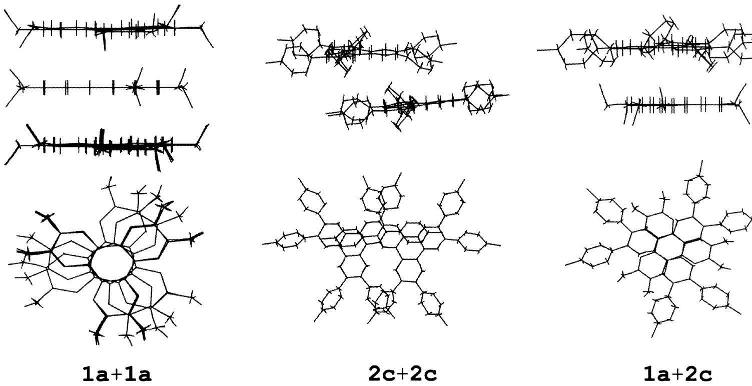

Figure 4. The elevation and plan views of the XED minimum energy dock of two molecules for a system which forms a stable mixture with **1b**. Left: **1b** + **1b**; middle: **3c** + **3c**; right: the mixture **1b** + **3c**.

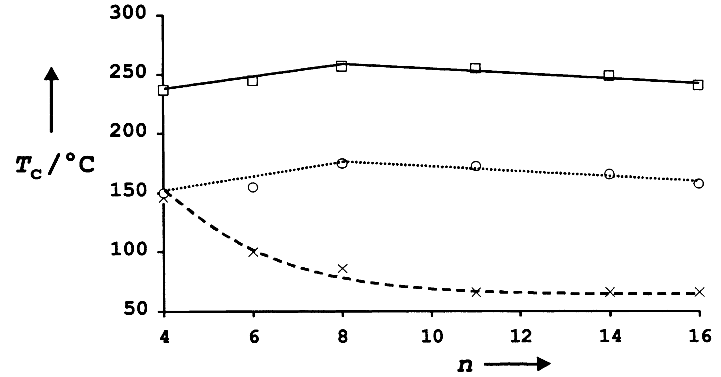

Figure 5. The trends in clearing temperature T_c for binary mixtures of the large core molecules (**2a** and **3a**) with discogen **1*n*** as a function of chain length *n*, measured by DSC and OPM. Upper line (——) = **1*n*** + **2a**; middle line (••••) = **1*n*** + **3a**; lower line (- - - -) = **1*n*** alone.

component, presumably corresponding to the same optimum packing. This stabilizing effect vanishes in those systems where the side chains are too long and no stable mixtures are obtained, or even predicted, for the systems **1a** + **2b** or **1a** + **3b** (**1b** + **2d**, **1b** + **3d**) in which the number of side-chain (x + y) is doubled to twelve. Hence, although the XED – CPI approach seems to be the only way to rationalize the stability of these mixtures, the packing of side chains is also important.

These mixtures not only provide a novel way of designing π-stacked systems but, from the standpoint of some applications, these particular systems are attractive. For example, mixtures obtained in this way are better photoconductors, with higher charge mobilities (for example, the mobility is $\sim 0.02\ \mathrm{cm^2V^{-11}s^{-11}}$ for **3a** + **1*n*** ($n = 11$)) than the discotic liquid crystal **1*n*** alone (**1*n*** ($n = 11$) is $3 \times 10^{-4}\ \mathrm{cm^2V^{-11}s^{-11}}$).[12] This enhanced mobility begins to approach the highest known values for discotic liquid crystals ($0.1\ \mathrm{cm^2V^{-11}s^{-11}}$).[13]

Received: December 14, 1999
Revised: April 13, 2000 [Z14395/Z14397]

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Rhodium – Rhodium Bonds in Edge-Sharing Coplanar Dinuclear Complexes**

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Dinuclear rhodium(II) complexes typically have face-to-face structures with both rhodium atoms in pseudooctahedral or pseudo-square-pyramidal environments. The rhodium – rhodium bond is systematically perpendicular to the two faces, which are disposed in eclipsed or staggered conformations.[1] These characteristics are found in complexes ranging from the large family of lantern complexes with four bridging ligands $[\mathrm{Rh_2}(\mu\text{-bridge})_4(\mathrm{L})_n]$ up to the cationic complex $[\mathrm{Rh_2(NCMe)_{10}}]^{4+}$ with no bridging ligands.[1c] Analogous rhodium – rhodium bonds are even formed in complexes in which the bridging ligands prevent face-to-face structures.[1d] Here we describe unprecedented dinuclear rhodium(II) complexes with a bond between two metal atoms in coplanar square-planar environments and an unusually low electron count of 30 valence electrons.

New starting materials with bulky $\mathrm{P}t\mathrm{Bu_2}^-$ ligands can be obtained by circumventing the inertness of known phosphido rhodium(I) complexes. In contrast to the partial replacement of 1,5-cyclooctadiene (COD) in $[\{\mathrm{Rh}(\mu\text{-PPh_2})_2(\mathrm{cod})\}_2]$ by

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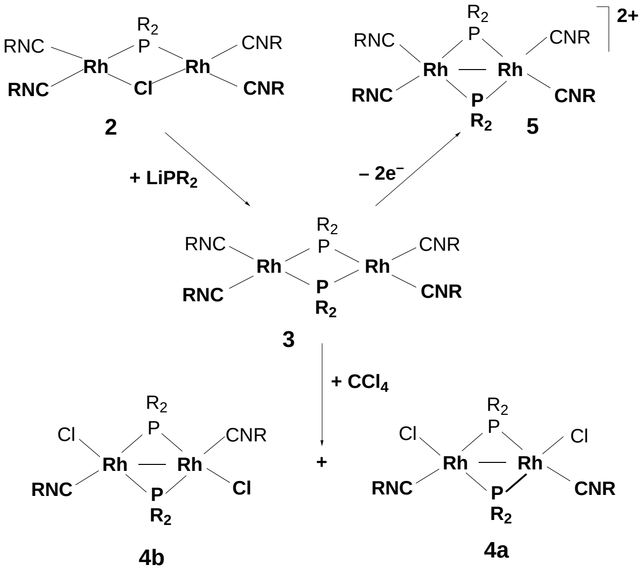
[**] Generous financial support from DGES (Projects PB98-641, PB95-318, and PB94-1186) and a fellowship (to M.S.) are gratefully acknowledged.

monodentate phosphanes,[2] the complete replacement of the diolefin in [{Rh(cod)}$_2$(μ-P*t*Bu$_2$)(μ-Cl)] (**1**)[3] by CN*t*Bu takes place smoothly to give the dinuclear complex [{Rh(CN*t*Bu)$_2$}$_2$(μ-P*t*Bu$_2$)(μ-Cl)] (**2**) in good yield. Complex **2** lacks a metal–metal bond, as revealed by the high-field chemical shift of the triplet ($\delta = 16.2$, $J_{P,Rh} = 100$ Hz) in the ^{31}P{^{1}H} NMR spectrum,[4] and the metal environments are square-planar, since the two signals observed for the CN*t*Bu groups in the ^{1}H NMR spectrum correspond to ligands *trans* to the P donor and Cl ligands (Scheme 1). Moreover, complexes **1** and **2** show distinct behavior with respect to the replacement of the chloride ligand. Whilst the cyclooctadiene complex **1** does not react with LiP*t*Bu$_2$ under prolonged reflux in THF, the isocyanide complex **2** reacts smoothly with equimolar amounts of LiP*t*Bu$_2$ in diethyl ether to give the new dinuclear bis-phosphido rhodium complex **3** (Scheme 1). Orange solutions of **3** in dichloromethane contain a single species with a planar Rh$_2$P$_2$ framework and no rhodium–rhodium bond. No changes in the ^{31}P{^{1}H} NMR spectrum were observed on varying the temperature in the range of −80 to 25°C, and therefore the geometric isomerization process involving exchange of the coordination sphere of one metal center from square-planar to tetrahedral that was reported for the related isoelectronic rhodium(I) complex [{Rh(μ-P*t*Bu$_2$)(CO)$_2$}$_2$][5] can be ruled out for **3**.



Scheme 1. Structural formulas of the new compounds and their transformations. R = *t*Bu.

Complex **3** reacts slowly with chloroform to give a red solution containing several complexes, which evolve into two major species over one day. Both compounds, **4a** and **4b** (Scheme 1), contain a rhodium–rhodium bond, as evidenced by the low-field chemical shift of the ^{31}P{^{1}H} NMR signals. Complex **4a** exhibits two triplets of doublets at $\delta = 431.6$ ($J_{P,Rh} = 89$, $J_{P,P} = 14$ Hz) and $\delta = 417.1$ ($J_{P,Rh} = 85$, $J_{P,P} = 14$ Hz), while **4b** shows a multiplet at $\delta = 399.7$, which corresponds to the AA′ part of an AA′XX′ spin system. Further evolution of this mixture at room temperature leads exclusively to **4b** after six days. At this point, the IR spectrum shows a single $\tilde{\nu}$(CN) band at 2160 cm^{-1}. Complex **4b** was obtained in one day by carrying out the reaction in carbon tetrachloride under argon at room temperature. Evaporation of the red solutions in chloroform or carbon tetrachloride and crystallization of the crude product from benzene/*n*-hexane gave red crystals (70% yield of isolated product) of the diamagnetic dirhodium(II) complex **4b**. Most probably, the intermediate **4a** is the *cis* isomer according to the above-described ^{31}P{^{1}H} NMR spectrum, since the phosphorus nuclei are inequivalent.

Complex **4b** was studied by single-crystal X-ray diffraction, and its novel structure is shown in Figure 1.[6] Excluding the intermetallic interaction, each metal atom is in a square-planar coordination environment and is bonded to two P*t*Bu$_2$ bridging ligands, a chloride ion, and a *t*BuNC group. The presence of a crystallographic inversion center makes the Rh$_2$P$_2$ core strictly planar; the angle between this plane and that defined by the remaining ligands (calculated through Rh, Cl, and C(9)) is 5.3(2)°. Apart from the coplanarity of the metal coordination planes, the most interesting feature of this complex is the short intermetallic distance of 2.7583(6) Å. This short distance suggests the existence of a Rh–Rh bond, as do the ^{31}P{^{1}H} NMR data, and is similar to the bond lengths in the two polymorphs of the square-planar/tetrahedral rhodium(I) complex [{Rh(μ-P*t*Bu$_2$)(CO)$_2$}$_2$] of 2.7609(9) and 2.748 Å, for which a rhodium–rhodium bond was postulated.[5a, 7] For comparison, the square-planar/square-planar isomer of this tetracarbonyl dimer, which does not have an intermetallic bond, has a metal–metal distance of 3.717(1) Å.[5a] In the former isomer the formation of the metal–metal bond was associated with the above-mentioned change of the coordination sphere of one metal center from square-planar to tetrahedral, whereas the intermetallic bond in **4** results from chemical oxidation of the metal centers. The only related example is the recently reported platinum(III) complex [{Pt(μ-PPh$_2$)(C$_6$F$_5$)$_2$}$_2$], which has a Pt–Pt bond length of 2.7245(7) Å.[8]

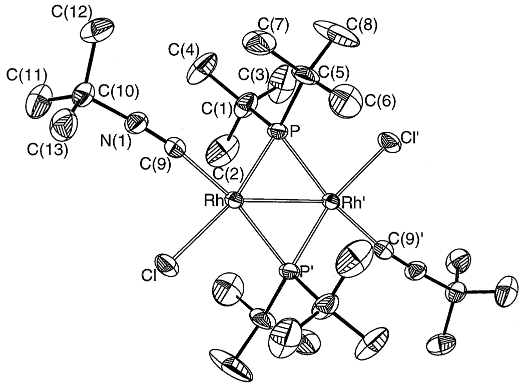


Figure 1. Molecular structure of **4b** (hydrogen atoms omitted; primed atoms are related to the unprimed ones by an inversion center). Selected bond lengths [Å] and angles [°]: Rh-Rh′ 2.7583(6), Rh-P 2.2168(10), Rh-P′ 2.2705(10), Rh-Cl 2.3962(10), Rh-C(9) 1.992(4); P-Rh-P′ 104.15(3), P-Rh-Cl 167.22(4), P-Rh-C(9) 88.67(11), P′-Rh-Cl 88.00(4), P′-Rh-C(9) 166.92(11), Cl-Rh-C(9) 79.41(11), Rh′-Rh-P 52.96(3), Rh′-Rh-P′ 51.20(3), Rh′-Rh-Cl 139.02(3), Rh′-Rh-C(9) 141.55(11), Rh-P-Rh′ 75.85(3).

In the search for additional complexes with this unusual structure, we realized that the reaction of **3** with chloroform or carbon tetrachloride to give **4** implies a formal oxidation of the metal centers and the removal of two CN*t*Bu ligands. Therefore, we investigated the potential generalization of this process by chemical oxidation of dirhodium(I) complexes. Thus, complex **3** was treated with [FeCp$_2$]OTf (OTf = trifluoromethanesulfonate) in 1:2 molar ratio in acetone. Upon mixing, the dark blue color of [FeCp$_2$]OTf faded almost immediately to give an orange solution. After evaporating the acetone and washing the crude product with diethyl ether, the residue was recrystallized from dichloromethane/diethyl ether to give orange crystals of [{Rh(μ-P*t*Bu$_2$)(CN*t*Bu)$_2$}$_2$](OTf)$_2$ (**5**) in 90 % yield. Spectroscopic data for **5**, especially the triplet at $\delta = 450.4$ ($J_{\text{P,Rh}} = 86$ Hz) in the ^{31}P{^{1}H} NMR spectrum, suggest a structure similar to that of **4b**, and thus the validity of this synthetic approach is confirmed.

The molecular structure of the dinuclear complex cation of **5** (Figure 2)[9] is very similar to that of the neutral complex **4b**. The cation also has a crystallographic inversion center at the midpoint of the Rh$_2$P$_2$ rhombus and a short intermetallic distance (2.7403(9) Å). Both metal centers have slightly distorted square-planar environments; the deviations from ideal square-planar coordination could be related to the dihedral angle between the Rh$_2$P$_2$ planar core and the plane through the terminal ligands [6.7(2)°, calculated through Rh, C(9), and C(14)].

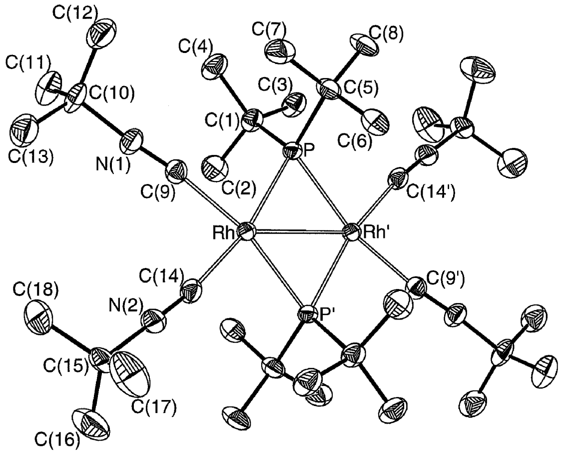


Figure 2. Molecular structure of the complex cation of **5** (hydrogen atoms omitted; primed atoms are related to the unprimed ones by an inversion center). Selected bond lengths [Å] and angles [°]: Rh-Rh' 2.7403(9), Rh-P 2.2764(10), Rh-P' 2.2744(10), Rh-C(9) 1.987(4), Rh-C(14) 1.996(4), P-Rh-P' 105.95(3); P-Rh-C(9) 85.64(11), P-Rh-C(14) 166.82(10), P'-Rh-C(9) 167.22(11), P'-Rh-C(14) 86.89(10), C(9)-Rh-C(14) 81.88(15), Rh'-Rh-P 52.94(3), Rh'-Rh-P' 53.01(3), Rh'-Rh-C(9) 138.27(10), Rh'-Rh-C(14) 139.80(10), Rh-P-Rh' 74.05(3).

The short metal–metal distances in **4b** and **5**, together with the diamagnetism of the complexes, clearly indicate some kind of Rh–Rh bonding. However, the way in which this spin pairing takes place is not completely clear, since two possibilities are conceivable. One is through a "direct" metal–metal σ bond, as suggested by density functional theory (DFT) calculations on the related diplatinum(III) complex.[8] However, the alternative "through-ring" bonding proposed by Alvarez et al.[10] should not be excluded, since both **4b** and **5** have a framework electron count (FEC) of six.

In conclusion, the combination of the bulky anionic P*t*Bu$_2^-$ ligands and the good σ donor CN*t*Bu promotes the formation of unprecedented coplanar square-planar dirhodium(II) complexes with a metal–metal bond.

Received: February 3, 2000 [Z14644]

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[6] Crystal data for **4b**·2 C$_6$H$_6$: $C_{26}H_{54}Cl_2N_2P_2Rh_2 \cdot 2\,C_6H_6$, $M_r = 889.59$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.4245(10)$, $b = 15.2523(14)$, $c = 12.5443(10)$ Å, $\beta = 99.369(10)°$, $V = 2156.7(3)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.370$ g cm^{-3}, $F(000) = 924$, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\mu(\text{Mo}_{K\alpha}) = 0.990$ mm^{-1}. Data were collected on a Siemens–Stoe AED2 diffractometer on a dark red crystal (0.44 × 0.30 × 0.22 mm). Of the 3865 reflections collected by $\omega/2\theta$ scans ($4 \leq 2\theta \leq 50°$), 3682 were unique ($R_{\text{int}} = 0.0235$) and 2844 observed with $I \geq 2\sigma(I)$. A Ψ scan absorption correction gave min./max. transmission factors of 0.6699/0.8117. The structure was solved by direct methods (A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined by full-matrix least-squares methods on F^2 for all reflections (G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**). Final agreement factors were $R_1 = 0.0334$ (observed reflections) and $wR_2 = 0.0687$ (all data) for 230 parameters; GOF: 1.014. Largest peak and hole in the final difference map: 0.701 and −0.447 e Å^{-3}.[9b]

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[9] a) Crystal data for **5**: $C_{38}H_{72}F_6N_4O_6P_2Rh_2S_2$, $M_r = 1126.88$, triclinic, $P\bar{1}$ (no. 2), $a = 10.752(2)$, $b = 11.3754(19)$, $c = 12.061(3)$ Å, $\alpha =$

63.021(10), $\beta = 82.579(14)$, $\gamma = 89.386(14)^\circ$, $V = 1301.7(5)$ Å^3, $Z = 1$, $\rho_{\text{calcd}} = 1.438\,\text{g}\,\text{cm}^{-3}$, $F(000) = 582$, $\lambda = 0.71073$ Å, $T = 293(2)$ K, $\mu(\text{Mo}_{\text{K}\alpha}) = 0.840\,\text{mm}^{-1}$. Data were collected on a Siemens–Stoe AED2 diffractometer on an orange crystal ($0.26 \times 0.25 \times 0.04$ mm). Of the 7336 reflections collected by $\omega/2\theta$ scans ($4 \leq 2\theta \leq 50^\circ$), 4586 were unique ($R_{\text{int}} = 0.0320$) and 4270 observed with $I \geq 2\sigma(I)$. Data were corrected for absorption (Gaussian face-indexed method) with min./max. transmission factors of 0.8113/0.9672. Structure solution and refinement were as described for **4b**. Final agreement factors were $R_1 = 0.0362$ (observed reflections) and $wR_2 = 0.0760$ (all data) for 296 parameters; GOF 1.024; largest peak and hole in the final difference map 0.737 and $-0.440\,\text{e}\,\text{Å}^{-3}$, respectively; b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-139639 (**4a**) and CCDC-139640 (**4b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Synthesis of Chiral, Enantiopure Zirconocene Imido Complexes: Highly Selective Kinetic Resolution and Stereoinversion of Allenes, and Evidence for a Stepwise Cycloaddition/Retrocycloaddition Reaction Mechanism**

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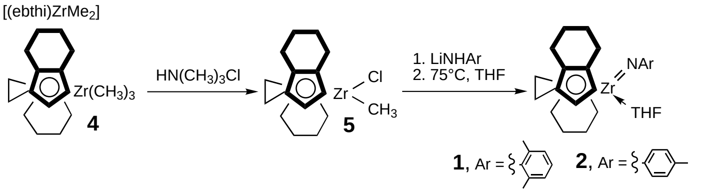
Richard A. Andersen,* and Robert G. Bergman*

Certain metal–carbon multiple bonds exhibit substantial reactivity toward organic compounds and are important intermediates in many catalytic processes.[1] The analogous reactivity of metal–heteroatom multiple bonds, such as those in metal–imido complexes, has been known for a much shorter time and has only relatively recently been utilized in synthetic applications.[2]

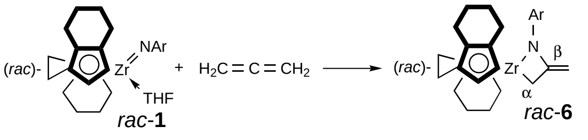
We wish to report a series of highly enantioselective reactions using isolable imido complexes with reactive metal–nitrogen double bonds.[3–9] These involve the reactions of enantiopure (ebthi)(L)Zr=NR complexes with 1,3-disubstituted allenes (L = tetrahydrofuran; ebthi = bis(tetrahydroindenyl)ethane). Our observations a) demonstrate the operation of a general and highly selective kinetic resolution, b) provide the first example of a reaction that can be used to selectively invert the absolute configuration of one (symmetrically or unsymmetrically 1,3-disubstituted) allene enantiomer within a racemic mixture, and c) provide strong mechanistic evidence for the stepwise nature of an organometallic cycloaddition reaction.

Previous work in our laboratories has shown that zirconocene–imido complexes undergo cycloaddition reactions with a wide range of unsaturated organic molecules including alkynes,[10] imines,[11] and certain alkenes.[12] Several of these reactions are important steps in catalytic transformations (for example, hydroamination or imine metathesis) mediated by the imido compounds. To extend this chemistry to systems capable of enantioselective reactions, we decided to examine the reactions of chiral disubstituted allenes with zirconium imido complexes bearing the C_2-symmetric ebthi ligand developed by Brintzinger.[13] The chiral imido complexes were synthesized in two steps from the known dimethyl complex **4**, as shown in [Eq. (1)].[14]



(1)

In order to investigate the products and diastereoselectivity of the chiral zirconocene–allene reactions, we first examined the stoichiometric reactions of racemic ebthi complexes **1** and **2** with achiral allenes and racemic chiral 1,3-disubstituted allenes. The purple metallacycle *rac*-**6** was formed rapidly upon condensation of allene onto a benzene solution of *rac*-**1** [Eq. (2)]. Production of an azametallacycle with the exocyclic methylene group in the β (as opposed to the α) position was indicated by its ^{1}H, ^{1}H NOESY spectrum, which featured a strong NOE between one of the exocyclic methylene protons and the methyl groups on the phenyl ring.



(2)

The reaction of *rac*-**1** with 1 equiv of racemic 1,3-diphenylallene, 3,4-heptadiene, 4,5-nonadiene, or 1,2-cyclononadiene at 23 °C provided a single diastereomeric product in each case, as determined by ^{1}H and ^{13}C NMR spectra ([Eq. (3)]). A bulky imido substituent is required for the selectivity in these transformations, as an 85:15 mixture of diastereomers was formed from the reaction of the *p*-tolylimido complex *rac*-**2** with diphenylallene. These results were encouraging because they suggested that the reactions are stereospecific: (*S*,*S*)-**1**

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[**] This work was supported by the US National Institutes of Health (grant no. GM-25459 to R.G.B.). Z.K.S. acknowledges a fellowship from the Chevron Co. We are grateful to Dr. Jeffrey S. Johnson and Mr. Stephen R. Jenkins for experimental assistance and helpful discussions, Prof. David MacMillan and his co-workers for extensive assistance with chiral gas chromatography, and Boulder Scientific Co. for a gift of *rac*-(ebthi)ZrCl$_2$.