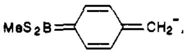
Table I. Summary of B–C Bond Lengths (Å) and C–B–C Bond Angles (deg) in Selected Mes_2BX Species[a]

	B–C(Mes)	B–C	C(Mes)–B–C(Mes)	C(Mes)–B–C	ref
$Mes_2BCH_2^-$, **3**	1.617 (7)	1.444 (8)	117.3 (5)	121.3 (5)	this work
, **1**	1.609 (2)	1.522 (10)	111.6 (6)	124.2 (7)	2
$Mes_3B^{\bullet -}$	1.597 (4)		120.0 (2)		5
Mes_2BCH_3, **2**	1.586 (3)	1.562 (3)	119.5 (2)	120.2 (2)	*b*
Mes_3B	1.579 (2)		120.0 (2)		5

[a] Average values are given where applicable. [b] P. P. Power and R. A. Bartlett, unpublished results.

average of 1.444 Å. The C_2BCH_2 core of the molecule is also planar with an essentially zero twist angle. This is in contrast to **1** which has a 25° twist angle between the planes at boron and carbon.[2] The BCH_2 bond length in the title compound is significantly shorter than the multiple bond in the ion **1** and also the ca. 1.5-Å distance found in the aromatic 2π-electron [cyclobutadiene]$^{2+}$ analogue[10] $Me_2N\overline{B-C(t\text{-}Bu)-B(NMe_2)-C}(t\text{-}Bu)$.[11] If a B–C double bond is assumed to be ca. 10% shorter than a B–C single bond, a value of 1.42–1.45 Å may be predicted for the B=C moiety, assuming a typical B–C single bond length (for three-coordinate boron) to be in the range 1.58–1.62 Å. The average distance of 1.444 Å in **3** is therefore consistent with a double bond formulation and in agreement with theoretical calculations.[12] Further supporting evidence for double bonding comes from the lowered CBC and HCH angles, which average 117° and 112°, respectively. A similar effect is seen in the structures of alkenes[13] (>C=C<), which, of course, are isoelectronic with the moiety [>B=C<]$^-$.[14] Trends in bonding are further illustrated in Table I where it can be seen that increasing bond order in one of the B–C bonds causes a regular decrease in the bond order of the remaining B–C bonds. The boron–carbon double bond in **3** may also be compared with that recently found by Nöth and co-workers in the compound tmpB=fluorenyl, **4**.[15] In **4** the B–C distance, 1.414 (3) Å, is slightly shorter than that in **3**. This is to be expected due to the two-coordinate nature of boron in **4**.

Finally, we draw attention to the trend in ^{11}B NMR chemical shifts on the deprotonation of Mes_2BMe to give **3**. A THF solution of Mes_2BMe displays a broad singlet at +83.6 ppm. The addition of 1 equiv of $LiN(C_6H_{11})_2$ in THF affords a new signal at +40.4 ppm due, presumably, to the solvated ions $[Li^+][Mes_2BCH_2]$. The addition of 2.2 equiv of 12-crown-4 to this solution results in a small upfield shift to +35.0 ppm. The upfield shifts[16] indicate increased electron density at boron due to the formation of the double bond. In addition the small (but significant) shift seen upon addition of 12-crown-4 seems to indicate that the $[Li]^+$ and $[Mes_2BCH_2]^-$ ions are associated in some way in THF solution in the absence of 12-crown-4. Further studies on the structures of related B–C double bonded species are in progress.

Acknowledgment. We thank Rasika Dias for experimental assistance and the National Science Foundation for financial support.

Supplementary Material Available: Details of data collection and refinement, and tables of atom coordinates and thermal parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (15 pages). Ordering information is given on any current masthead page.

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(14) A [>B=C<]$^-$ moiety should also be capable of behaving as an η^2 ligand to transition metals like ethylenes. An example of such a complex, $[Ir(H)_2(PMe_3)_3[BC_8H_{14}CH_2]]$, has been synthesized and characterized spectroscopically. Baker, R. T., personal communication.

(15) tmp = 2,2,6,6-tetramethylpiperidine. Glaser, B.; Nöth, H. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 416. This reference contains the spectroscopic characterization of this compound. We are grateful to Professor Nöth for providing us with some details of his recent structural determination of this interesting species. Nöth, H. "Symposium on Multiple Bonding Involving the Heavier Main Group Elements", 192nd National Meeting of the American Chemical Society, Anaheim, Sept 7–12, 1986; American Chemical Society: Washington, DC.

(16) Similar upfield shifts were seen in the ^{11}B NMR spectra of $[Mes_2BPR]^-$ (R = Ph, C_6H_{11}, or Mes) relative to their neutral Mes_2BPHR precursors. However, little change was observed except a broadening of the peaks when 12-crown-4 was added. Likewise their ^{31}P NMR spectra showed considerable downfield shifts when metalated and further downfield shifts when 12-crown-4 was added. See also: Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817.

Asymmetric Induction in the Formal Iron-Catalyzed [4 + 4] Ene Reaction: The Highly Diastereoselective Cross-Coupling of 1,3-Dienes to Chiral Cyclic Acetals

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The design of new transition-metal catalysts for asymmetric organic synthesis has proven to be a challenging but nonetheless exceptionally powerful approach to the problem of controlling absolute stereochemistry.[1-3] We have recently reported the chemo- and regioselective formal [4 + 4] ene and 1,4-hydrovinylation reactions of 1,3-dienes with allyl benzyl ether catalyzed by soluble iron(0) complexes, L·Fe(0).[4] We now wish to report the first examples in which a remote stereocenter, specifically a remote acetal substituent, is used to direct the stereochemical course of the carbon–carbon bond construction in an L·Fe(0)-catalyzed [4 + 4] ene reaction.

Homochiral five- and six-membered-ring acetal subunits have been widely used as removable chiral auxiliaries to direct diastereoselective carbon–carbon bond-forming reactions.[5] While the

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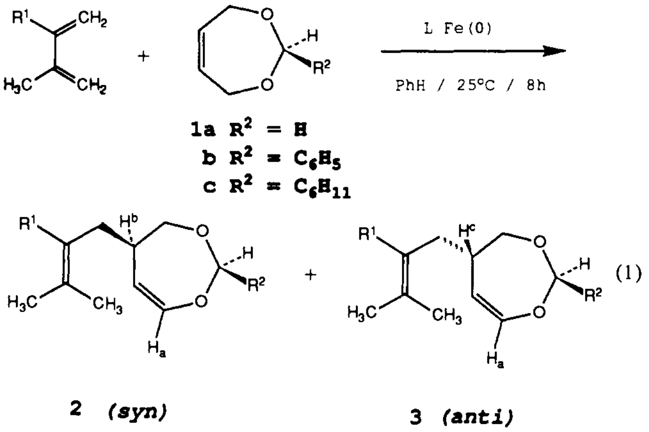
chemistry of the 1,3-dioxacyclohept-5-ene (4,7-dihydro-1,3-dioxepin) ring system has been widely investigated, the use of this seven-membered-ring acetal as a chiral template for asymmetric synthesis is unknown.[6] In part, this lack of utility reflects the failure of classical electrophilic reagents to distinguish between the diastereotopic faces of the olefin within this ring system. For example, hydroboration/oxidation ((1) $BH_3 \cdot THF$ or 9-BBN, THF, 25 °C; (2) H_2O_2/OH^-) of 2-phenyl-1,3-dioxepin (**1b**) yields a 60:40 (cis/trans) mixture of diastereomeric alcohols.

In the course of exploring the scope of our new L·Fe(0)-catalyzed [4 + 4] ene reactions, we made the observation that unlike some 3-substituted allylic ethers (e.g., (*E*)-1-(benzyloxy)-2-butene, (*E*)- or (*Z*)-2-butene-1,4-diol dibenzyl ether) 1,3-dioxepins are good substrates for *bimolecular* coupling reactions with 1,3-dienes. For example, the parent 4,7-dihydro-1,3-dioxepin (**1a**) reacts with 2,3-dimethyl-1,3-butadiene in the presence of 10 mol % of the bpy·Fe(0) catalyst (bpy = 2,2′-bipyridine, benzene, 25 °C, 8 h, 45%) to yield the 6-substituted 6,7-dihydro-1,3-dioxepin **2a**. 6,7-Dihydro-1,3-dioxepins can be converted via Lewis acid catalyzed rearrangement or via simple hydrolysis to tetrahydrofurans or 2-furanones, subunits which are found in many natural products,[7]



1a R^2 = H
b R^2 = C_6H_5
c R^2 = C_6H_{11}

(1)

2 *(syn)* **3** *(anti)*

Dioxepins **1a–c** exist as equilibrium mixtures of rapidly interconverting chair and twist boat conformers.[8,9] In the chair conformer we reasoned that the axially disposed oxygen lone pairs could be serving as remote ligation sites for the metal, thereby facilitating the reaction of these substrates. The accessible chair conformer of 2-substituted dioxepins **1b** and **1c** has the alkyl group preferentially occupying a pseudoequatorial position. We postulated that the axially disposed lone pairs might not only facilitate the reaction of these substrates but also direct the stereochemical course of the carbon–carbon bond construction syn relative to the acetal substituent. The bpy·Fe(0)-catalyzed reactions of **1b** and **1c** with 2,3-dimethyl-1,3-butadiene proceed readily and with high diastereoselectivity (>95:5) to yield (70–80%) the [4 + 4] ene product **2** (eq 1, $R^1 = CH_3$, $R^2 = C_6H_5$, C_6H_{11}). The carbon–carbon bond formation proceeds almost exclusively syn with respect to the alkyl substituent of the acetal stereocenter.[10]

The choice of ligand is critical in determining the sense and degree of diastereoselection in this process. Coupling reactions promoted by L·Fe(0) catalysts modified with 1,10-phenanthroline or with 4,4′-dimethyl-2,2′-bipyridine yield **2** and **3** in approximately an 80:20 ratio. Reactions run in the presence of an iron catalyst modified by 2,2′-biquinoline or 2,9-dimethyl-1,10-phenanthroline (dmph) show a reversal in the sense of asymmetric induction. These coupling reactions proceed with a slight preference for formation of the anti stereoisomer **3** (**2**;**3** = 40:60). The L·Fe(0)-catalyzed [4 + 4] ene reactions of **1b** with 2-substituted 1,3-dienes (e.g., isoprene, myrcene) are qualitatively similar to those described above. Each unsymmetrically substituted diene reacts with high regioselectivity (>95:5); however, we find that the stereoselectivity is somewhat lower than with dimethylbutadiene. For example, the coupling of dioxepin **1b** to isoprene catalyzed by bpy·Fe(0) yields (60%) an 80:20 mixture of [4 +

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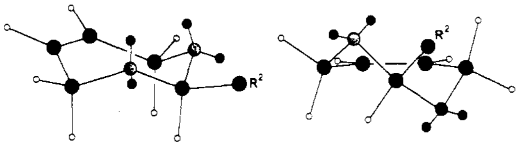
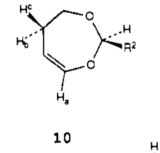
(9) We have estimated the relative energies of chair and twist boat conformers **4** for compounds **1**, **5**, and **6** by using MM2 calculations. The MM2 calculated (chair–twist boat) energy differences (kcal/mol) are: **1a**, +0.20; **1b**, +0.03; **1c**, –0.80; **5a**, –0.17; **5** ($R^1 = CH_3$, $R^2 = C_6H_5$), +0.25; and **6** ($R^1 = CH_3$), +1.70.

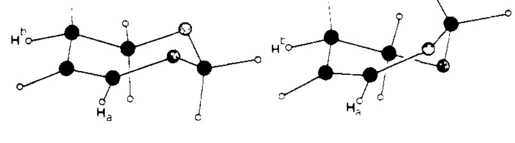


CHAIR-4 TWIST BOAT-4

(10) (a) Product ratios are determined by ^1H NMR integration. We assign a limiting value of >95:5 in cases where the resonances of the minor diastereomer cannot be distinguished from baseline noise. The stereochemical assignments of **2**, **3**, **7**, **8**, and **9** are based upon a consideration of the available conformations, detailed analysis of the 300-MHz ^1H NMR spectra, and by spectral comparison to the model compound, the unsubstituted 6,7-dihydro-1,3-dioxepin **10** (R = C_6H_5, C_6H_{11}). In particular, key to our stereochemical assignment is the presence or absence of an allylic coupling to the vinyl proton, Ha. By MM2 calculation the chair and twist boat conformers are close in energy in these ring systems. Considering either the chair or twist boat conformer **10**, only Hc has the correct angular relationship to Ha to exhibit strong allylic coupling, giving a stereochemical handle to which the other stereocenters can be easily related.



10

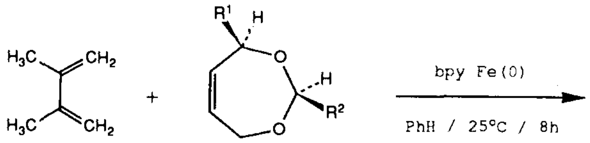


CHAIR-10 TWIST BOAT-10

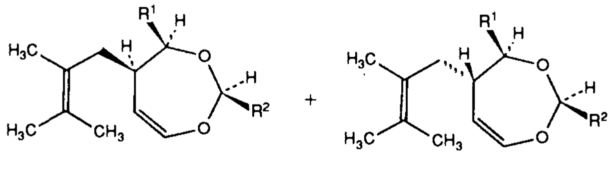
(b) Jackman, L. M.; Sternhell, S. "International Series of Monographs in Organic Chemistry", *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: New York, 1969.

4] ene products **2** and **3** (R^1 = H, R^2 = C_6H_5). The isoprene reaction catalyzed by dmph·Fe(0) is also slightly more anti selective, yielding a 30:70 syn/anti mixture.

While the parent acetals **1** are achiral, homochiral 2,4-disubstituted 1,3-dioxepins can be easily prepared by starting with the asymmetric reduction of an appropriate propargylic ketone.[11] Acetalization of 2-substituted *cis*-1,4-but-2-ene diols with benzaldehyde dimethyl acetal yields a thermodynamic mixture of *cis*- and *trans*-phenyl acetals.[12] The 56:44 mixture of diastereomers **5** and **6** (R^1 = C_2H_5 or CH_2Ph, R^2 = Ph) can be separated by chromatography on silver nitrate impregnated silica gel and the unwanted isomer reequilibrated to the thermodynamic mixture. Each of the phenyl acetal diastereomers **5** and **6** reacts with 2,3-dimethyl-1,3-butadiene in the presence of bpy·Fe(0) to yield (40–60%) a [4 + 4] ene product, **7** and **9**, respectively (eq 2 and 3). Each coupling reaction proceeds highly diastereoselectively

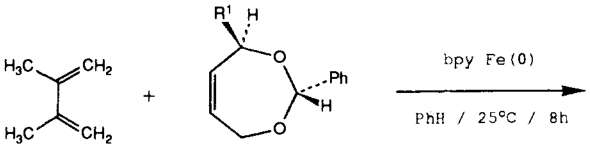


5a R^1 = C_2H_5, R^2 = Ph
b R^1 = CH_2Ph, R^2 = Ph
c R^1 = C_2H_5, R^2 = H

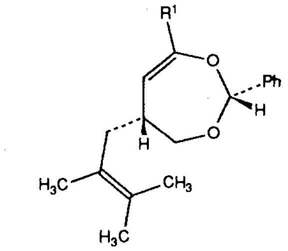


(2)

7 **8**



6a R^1 = C_2H_5, R^2 = Ph
b R^1 = CH_2Ph, R^2 = Ph



(3)

9

(>95:5), with the isomeric all-cis [4 + 4] ene products **7** and **9** differing only with respect to the regiochemistry of carbon–carbon bond formation. Most significantly, the stereochemistry of carbon–carbon bond construction proceeds independent of the stereochemistry of the substituent (R^1) at the 4-position of the 1,3-dioxepin ring and is directed greater than 95% syn with respect to the remote phenyl substituent. The acetal substituent is critical to the asymmetric induction. In contrast to the reactions of **5a** and **5b**, the bpy·Fe(0)-catalyzed reaction of the unsubstituted acetal **5c** (R^1 = C_2H_5, R^2 = H) proceeds in poor yield (10%) and with low stereoselectivity to give a 2:3 mixture of **7c** and **8c**.

Further studies of the effect of remote substituents on the stereochemistry of this new carbon–carbon bond-forming reaction and on the applications of this methodology to asymmetric synthesis are in progress.[13]

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[12] The energy difference between the lowest energy conformers of **5** and **6** is estimated by MM2 to be +0.10 kcal/mol, consistent with the slight thermodynamic preference for formation of the cis diastereomer. The structural assignments of **5** and **6** are based upon the detailed analysis of the 300-MHz ^1H NMR spectra and from NOE experiments. In an NOE difference experiment (irradiating the acetal proton), the methine hydrogen in **5**, but not in **6**, shows a strong signal enhancement, confirming the cis relationship between those two protons.

[13] We thank the National Institutes of Health (GM 34927), the donors of Petroleum Research Fund, administered by the American Chemical Society, and the University of Utah Research Committee, for support of this work.

The Synthesis, Reactions, and Molecular Structure of Zirconocene–Alkyne Complexes

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Transition metal complexes of alkynes have been reported for a large number of metals, including examples of both early and late transition metals.[1] We have recently reported the preparation and reaction chemistry of the zirconocene complexes of cyclohexyne[2a] and benzyne.[2b] We have now developed a general route to zirconocene complexes of both terminal and internal acyclic alkynes and herein we report on their synthesis and reactions. In addition we have determined the X-ray crystal structure of the trimethylphosphine adduct of the zirconocene complex of 1-hexyne **2b** which shows several interesting differences in structure from the cyclohexyne and benzyne complexes and which is, to our knowledge, the first structurally characterized acyclic alkyne complex of zirconium to be reported.

Zirconocene alkyne complexes can be prepared as shown in Scheme I. Hydrozirconation of an alkyne[3] followed by the addition of methyllithium produces intermediate **1** which loses methane,[4] and the resulting alkyne complex is trapped with trimethylphosphine. These complexes can be isolated in ca. 70% yield and can be further purified by recrystallization from ether/hexane at low temperature.

The X-ray crystal structure of **2b** is shown in Figure 1. Of note is the C6–C7–C8 bond angle of 135.8 (3)°. This should be compared with the corresponding angles of 126.0 (1.2)° and 122.1

Scheme I