the proton at C2 of ester **4b** appears as a sharp singlet at δ 4.81, while the C2 proton of ester **5b** appears as a sharp singlet at δ 4.85. In mixtures of these esters, the resonances for the C2 protons are completely resolved.

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[16] Walba, D. M.; DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M. *Organometallics* **1984**, *3*, 498-499.

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[18] Dienoates **11** and **13** were prepared from hexadiyne. The tetrahedral stereocenters of dienoate **11** were introduced enantioselectively by means of standard Evans aldol chemistry (ref 4, for detailed experimental procedures used in our group see ref 1e), and the trigonal stereocenters of both **11** and **13** were introduced diastereoselectively by hydrogenation of triple bonds with 5% Pd/$BaSO_4$ poisoned with quinoline. All intermediates in the routes to dienoates **11** and **13**, and materials in the route leading from **13** to **14**, were characterized spectroscopically.

[19] The face selectivity in the oxidative cyclization of dienoate **13** was assigned by analogy to that for the neroate system, and the relative stereochemistry of the aldol process was assigned by analogy with similar Evans aldol processes.

Photoluminescence of $[Pt^{II}(4,7\text{-diphenyl-1,10-phenanthroline})(CN)_2]$ in Solution

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Aromatic molecules are well-known to undergo excited-state dimerization in solution.[1,2] Under suitable conditions the formation of excited dimers (excimers) can be monitored by the simultaneous appearance of the monomer and excimer luminescence. With regard to coordination compounds, Pt^{II} complexes are promising candidates for the observation of emissive monomers and excimers.[3,4] Unfortunately, the majority of mononuclear Pt^{II} complexes are not luminescent in fluid solution. This seems to be associated with the presence of low-energy dd states. The few mononuclear Pt^{II} complexes that are indeed luminescent in solution[5-9] emit from intraligand (IL) $\pi\pi^*$ or metal to ligand charge transfer (MLCT) states. In addition to these mononuclear com-

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[2] Birks, J. B. *The Photophysics of Aromatic Molecules*; Wiley and Sons: New York, 1970.

[3] An excimer of $[Pt(o\text{-phen})_2]^{2+}$ in the solid state has been reported recently.[4]

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plexes, several binuclear Pt^{II} compounds such as $[Pt_2(P_2O_5H_2)_4]^{4-}$[10] and $[Pt_2[bis(diphenylphosphino)methane]_2(CN)_4]$[11] and the oligomeric anion $[Pt(CN)_4]_n^{2-}$[12,13] are known to be intensely luminescent in solution. In these cases the emission originates from excited states which are characterized by strong metal–metal bonding. This metal–metal bond which is essentially absent in the ground state may thus promote a dimerization of excited mononuclear Pt^{II} complexes in solution. We explored this possibility and selected the compound $[Pt(bathophen)(CN)_2]$ with bathophen = bathophenanthroline (4,7-diphenyl-1,10-phenanthroline) for the present study. The ligand field (LF) states of this compound occur certainly at very high energies and should thus not interfere with an emitting IL state of the coordinated bathophen. It is also important that the complex is neutral since excimer formation of charged complexes should be hindered by electrostatic repulsion. Finally, excimer formation requires a relatively high concentration of the monomer. While some $[Pt^{II}(diimine)(CN)_2]$ complexes have been recently reported to emit in the solid state,[14] their investigation in solution is hampered by their very low solubility in all common solvents. Interestingly, the complex $[Pt(5,5'\text{-}Me_2bpy)(CN)_2]$ is indeed soluble in acetonitrile and shows a luminescence in solution,[9] but its solubility may be too low to observe an excimer emission. For the complex $[Pt(bathophen)(CN)_2]$, an enhanced solubility in nonaqueous solvents was expected in analogy to the compound $[Re(bathophen)(CO)_3Cl]$.[15]

The compound $[Pt(bathophen)(CN)_2]\cdot H_2O$ was prepared and obtained analytically pure in analogy to the synthesis of $[Pt(2,2'\text{-}bipyrimidine)(CN)_2]$.[16] In CH_2Cl_2, the complex $[Pt(bathophen)(CN)_2]$ was soluble up to concentrations of about 6×10^{-4} M. In PEG (polyethylene glycol), higher concentrations up to 9×10^{-3} M were obtained. This was facilitated by heating. It is possible that these solutions were oversaturated, but they remained homogeneous.

The absorption spectra of $[Pt(bathophen)(CN)_2]$ in CH_2Cl_2 and PEG are very similar. In PEG absorption maxima appear at $\lambda = 375$ ($\epsilon = 5900$), 357 (7500), ~336 (shoulder, 12 400), ~304 (shoulder, 36 100), and 293 nm (41 300). The absorption spectrum was not concentration dependent. When saturated CH_2Cl_2 or PEG solutions were diluted, the Lambert–Beer law was obeyed.

In solutions of CH_2Cl_2 and PEG, the complex showed an emission that varied with the concentration. The excitation spectrum matched the absorption spectrum, indicating a genuine emission of the complex. In CH_2Cl_2 at low complex concentrations (~10^{-5} M), only a green luminescence at $\lambda_{max} = 520$ nm appeared. An increase of the concentration to its upper limit (6×10^{-4} M) was associated with the appearance of a red emission at $\lambda_{max} = 615$ nm which grew at the expense of the green emission. Due to limited solubility of $[Pt(bathophen)(CN)_2]$ in CH_2Cl_2, a complete conversion of the green to the red luminescence was not achieved. However, in PEG the green emission ($\lambda_{max} = 530$ nm, $\tau = 0.1$ μs) could be completely replaced by the red luminescence ($\lambda_{max} = 630$ nm, $\tau = 1$ μs) since higher concentrations than those in CH_2Cl_2 were obtained. At intermediate concentrations in PEG, both emissions were present. When the light absorption was complete ($A > 2$), the variation of the concentration led to the occurrence of an isoemissive point at $\lambda = 586$ nm (Figure 1).

The bathophen and cyanide ligands of $Pt(bathophen)(CN)_2$ should cause a large LF splitting of the d orbitals due to strong σ bonding as well as π back-bonding in the complex. LF and metal to ligand charge transfer (MLCT) transitions are then not expected to occur at low energies. The absorption spectrum of the complex indeed does not contain the solvatochromic MLCT bands which are characteristic for complexes of the type $[Pt(diimine)X_2]$ with X^- = halide.[17] In analogy to the complexes $[Pt(5,5'\text{-}Me_2bpy)(CN)_2]$[9] and $[Pt(o\text{-}phen)_2]^{2+}$,[4] we assign the absorption bands of $[Pt(bathophen)(CN)_2]$ to IL $\pi\pi^*$ transitions of the coordinated bathophen. This IL assignment of the lowest excited state is also supported by the emission properties of $[Pt(bathophen)(CN)_2]$ in dilute solution. The observation of a solution luminescence indicates the absence of low-energy LF states.[7,8] The IL luminescence of $[Pt(bathophen)(CN)_2]$ appears at a wavelength ($\lambda_{max} = 530$ nm) that is very close to that of the low-temperature IL emission of $[Pt(o\text{-}phen)_2]^{2+}$[4] and the phosphorescence of *o*-phen complexes of Zn^{2+}.[18]

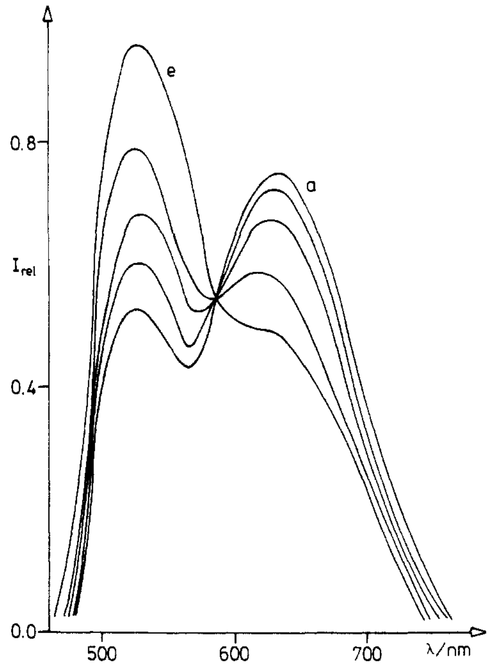

Figure 1. Concentration dependence of the emission spectra of $[Pt^{II}(4,7\text{-}diphenyl\text{-}1,10\text{-}phenanthroline)(CN)_2]$ in polyethylene glycol at room temperature: 4×10^{-3} M (a), 3×10^{-3} M, 2×10^{-3} M, 1×10^{-3} M, and 5×10^{-4} M (e); $\lambda_{exc} = 360$ nm, 1-cm cell, intensity in arbitrary units.

While the absorption spectrum of $[Pt(bathophen)(CN)_2]$ in solution obeys the Lambert–Beer law, the emission spectrum undergoes a considerable change in the same concentration range (Figure 1). We suggest that this concentration dependence is due to the formation of an excimer.

In dilute solution the IL $\pi\pi^*$ state of the mononuclear complex is deactivated by emission and nonradiative deactivation. With increasing concentration, an association to an excimer takes place. The excimer emits at lower energies. It may also undergo a radiationless deactivation or dissociate into an excited-state and a ground-state monomer. In the ground state the dimer is not stable but dissociates to its mononuclear components.

It is assumed that the excimer is characterized by a metal–metal bond which promotes the dimerization.[19] The formation of a strong metal–metal bond in the excited state also has been observed for Pt^{II} complexes which are already binuclear in the ground state due to the presence of bridging ligands.[10,11] Compared to the IL emission of the monomeric $[Pt(bathophen)(CN)_2]$, the luminescence of the excimer is shifted to a longer wavelength since the dimerization generates a new low-energy excited state which

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(19) The existence of an excimer of $[Pt(o\text{-}phen)_2]^{2+}$ in the solid state has been attributed to ligand–ligand interaction in the excited state.[4] While this is also possible for $[Pt(bathophen)(CN)_2]$, we consider the formation of a metal–metal bond as a more probable alternative.

is associated with the metal–metal interaction.[10,11] The excimer formation is certainly facilitated by the relatively long lifetime of the monomer ($\sim 10^{-7}$ s). With increasing concentration, the excimer formation competes successfully with the emission and radiationless deactivation of the monomer. The isoemissive point at λ = 586 nm (Figure 1) indicates the presence of only two emitting species.[1,2]

If the excimer is indeed rather stable, its dissociation may not be important. This assumption is supported by a simple calculation. Provided the excimer dissociation can be neglected, the second-order rate constant k_A for the excimer formation can be calculated from the half-concentration C_h.[1,2] At an estimated half-concentration $C_h = 1.8 \times 10^{-3}$ M, a reasonable value of $k_A = 5.6 \times 10^9$ s^{-1} M^{-1} is obtained, indicating a diffusion-controlled process.

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Catalytic Asymmetric Induction in the Homo Diels–Alder Reaction

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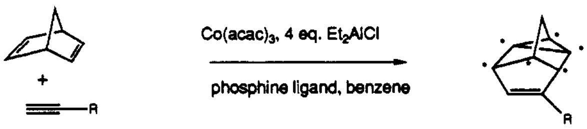
Enantioselective carbon–carbon bond-forming reactions can proceed in >95% ee for reactions such as the aldol condensation, the Diels–Alder reaction, and others through careful choice of one of a number of readily available chiral auxiliaries.[2-4] Despite the progress made in the last ten years in this area of *stoichiometric* asymmetric synthesis, there remains a continuing need for the development of new reactions where high levels of *catalytic* asymmetric induction occur.[5,6] There is great interest in developing *cycloadditions* where control is achieved through the presence of catalytic amounts of an external ligand.[7-10]

Table I. Cycloaddition of Norbornadiene and Acetylenes with Chiral Phosphines

entry	adduct	ligand[a,b]	temp, °C	yield, %	rotation,[c] deg	alcohol	ester de[d,l]
1	**1a**	A	80	34		**2a**	41 (*R*)
2	**1a**	A	25–27	37	+37.7	**2a**[g]	**69** (*R*)
3	**1a**	B	25–32	93	−34.4	**2a**	48 (*S*)
4	**1b**	A	27–33	88		**2b**	78 (*R*)
5	**1b**	A[e]	25–26	83	−0.8	**2b**[h]	**91** (*R*)
6	**1b**	B[e]	25–27	87	+0.4	**2b**	**78** (*S*)
7	**1b**	A[f]	25–28	64		**2b**	80 (*R*)
8	**1c**	A	25–33	75	−1.9	**2c**	36 (*R*)
9	**1c**	B	30–40	33		**2c**[i]	**55** (*S*)
10	**1d**	A[j]	28–32	85	−0.3	**2e**[k]	**85** (*R*)
11	**1e**	A[j]	28–32	67		**2e**	18 (*S*)
12	**1e**	A[f,j]	28–30	60	−0.3	**2e**	**80** (*R*)

[a] A = *S,S*-chiraphos, B = *R*-prophos. [b] 2% Co(acac)$_3$, 2% ligand, 4 equiv Et$_2$AlCl in benzene, reaction times of 3–20 h followed by purification by flash chromatography or bulb-to-bulb distillation. [c] Measured in CH$_2$Cl$_2$ at 25 °C. [d] Ester de = olefin ee, see text. [e] 1% catalyst used. [f] Reaction run in THF/toluene (3/1). [g] $[\alpha]_D = +99.4°$ (c = 1.0). [h] $[\alpha]_D = +56.4°$ (c = 1.1). [i] $[\alpha]_D = -39.1°$ (c = 1.0). [j] 4% catalyst used. [k] $[\alpha]_D = +26.9°$ (c = 0.5) as TBDMS derivative. [l] *R* or *S* refers to the stereochemistry of the carbon bearing the hydroxyl group in alcohols **2a–e**.

We have recently begun a program to develop the homo Diels–Alder reaction into a viable approach to polycyclic natural product synthesis. We have reported that cobalt acetylacetonate, Co(acac)$_3$, upon reduction in the presence of 1,2-bis(diphenylphosphino)ethane, is extremely effective in promoting a cycloaddition between norbornadiene and a variety of monosubstituted acetylenes to yield deltacyclenes (eq 1).[11] Importantly, a total of six new stereocenters (represented by an asterisk) are created in this transformation. In this communication, we address the question of enantioselectivity in the cycloaddition through the use of chiral phosphines. We are aware of no previous studies in this area.



(1)

We first surveyed the enantioselectivity in the reaction of phenylacetylene and norbornadiene as a function of chiral phosphine. The ligands were examined under the standard cycloaddition conditions (2 mol % azeotropically dried Co(acac)$_3$, 2 mol % phosphine, 4 equiv of Et$_2$AlCl based on cobalt, 1.5 equiv of acetylene, 1 equiv of norbornadiene, reaction warms to ca. 45 °C). *S,S*-Chiraphos[12] and *R*-prophos[12] gave **1a** in good to excellent chemical yield,[12] while *R*-BINAP and (+)-DIOP gave no cycloadduct.[13] To determine the degree and sense of induction we used a combination of spectroscopic and chemical techniques. A standard protocol was developed: racemic and chiral **1a** were subjected to hydroboration–oxidation[14] and the resulting alcohols, **2a**, were converted to the Mosher esters **3a**.[15a] For adduct **1c**

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(8) High enantioselectivity has recently been reported in the hetero-Diels–Alder reaction using 10 mol % of a chiral aluminum reagent, see: Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310. For earlier reports see: Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 3716.

(9) Low (7%) to good (73%) enantiomeric excesses have been reported in the [3 + 2] cycloaddition catalyzed by Pd. In the latter case a 4:1 mixture of stereoisomers diminishes the utility of this approach: (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1983**, *105*, 2326. (b) Yamamoto, A.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1989**, *30*, 375. Reaction with a chiral auxiliary furnishes the cycloadduct with much higher ee's, see: Binger, P.; Schaefer, B. *Tetrahedron Lett.* **1988**, *29*, 529.

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(12) Abbreviations: *S,S*-chiraphos, (2*S*,3*S*)-(−)-bis(diphenylphosphino)butane; *R*-prophos, (*R*)-(+)-1,2-bis(diphenylphosphino)propane. Satisfactory NMR, IR, optical rotations, and mass spectral data were obtained for all new compounds.

(13) From a detailed study of phosphine ligands, it is clear that the maximum number of atoms from P to P must not exceed 4 (unpublished work of C. M. Crudden).

(14) The hydroboration with 3 equiv of BH$_3$ or 9-BBN gave a single regio- and stereoisomeric alcohol. Excess borane was used to avoid any resolution. The measured ee's were identical regardless of the yield in a particular run of the hydroboration. 9-BBN was not routinely used due to the difficulty encountered in separating 1,5-cyclooctanediol from the desired product. For the preparation of optically pure alkyl boranes via kinetic resolution see: Brown, H. C.; Schwier, J. R.; Singaram, B. *J. Org. Chem.* **1978**, *43*, 4395.

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