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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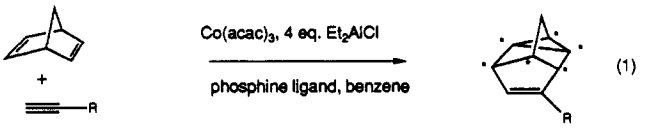
Enantioselective carbon-carbon bond-forming reactions can proceed in >95% ee for reactions such as the aldol condensation, the Diels-Alder reaction, and others through careful choice of one of a number of readily available chiral auxiliaries.[2-4] Despite the progress made in the last ten years in this 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_2AlCl in benzene, reaction times of 3-20 h followed by purification by flash chromatography or bulb-to-bulb distillation. [c] Measured in CH_2Cl_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_2AlCl 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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(6) Reactions where catalytic asymmetric induction has been achieved include the Sharpless epoxidation ((a) Rossiter, B. E., ref 2, Vol. 5, Chapter 7. (b) Finn, M. G.; Sharpless, K. B., ref 2, Vol. 5, Chapter 8), the asymmetric hydrogenation ((c) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106), and the dihydroxylation of olefins ((d) Jacobsen, E. N.; Marko, I.; Mungall, W. S.; Schroder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968 and ref 2).

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(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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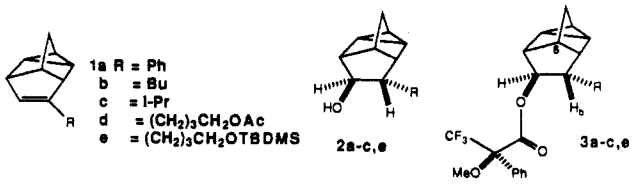
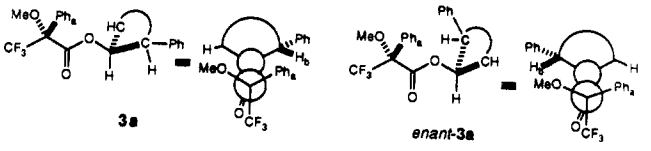
the ee's were confirmed by integration of the NMR shifts of the diastereotopic protons formed upon complexation with Ag(FOD)/Eu(hfbc)$_3$.[16]



In **3a**, the benzylic proton, H_b, in the diastereomers was clearly resolved at 200 MHz. Integration of the resonances appearing at 3.40 and 3.29 ppm provided a measure of the diastereomeric excess, which then gave the ee.[15a] The absolute stereochemistry of the cycloadducts can be assigned by using the method first described by Mosher.[15b,17] In the extended conformations depicted in **3a** and *enant*-**3a**, or their corresponding Newmann projections, the proton syn to the phenyl ring, H_b, is further upfield in **3a** due to through-space interaction with Ph_a. The assignment of the absolute stereochemistry was confirmed by X-ray crystallography.[18] *S,S*-Chiraphos gives the cycloadduct with the absolute



stereochemistry as depicted in **1a**, while *R*-prophos gives *enant*-**1a** as the predominant product. The ratios of diastereomers for **3b**, **3c**, and **3e** were easily measured by integration of the H_6 resonances, which were well-resolved at 400 MHz, at ca. 2.05 and ca. 2.15 ppm for the two diastereomeric esters.[19] The absolute stereochemistry of these derivatives was assumed by analogy to be the same as that determined for **3a** since the downfield resonance (for H_6) was the major signal observed in **3a** as well as in the other adducts prepared with *S,S*-chiraphos.

The effects of temperature, solvent, amount of catalyst, and acetylene structure on the enantioselectivity were examined (Table I). The ee of **1a**, using *S,S*-chiraphos, improved as the temperature was decreased, entries 1 and 2. Reaction at <20 °C gave little cycloadduct. Hexyne and norbornadiene gave **1d** in high chemical and optical yield in the presence of 2 mol % of catalyst at ca. 30 °C, entry 4, which rose to 91% ee when less catalyst was used, entry 5. Since the reaction is quite exothermic, this increase in ee is presumably a result of maintaining the internal reaction temperature closer to the optimum value of ca. 27 °C. The amount of catalyst used was varied as a means of obtaining optimal ee's. There is a trade-off between high chemical yields that tend to occur with higher amounts of catalyst and high ee's that arise from lower reaction temperatures. *R*-Prophos gave the enantiomeric adduct with good levels of selectivity. We noted a decrease in the ee in a coupling between NBD and hexyne with THF as solvent; this may be due to complexation of the solvent oxygen, entries 5 and 7. Increasing steric bulk near the acetylene also results in lower selectivity or no reaction. For example, cycloaddition between norbornadiene and 3-methylbutyne in benzene gave **1c** in high chemical yield but relatively low ee, 36%. In this instance the use of *R*-prophos was marginally more effective than *S,S*-chiraphos.

An acetylene bearing a remote oxygen also reacted with high enantioselectivity. However, we have found the choice of protecting group and solvent to be critical variables, entries 10–12. A side-chain oxygen which is capable of intramolecular coordination to the cobalt, entry 11, disrupts the complexation of the phosphine, NBD, and acetylene, which appears to be required for highly selective reactions. This effect was overcome through the use of a protecting group bearing a more remote oxygen, entry 10, or by carrying out the reaction in THF, which competes for a coordination site and displaces the OTBDMS group (entries 5 and 7 vs 11 and 12). In these reactions 4 mol % of catalyst was used so as to obtain reasonable yields and reactions times.

From these data we conclude that the structure of the active complex is similar to that first proposed by Lyons[11a,b] in which the chelating phosphine, norbornadiene, and acetylene are simultaneously coordinated to the cobalt. The methyl(s) in the connecting chain of the chiral phosphine ligand control the orientation of the phenyl rings, which in turn determines the position of the acetylene R group so as to minimize nonbonding interactions. Similar arguments have been used to explain enantioselectivity observed in other systems with *S,S*-chiraphos.[20]

In conclusion, we have demonstrated for the first time that a highly enantioselective cobalt-catalyzed homo Diels–Alder reaction can be performed with chiral phosphines.

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Supplementary Material Available: General experimental procedures, specific details for representative reactions, and isolation and spectroscopic information for the prepared compounds (9 pages). Ordering information is given on any current masthead page.

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(18) The crystal used for the structure determination was obtained by crystallization of a diastereomeric mixture of **3a** and *enant*-**3a** from pentane. *enant*-**3a** crystallized selectively as colorless needles. ^{1}H NMR showed the crystals had the sense of induction that is predominant from reactions with *R*-prophos. Details of the structure will be reported by Dr. Alan Lough.

(19) The values were consistent with those obtained from the ^{19}F spectrum. The upfield peak was the major signal in the ^{19}F spectrum for samples prepared with *S,S*-chiraphos.

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Selective Hydroxylation of Methyl Groups by Platinum Salts in Aqueous Medium. Direct Conversion of Ethanol to Ethylene Glycol

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Many intriguing examples of the activation of C–H bonds in alkanes by transition-metal complexes, often under remarkably mild conditions, have appeared in the last few years.[1] However, major barriers to development of a practical alkane conversion process remain. In particular, most systems studied are incompatible with O_2, the most desirable co-reagent to obtain a thermodynamically favored, economically viable catalytic reaction. Also, potential products (alcohols, alkenes, etc.) are often more reactive than the starting alkanes, which limits achievable yields. The latter is especially problematical when a hydrogen atom abstraction route is involved, as with P-450 and models thereof.

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