others with isotropic ones). The six platinum atoms, shown in Figures 1 and 2, define a trigonal prism whose edges are associated with bridging isocyanide groups; the remaining six isocyanide ligands are terminally bonded one per each platinum atom. The mercury atom occupies the pseudocenter of the prism. The molecule shows a small but significant rotational distortion of the two related Pt_3 fragments from an eclipsed pseudo-D_{3h} conformation by ca. 11° along one of the triangular Pt-Pt edges. The mean Hg-Pt and intratriangular Pt-Pt distances are 2.943 and 2.643 Å, respectively. The former distance is slightly longer than the sum (2.88 Å) of each of the covalent radii, suggesting relatively weak bond strength. The Pt-Pt distance is comparable to those found in $Pt_3(t\text{-BuNC})_6$[6] and $Pt_7(2,6\text{-Me}_2C_6H_3NC)_{12}$.[3] The closest intertriangular Pt-Pt distance, Pt(1)-Pt(4), is 4.954 Å, suggesting the absence of interaction between both platinum triangles. The dihedral angle between two triangles is ca. 7.4°, lying in the nearly parallel plane. The Hg atom is nearly equiv distant (ca. 2.51 Å) from each of two Pt_3 planes. The average distances for Pt-C(terminal) and Pt-C(bridge) bonds are 1.914 and 2.096 Å and resemble closely those found in other platinum isocyanide complexes.[3,6]

The infrared spectrum of **1** showed the presence of terminal and bridging isocyanide groups at 2095 and 1720 cm^{-1}, respectively. The ^1H NMR spectrum in C_6D_6 at ambient temperature showed two kinds of resonances due to *o*-methyl groups at δ 2.16 and 2.52 in a 1:1 ratio, assignable to the bridging and terminal isocyanide ligands. Intermolecular exchange between [1] and added 2,6-xylyl isocyanide was observed. The ^1H NMR spectrum at −77 °C in CD_2Cl_2 showed three resonances, at δ 2.06, 2.23, and 2.37, due to the bridging, terminal, and free isocyanide ligands, respectively.[7] The signals broaden on warming, and the latter two signals coalesce at ca. −30 °C, sugesting the presence of intermolecular ligand exchange between the terminal and free isocyanides. The spectrum at ca. −19 °C leads to coalescence of two broad resonances to a broad singlet, due to the intramolecular ligand exchange between the terminal and bridging isocyanide ligands. Further warming gives a sharp singlet at δ 2.24 (25 °C), suggesting the presence of a rapid intra- and intermolecular ligand exchanges. The activation free energies at coalescence temperatures are ca. 12.7 kcal/mol (T_c = −30 °C) for the intermolecular ligand-exchange process and ca. 12.9 kcal/mol (T_c = −19 °C) for the intramolecular process.[8] Although we have no detailed information for the mechanism of exchange processes, the exchange observed is probably an intermolecular process, catalyzed by free isocyanide ligand. A similar phenomenon has been observed in the $Pt_3(t\text{-BuNC})_6$-*t*-BuNC system.[6]

When 1 was heated in toluene at reflux, elimination of a mercury atom occurred to give $Pt_3(2,6\text{-Me}_2C_6H_3NC)_6$. The reactions with fumaronitrile and methyl iodide led to fragmentation of Pt-Pt and Hg-Pt bonds to produce $Pt(2,6\text{-Me}_2C_6H_3NC)_2(NCHC{=}CHCN)$[9] and *cis*-$Pt(2,6\text{-Me}_2C_6H_3NC)_2(CH_3)I$,[10] respectively.

Supplementary Material Available: Table of atomic positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

Enantioselective Allylborane Condensations

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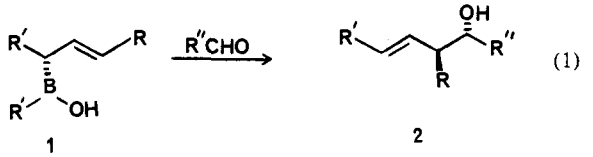
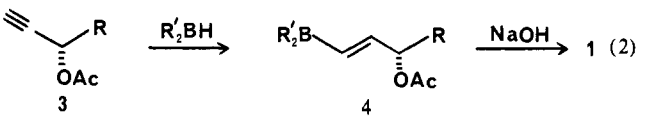
The control of stereochemistry during carbon-carbon bond formation is of great importance in synthesis. Recently a high degree of selectivity has been reached in aldol-type reactions.[2] We report that condensations of aldehydes with enantiomerically enriched allylboranes of type **1** provide homoallylic alcohols with



1 2 (1)

a high degree of enantio- and diastereoselectivity. The enantiomeric purities obtained range from 50% to 85% ee. the diastereoselectivities are >95% of the less commonly produced[2] threo isomer **2** (eq 1). Results for representative aldehydes are illustrated in Table I.

The reactions are carried out by first generating the allylborane **1**.[3] Hydroboration of optically active propargylic acetate **3**[4] with



3 4 1 (2)

1.0 equiv of either dicyclohexyl- or diisopinocampheylborane[5] (1.0 M in THF) proceeds smoothly to form the vinylborane **4**. The intermediate **4** is not isolated but treated directly with 3.0 eq of 3.0 N sodium hydroxide (−15 °C for 15 min, room temperature for 5 min). Again the allylborane **1** is not isolated but treated with 2.0 eq of an aldehyde (−15 °C for 15 min, room temperature for 2 h). Oxidative workup (100% excess 30% hydrogen peroxide, 2 h, 40 °C) is followed by extraction with ether, washing with water, and drying over potassium carbonate. The solvents are removed under vacuum, and the alcohol **2** is isolated by bulb to bulb distillation.

The threo configuration for *trans*-allylborane condensations has been determined previously.[6] Nevertheless, for confirmation of

(6) Green, M.; Howard, J. A.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1509-1514.

(7) Our assignment may be incompatible with the fact that the chemical shifts of the terminal isocyanide groups appear in a higher field than those of the bridging ones.[11] However, we assigned them on the basis of the general assessment that the intermolecular exchange is faster for the terminal than for the bridging ligands.[6]

(8) The temperatures were calibrated by using the chemical-shift separation obtained from a methanol solution. The activation energies were calculated by the following equations, and their uncertainties are within ca. 10%: $\Delta G^* = 2.3RT(10.3 + \log T - \log k)$ and $k = (\Delta h)\pi/\sqrt{2}$, where T represents the coalescence temperature, and Δh represents the chemical shift difference of the peaks in the absence of exchange, and k is the rate constant in the coalescence temperature.

(9) Mp 197-198 °C(dec). Anal. Calcd for $C_{22}H_{20}N_4Pt$: C, 49.34; H, 3.76; N, 10.46. Found: C, 49.21; H, 3.77; N, 10.56. IR (KBr) 2225 (C≡N), 2180, 2150 (N≡C) cm^{-1}; NMR ($CDCl_3$) δ 2.49 (s, 4, CH_3), 2.94 (s, J_{Pt-H} = 32.4 Hz, 2, CH), ca. 7.20 (c, aromatic protons).

(10) Mp 180-182 °C(dec). Anal. Calcd for $C_{19}H_{21}N_2IPt$: C, 38.07; H, 3.53; N, 4.67. Found C, 38.08; H, 3.50; N, 4.28. IR (KBr) 2175, 2146 (N≡C) cm^{-1}; NMR ($CDCl_3$) δ 1.15 (t, J_{Pt-H} = 39.6 Hz, Pt-CH_3), 2.51 (s, 4, CH_3), ca. 7.1 (c, aromatic protons).

(11) For example: Basset, J. M.; Barker, G. K.; Green, M.; Howard, J. A. k.; Stone, F. G. A.; Wolsey, W. C. *J. Chem. Soc., Dalton Trans.* **1981**, 219-227.

(1) (a) Alfred P. Sloan Foundation Fellow, 1978-1982. (b) University of California Regents Fellow, 1979-1981.

(2) (a) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127. (b) Evans, D. A.; McGee, L. R. *Ibid.* **1981**, *103*, 2876. (c) Pirrung, M. C.; Heathcock, C. H. *J. Org. Chem.* **1980**, *45*, 1727. (d) Meyers, A. I.; Yamamoto, Y. *J. Am. Chem. Soc.* **1981**, *103*, 4278. (e) Nagaoka, H.; Rutsch, W.; Schmid, G.; Iio, H.; Johnson, M. R.; Kishi, Y. *Ibid.* **1980**, *102*, 7965. (f) Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *Ibid.* **1981**, *103*, 1566. (g) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3 and references cited therein.

(3) Midland, M. M.; Preston, S. B. *J. Org. Chem.* **1980**, *45*, 747.

(4) (a) Midland, M. M.; McDowell, D. C.; Hatch, R. L.; Tramontano, A. *J. Am. Chem. Soc.* **1980**, *102*, 867. The propargylic alcohols can be further purified to >99% ee by recrystallization: (b) Fried, J.; Lin, C. H.; Mehra, M. M.; Kao, W. L.; Daven, P. *Ann. N.Y. Acad. Sci.* **1971**, *180*, 38.

(5) Brown, H. C.; Mandal, A. K.; Kulkarni, S. V. *J. Org. Chem.* **1977**, *42*, 1391.

(6) (a) Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1980**, *21*, 4883. (b) Hoffmann, R. W.; Zeiss, H. J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 218. (c) Hoffmann, R. W.; Ladner, W. *Tetrahedron Lett.* **1979**, 4653. (d) Hoffmann, R. W.; Ladner, W.; Steinbach, K.; Massa, W.; Schmidt, R.; Snatzke, G. *Chem. Ber.* **1981**, *114*, 2786. (e) Hoffmann, R. W.; Helbig, W. *Ibid.* **1981**, 2802. (f) Hoffmann, R. W.; Weidemann, W. *J. Organomet. Chem.* **1980**, *195*, 137. (g) Tasai, D. J. S.; Matteson, D. S. *Tetrahedron Lett.* **1981**, *22*, 2751. (h) Yamaguchi, M.; Mukaiyama, T. *Chem. Lett.* **1980**, 993. (i) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 3229.

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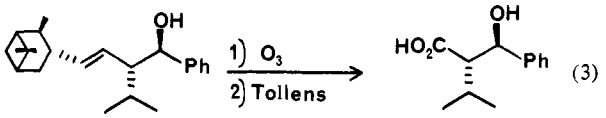
Table I. Optically Active Threo Homoallylic Alcohols 2 from Propargylic Acetates 3

config of 3[a,c]	R	R′	R″	% yield[d] of 2	% ee of 2	threo/erythro[f]	config of 2	entry
S	n-C_5H_{11}	cyclohexyl	CH_3	76	50.2[e]	96/4	S,R	a
R	i-Pr	cyclohexyl	Ph	70	60[b]	99/1	R,R[g]	b
S	n-C_5H_{11}	isopinocampheyl	i-Pr	63	80[a]	96/4	S, R	c
S	n-C_5H_{11}	isopinocampheyl	n-C_5H_{11}	62	85[a]	96/4	S,R	d
S	n-C_5H_{11}	isopinocampheyl	Ph	72	79[a]	98/2	S,S[g]	e

[a] Optical purities determined by 90-MHz ^{1}H NMR spectroscopy with tris[d,d-dicampholylmethanato]europium(III). [b] Shift reagent used is tris[3-[(heptafluoropropyl)hydroxymethylene]-d-camphorato]europium(III). [c] All % ee >99% except for 3b, which is 90% ee. [d] All yields are isolated. [e] Determined by HPLC separation of the ester from (S)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride.[11] [f] Determined via ^{13}C NMR comparison with threo/erythro mixtures. [g] Note change in priority: phenyl > alkyl.

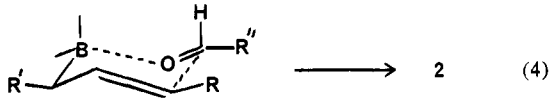
our results, **2c** was converted to *threo*-1-isopropyl-2-hydroxyhydrocinnamic acid via ozonolysis followed by Tollens oxidation (eq 3).[7] The structure of this acid has previously been unam-



(3)

2c

biguously determined.[8] The relative amounts of threo to erythro **2a–2e** were determined by comparison of the 22.6-MHz ^{13}C spectra of **2a–2e** and of a mixture of threo and erythro **2a–2e**.[9] The ratios in **2a** were further confirmed by VPC and in **2b** by ^{1}H NMR spectroscopy. The absolute configuration was determined by mechanistic considerations of the established "chair" transition state[6] for allylborane condensations with the assumption that all groups occupy an equatorial position as depicted in eq 4. The



(4)

absolute configuration was further confirmed by comparison of the NMR spectrum in the presence of chiral shift reagents to the NMR spectrum of similar compounds of known configuration in the presence of chiral shift reagents. The trans geometries of **2a–2e** were determined by ^{1}H vinyl coupling constants (15.3–15.6 Hz), IR data, and ^{13}C calculations.[10] It should be noted that Yamamoto[6i] obtains cis olefins from condensations of α-silyl- or α-stannyl-substituted crotylboranes with aldehydes and that Hoffmann[6f] obtains predominately cis products from condensations with esters of 1-butenyl-3-boronic acid. Presumably steric factors in their examples force R′ into an axial position.

The enantiomeric purity of the final product **2** is essentially the same as the enantiomeric purity of the allylborane **1**. Thus the chirality of the boron–carbon bond of **1** is transferred to the two new centers of **2** with essentially 100% efficiency. Since the loss of enantiomeric purity occurs during the transformation of **4** to **1**, development of more efficient processes for preparing enantiomerically enriched allylboranes should led to an additional increase in the enantiomeric purity of the final product. In a previous study in our laboratories[3] it was found that the enantiomeric enrichment of allylborane **1** (and hence the alcohol **2**) increased with the steric bulk of the migrating species R′. Table I illustrates that a large increase in % ee is obtained by using isopinocampheyl as the migrating species, instead of cyclohexyl. The increased % ee is evidently due to steric effects and not to the chirality of the isopinocampheyl group. Thus when diisopinocampheylborane is used with racemic acetate, the allylborane is racemic at the boron–carbon bond as shown by oxidation of the allylborane to an alcohol that is racemic at the alcohol center.

This procedure thus makes available a "one-pot" method (starting from the propargylic acetate) for carbon–carbon bond formation that is both enantio- and diastereoselective. The selectivity is for threo isomers, which nicely compliments the many existing methods for generating erythro isomers. The homoallylic alcohols formed can be cleaved to form aldol-type products, which we are currently studying as possible precursors to natural products.

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Registry No. 1a, 81206-09-9; **1b**, 81206-10-2; **1c**, 81206-11-3; **2a**, 81206-12-4; **2b**, 81206-13-5; **2c**, 81206-14-6; **2d**, 81206-15-7; **2e**, 81206-16-8; **3a**, 54315-38-7; **3b**, 81206-17-9; dicyclohexylborane, 1568-65-6; diisopinocamphenylborane, 24041-59-6; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; 2-methylpropanol, 78-84-2; hexanal, 66-25-1.

(7) Barua, R. K.; Barua, H. B. *Biochem. J.* **1964**, *92*, 21c.
(8) Mulzer, J.; Zippel, M.; Bruntrup, G.; Segner, J.; Finke, J. *Liebigs Ann. Chem.* **1980**, 1108.
(9) Mixtures were prepared by Jones oxidation followed by lithium aluminum hydride reduction of **2a–2e**.
(10) Silverstein, R. M.; Bassler, C. G.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; pp 260–264.
(11) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

Polymerization of Ethylene by an Alkylidene Hydride Catalyst

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In spite of the fact that transition-metal-catalyzed polymerizations of ethylene and propylene were discovered more than 25 years ago, surprisingly little is known about the most important step in the polymerization reaction, the mechanism of forming the carbon–carbon bond.[1] There is overwhelming evidence that the polymerization process consists of what is overall "insertion" of an olefin into a metal–alkyl bond or, perhaps more accurately, migration of the alkyl to a coordinated olefin. Yet a nagging question is why do the vast majority of *isolable* metal alkyl complexes not react with ethylene readily, while many which are presumably prepared in situ (using a main-group alkylating agent) react rapidly to produce ethylene oligomers or polymers? We report here what we believe to be the first example of a well-characterized ethylene polymerization catalyst, one that happens to be slow enough so that polymer-chain growth can be monitored and that does not require a Lewis Acid cocatalyst. The fact that the catalyst is an alkylidene hydride complex should justify a reevaluation of the possible mechanisms for polymerizing ethylene and propylene.

Tantalum neopentylidene hydride complexes have been prepared by reducing tantalum(V) neopentyl complexes by two electrons.[2] We discovered that although one of these, $Ta(CHCMe_3)(H)L_3Cl_2$

(1) Boor, John, Jr. "Ziegler–Natta Catalysts and Polymerizations"; Academic Press: New York, 1979.
(2) Fellmann, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608.

0002-7863/82/1504-2331$01.25/0