2 H), 0.97 (d, J_{HH} = 6.1 Hz, CHCH_3).

(z) ***trans*- and *cis*-1-Acetoxy-1,2-dimethylcyclopropanes.** *cis*-1-Acetoxy-1,2-dimethylcyclopropane: ^{1}H NMR ($CDCl_3$, 25 °C) δ 0.20 ppm (m, 1 H), 0.90-1.10 (m, 2 H), 1.05 (d, CH_3CH), 1.43 (s, CH_3COC(O)-), 1.95 (s, COCH_3).

trans-1-Acetoxy-1,2-dimethylcyclopropane: ^{1}H NMR (C_6D_6, 25 °C) δ 0.36 ppm (m, 1 H), 0.53 (m, 1 H), 0.65 (m, 1 H), 1.05 (d, J_{HH} = 7.0 Hz, CH_3CH), 1.43 (s, 3 H, CHCOC(O)-), 1.64 (s, COCH_3).

(aa) ^{1}H NMR Shift Experiments on *trans*- and *cis*-1-Acetoxy-2-methylcyclopropanes and *trans*- and *cis*-1-Acetoxy-1,2-dimethylcyclopropanes. *trans*-1-Acetoxy-2-methylcyclopropane (5.2 mg) collected by GC was dissolved in 0.5 mL of C_6D_6. Addition of 28 mg of (+)-Eu(hfc)$_3$ resulted in baseline separation of the signals of the OC(O)CH_3 group for each enantiomer. The OC(O)CH_3 signal for (1*S*,2*R*)-*trans*-1-acetoxy-2-methylcyclopropane shifted to 8.27 ppm (major), and the OC(O)CH_3 signal for (1*R*,2*S*)-*trans*-1-acetoxy-2-methylcyclopropane shifted to 8.12 ppm.

cis-1-Acetoxy-2-methylcyclopropane (2.9 mg) collected by GC was dissolved in 0.5 mL of $CDCl_3$. Addition of 36mg of (+)-Eu(hfc)$_3$ resulted in baseline separation of the signals of the CH_3 groups for each enantiomer. The CH_3 signal for (1*R*,2*R*)-*cis*-1-acetoxy-2-methylcyclopropane shifted to 3.53 ppm (doublet), and the CH_3 signal for (1*S*,2*S*)-*trans*-1-acetoxy-2-methylcyclopropane shifted to 3.46 ppm (doublet).

Similar results were obtained on the *trans*- and *cis*-1-acetoxy-1,2-dimethylcyclopropanes by using the shift reagent (+)-Eu(hfc)$_3$.

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Investigation of the Stereochemistry of Fe-C_α Bond Cleavage When Phenylcyclopropane Is Generated by γ-Ionization of Stereospecifically Deuterated $C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$ Complexes. A Transition-State Model for Transfer of the Carbene Ligand from $C_5H_5(CO)_2Fe{=}CHR^+$ to Alkenes

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Abstract: $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, **4**, and stereospecifically deuterium labeled *threo*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, **7a,b** and *erythro*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, **8a,b** were synthesized. Treatment of compound **4** with trimethylsilyl triflate results in ionization of the γ-methoxy group and formation of phenylcyclopropane in good yields. Ionization of **7a,b** gives a 1:1 mixture of *cis*-2,*cis*-3-dideuterio- and *trans*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropane, while ionization of **8a,b** gives *cis*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropane. These results established that the cyclopropane ring is formed by backside attack of electrophilic C_γ on C_α with net inversion of stereochemistry at C_α. These reactions serve as models for the reactions of carbene complexes $C_5H_5(CO)_2Fe{=}CHR^+$ with alkenes to give cyclopropanes and suggest that in the transfer reactions Fe-C_α is cleaved with inversion.

Introduction

The carbene ligands of electrophilic iron-carbene complexes of the general type $C_5H_5(CO)(L)Fe{=}CRR'^+$ can be transferred to alkenes to generate cyclopropanes.[1] The initial stage of the transfer reaction involves attack of electrophilic C_α of the iron complex on the alkene to generate positive charge at C_γ. Several studies support this contention,[1a,2-4] the most compelling of which is the demonstration that the reaction of $C_5H_5(CO)_2Fe{=}CHCH_3^+$ with *p*-methoxystyrene generates a γ-benzyl carbocation intermediate, $C_5H_5(CO)_2FeCH(CH_3)CH_2C^+(H)(C_6H_4OCH_3)$, prior to formation of cyclopropane products.[3]

Shown in Scheme I are two mechanisms for attack of electrophilic C_γ on C_α which result in generation of the cyclopropane through C_γ-C_α bond formation and Fe-C_α bond cleavage. One involves frontside attack of the electrophilic C_γ at the Fe-C_α bond and cleavage with retention of C_α stereochemistry.[5] The second involves backside attack of C_γ on Fe-C_α and cleavage with inversion of C_α stereochemistry. The plausibility of the inversion mechanism was initially noted by us[6] based on analogy with solvolysis of γ-Sn derivatives in which the Sn-C_α bond is cleaved with inversion at C_α.[7] This mode of cleavage is suggested by a combination of stereochemical and relative reactivity studies on

(1) For a complete tabulation of references concerning carbene transfer reactions of iron-carbene complexes, see: (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) References 1-5 in the preceding paper in this issue.

(2) Brookhart, M.; Liu, Y. *Advances in Metal Carbene Chemistry*; Schubert, U.; Kluwer Academic Publishers: 1989; pp 251-270.

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(4) Relative rates of the reactions of $Cp(CO)_2Fe{=}CHCH_3^+$ with a series of para-substituted styrenes have been examined, and a good σ^+-ρ correlation was observed with $\rho = -2.2$ which implies that substantial positive charge buildup at C_γ in the transition state: Kegley, S. E. Ph.D. Dissertation, 1982, University of North Carolina.

(5) A concerted frontside closure cannot be stereochemically distinguished from formation of an Fe(IV) metallacyclobutane intermediate followed by reductive elimination.

(6) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

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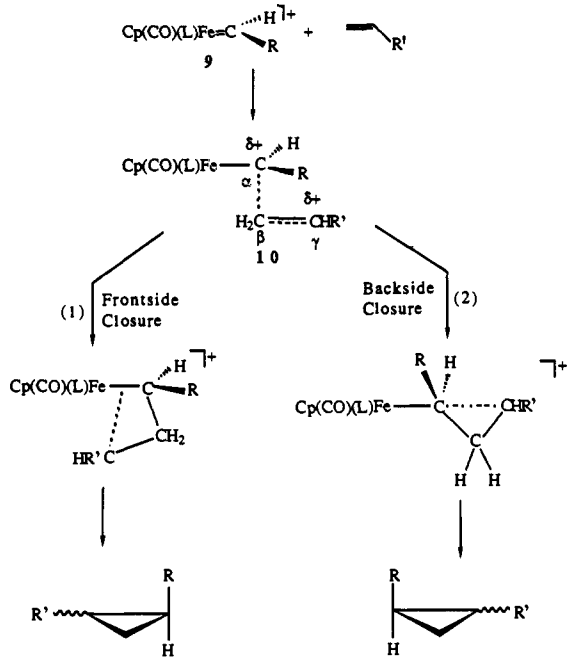
Scheme I



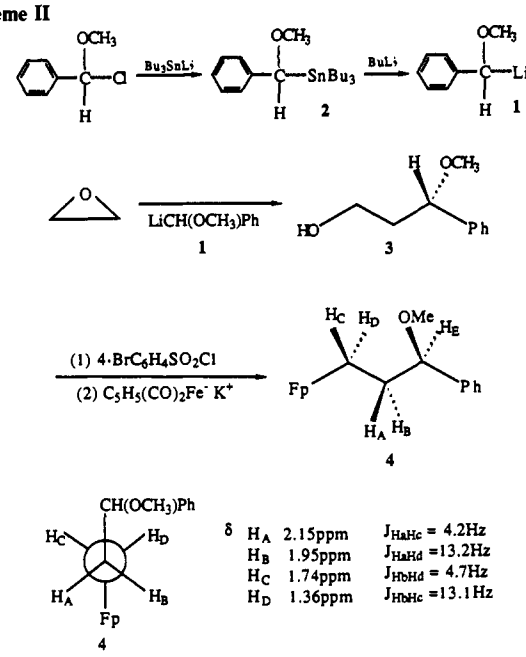
chiral systems of the type $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$. These results, which are summarized in the preceding paper in this issue,[8] suggest transfer occurs through reaction of alkenes with the minor but more reactive synclinal isomers of $C_5H_5(CO)(PR_3)Fe{=}CHCH_3^+$ followed by backside attack of electrophilic C_γ on C_α and cleavage with inversion.

As a definitive test of the stereochemistry of the Fe–C_α bond cleavage, we report here the stereochemical results of the ionization of γ-iron derivatives stereospecifically deuterium labeled at C_α and C_β. Specifically we have examined the reactions of *threo*- and *erythro*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$ with trimethylsilyl triflate to give stereospecifically labeled 2,3-dideuterio-1-phenylcyclopropanes. The generation of cyclopropanes from ionization of γ-iron derivatives was first reported by Casey[9] who showed that cyclopropane is produced from the reaction of $C_5H_5(CO)_2FeCH_2CH_2CH_2Br$ with Ag^+. A preliminary communication on results reported here has appeared.[10] Casey has reported a similar stereochemical investigation by using stereospecifically labeled $C_5H_5(CO)_2FeCHDCHDCH_2S(Ph)(CH_3)^+$.[11]

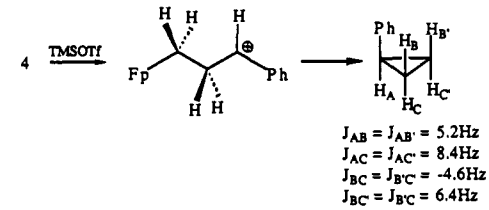
Results and Discussion

Synthesis of $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, 4. The γ-methoxy iron derivative, $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, **4**, was synthesized as shown in Scheme II. $LiCH(OCH_3)C_6H_5$, **1**, was generated in situ by treatment of $Bu_3SnCH(OCH_3)Ph$, **2**, with *n*-butyllithium at −78 °C.[12] Ethylene oxide was condensed into the solution of α-lithio ether **1** at −78 °C, and after workup 3-methoxy-3-phenylpropan-1-ol, **3**, was purified by column chromatography. Alcohol **3** was converted to the corresponding brosylate, and $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, **4**, was formed by displacement of brosylate with $C_5H_5(CO)_2Fe^-K^+$. This reaction occurs with inversion at carbon in close analogy to the stereochemistry previously demonstrated in the reaction of $C_5H_5(CO)_2Fe^-K^+$ with stereospecifically labeled brosylate $BsOCHDCHDC(CH_3)_3$.[13] ^1H NMR spectra of compound **4** are well-resolved, and the chemical shifts and coupling

Scheme II



Scheme III



constants are listed in Scheme II. Assignments are verified by observation of expected J_{HH} values and $\{^1H,^1H\}$ COSY 2D NMR spectra.[14]

Generation of Phenylcyclopropane by γ-Ionization of $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, 4. Compound **4** was treated with trimethylsilyl triflate at −78 °C in CH_2Cl_2 and allowed to warm to room temperature overnight. Phenylcyclopropane (75%) was isolated by preparative GC. A well-resolved ^1H NMR spectrum of phenylcyclopropane was obtained, and precise chemical shifts and coupling constants were determined by decoupling techniques and confirmed by spectral simulation. While phenylcyclopropane is formed via ionization of the γ-methoxy group and attack of electrophilic C_γ at C_α, it is not possible to specify whether ionization and C_α–C_γ bond formation are synchronous or whether a discrete benzylic carbocation is formed prior to Fe–C_α bond cleavage. For simplicity in Scheme III and mechanistic schemes which follow, a discrete carbocation is illustrated.

Synthesis of *threo*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, 7a,b, and *erythro*-$d_2$-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, 8a,b. Similar to the preparation of unlabeled **4**, *threo*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, **7a,b**, and *erythro*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, **8a,b**, were prepared as shown in Scheme IV. The *cis*-dideuterio- and *trans*-dideuterioethylene oxides[15] were prepared via conversion of *cis*- and *trans*-dideuterioethylene[16] to *threo*- and *erythro*-dideuteriobromohydrins followed by base-induced closure to ethylene oxides. The yields for dideuteriobromohydrins and dideuterioethylene oxides were much improved by modification of previously reported reaction conditions and workup procedures. Treatment of *trans*-dideuterioethylene oxide and α-lithio ether **1** produces *erythro*(*anti*)-d_2 alcohols **5a,b** (80%). Similarly, *cis*-dideuterioethylene oxide leads to *threo*(*syn*)-d_2 alcohols **6a,b** (75%). Mass spectral analysis shows **5a,b** and **6a,b** to have greater than 95%

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(14) See supplementary material for complete NMR spectra.
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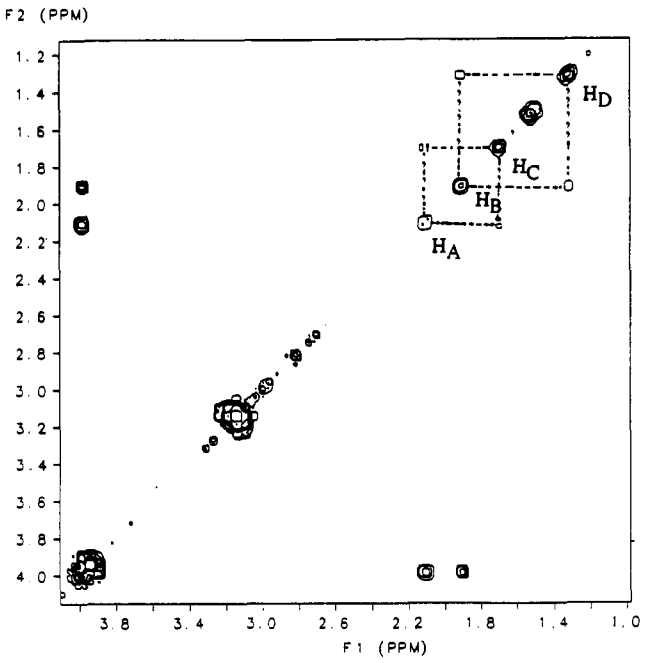


Figure 1. {^{1}H,^{1}H} COSY 2D NMR spectrum of **7a,b**.

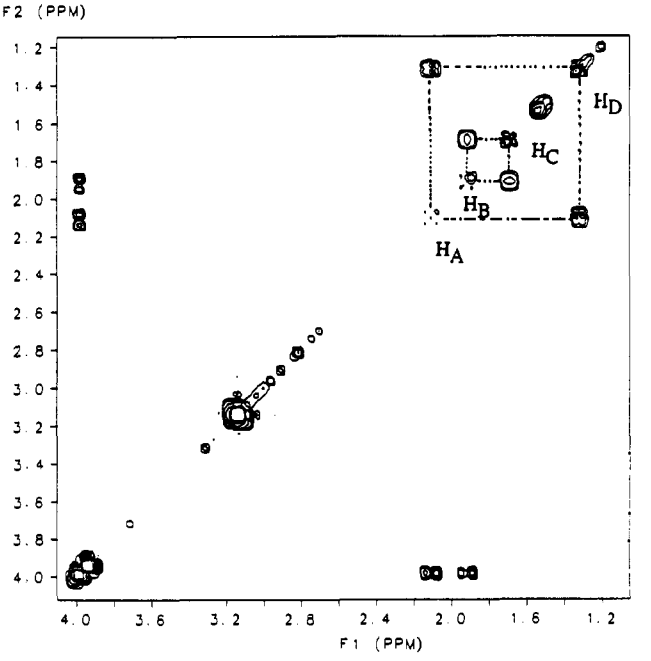
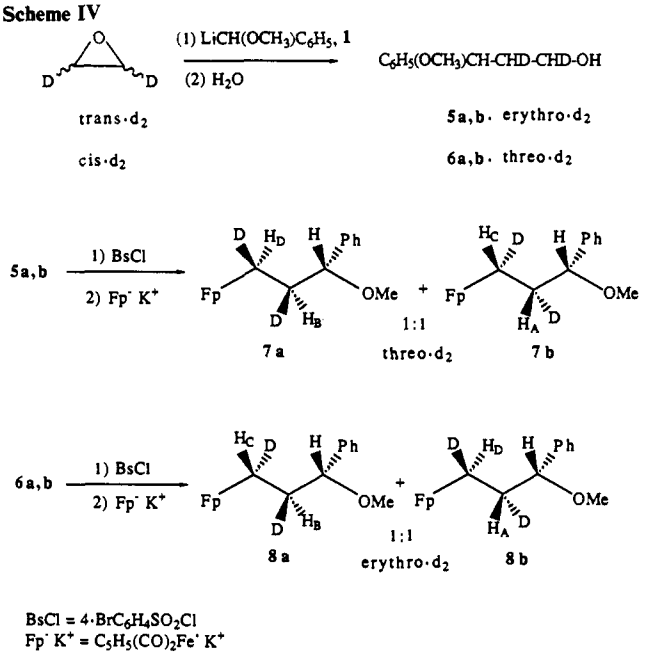
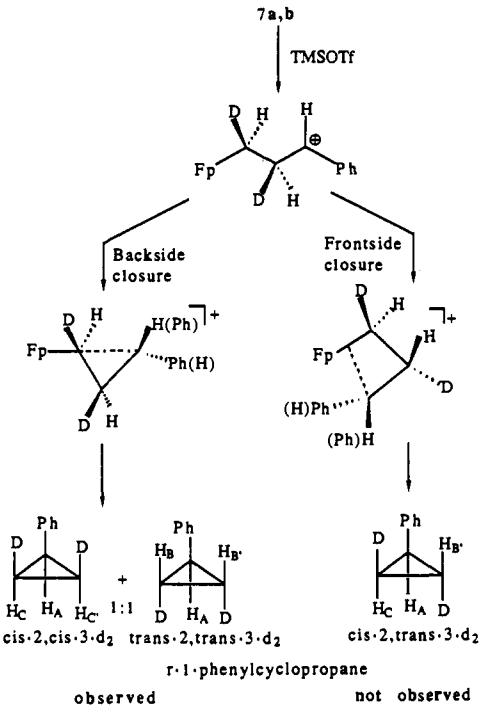


Figure 2. {^{1}H,^{1}H} COSY 2D NMR spectrum of **8a,b**.

Scheme IV



Scheme V



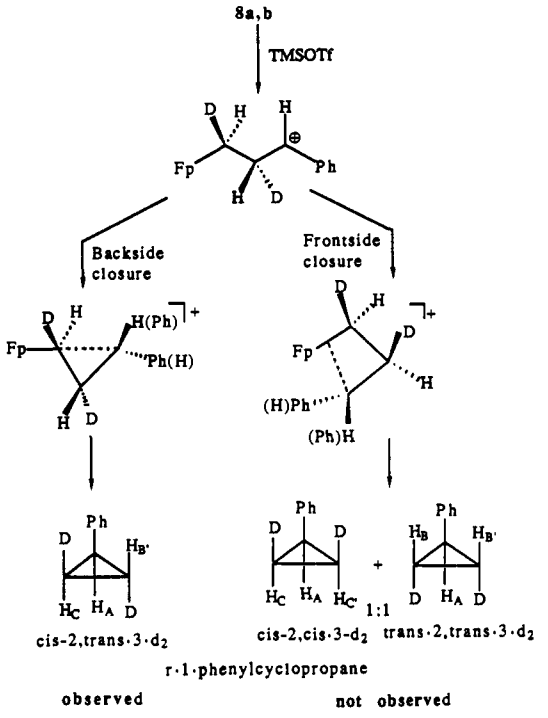
d_2 incorporation. Conversion of **5a,b** and **6a,b** to brosylates followed by S_N2 displacement using $C_5H_5(CO)_2Fe^-K^+$ yields **7a,b** and **8a,b**, respectively (60%).

The stereochemistry of each step had literature precedent,[13] and the expected configurations of **7a,b** and **8a,b** were verified by ^{1}H NMR and {^{1}H,^{1}H} COSY 2D NMR experiments. In **7a,b**, the {^{1}H,^{1}H} COSY 2D NMR spectrum (Figure 1) shows that H_A correlates with H_C and H_B with H_D. H_A and H_C appear as doublets with $J(H_AH_C)$ = 4.2 Hz, and H_B and H_D appear as doublets with $J(H_BH_D)$ = 4.7 Hz verifying structures **7b** and **7a**, respectively. In **8a,b**, the {^{1}H,^{1}H} COSY 2D NMR spectrum (Figure 2) shows that H_A correlates with H_D and H_B with H_C. H_A and H_D appear as doublets with $J(H_AH_D)$ = 13.2 Hz, and H_B and H_C appear as doublets with $J(H_BH_C)$ = 13.1 Hz establishing structures **8b** and **8a**, respectively.

Ionization of *threo*-d_2-$C_5H_5(CO)_2$FeCHDCHDCH-$(OCH_3)C_6H_5$, 7a,b, and *erythro*-$d_2C_5H_5(CO)_2$FeCHDCHDCH-$(OCH_3)C_6H_5$, 8a,b to give Dideuteriophenylcyclopropanes. Formation of dideuteriophenylcycolopropanes by ionization of **7a,b** and **8a,b** was carried out by addition of TMS-OTf (1.0 equiv) to CH_2Cl_2 solutions of **7a,b** and **8a,b** containing triethylamine (0.1 equiv) at −78 °C followed by warming to 25 °C overnight. The crude dideuteriophenylcyclopropanes were purified by preparative GC; yields were determined to be 70–75% by use of an internal standard.

As illustrated in Scheme V, the *threo*-d_2 isomers, **7a,b**, yield a 1:1 mixture of *cis*-2,*cis*-3-dideuterio- and *trans*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropanes. The configurations of deuterium-labeled phenylcyclopropanes are readily assigned by ^{1}H NMR analysis. Decoupling of H_A applied to the 1:1 mixture of *cis*-2,*cis*-3-dideuterio- and *trans*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropanes results in the H_C, $H_{C'}$ and H_B, $H_{B'}$ signals appearing as sharp singlets. Decoupling of H_B, $H_{B'}$ of 1:1 mixtures results in simplification of H_A to a singlet (overlapped with H_A of the other isomer) while H_C, $H_{C'}$ are not affected.[14]

Scheme VI



cis-2,*trans*-3-Dideuterio-*r*-1-phenylcyclopropane was generated by ionization of the *erythro*-d_2 isomers **8a,b** (as shown in Scheme VI). *cis*-2,*trans*-3-Dideuteriophenylcyclopropane can be distinguished from other isomers by ^{1}H NMR analysis by using decoupling techniques. Upon decoupling H_A in *cis*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropane, $H_{B'}$ and H_C become doublets. Upon decoupling $H_{B'}$, H_A and H_C were simplified from broad doublets of doublets to clean doublets.[14]

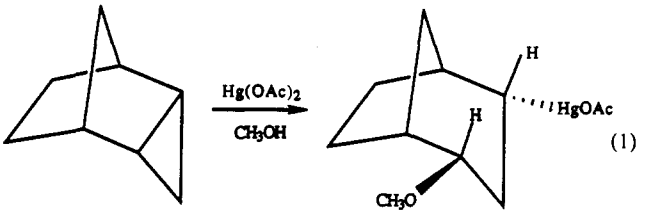
The deuterium-labeling patterns observed are consistent only with cyclopropane ring formation by backside attack of electrophilic C_γ on C_α with net inversion of stereochemistry at C_α (mechanism 2 in Scheme I). Frontside attack of C_γ on the Fe–C_α bond and cleavage with retention of configuration leads to converse labeling results.

Summary

When phenylcyclopropanes are generated by γ-ionization of *threo*-d_2- and *erythro*-d_2-$C_5H_5(CO)_2$FECHDCHDCH-$(OCH_3)C_6H_5$, cleavage of the Fe–C_α bond occurs with inversion of configuration of C_α. On the basis of the fact that γ-benzyl carbocations have been demonstrated to be intermediates in ethylidene transfer reactions from $C_5H_5(CO)_2Fe{=}CHCH_3^+$ to *p*-methoxystyrene,[3] the transition state for this γ-ionization and ring closure is clearly a good model for the transition state for the carbene transfer reaction. Thus, these observations combined with earlier results lead to a detailed mechanistic description of the carbene transfer reaction. The electrophilic iron carbene, **9**, attacks the alkene to generate an electrophilic center at C_γ. In cases where C_γ possesses a strongly electron-donating group, a stabilized carbocation intermediate is formed with sufficient lifetime to allow C_γ–C_β bond rotation.[3] The developing (or full)[17] γ-carbocation then attacks the Fe–C_α bond at the backside such that C_α stereochemistry is inverted. When substituted carbene complexes of the type $C_5H_5(CO)(L)Fe{=}CHR^+$ are employed, the transfers proceed primarily via the less stable but more reactive synclinal isomers as opposed to the major anticlinal isomers. In the case of enantiomerically pure systems $C_5H_5(CO)(L)Fe^*{=}CHR^+$, the absolute stereochemistry and high enantiomeric excesses of the cyclopropane products are completely consistent with reaction through the synclinal isomers via mechanism 2. A more detailed description of the transfer mechanism is presented in the preceding paper in this issue.[8]

The results described here and the analogous results obtained by Casey[11] using γ-iron derivatives are closely related to investigations of ionizations of γ-derivatives of main group elements. Results of studies of the formation of cyclopropanes from ionization of γ-Sn,[7,18] γ-Si,[19] and γ-B[20] derivatives suggest that inversion occurs at C_α through transition states similar to those described here. A counterexample is the demonstration by Grubbs[21] that thermolysis of stereospecifically deuterium-labeled $Cp_2Ti(I)CH_2CH(R)CH_2I$ leads to cyclopropane formation with retention at C_α. This reversal in stereochemistry may suggest a radical rather than an ionic pathway.

Electrophilic cleavage of cyclopropane rings (formally the reverse reaction) often follows a similar stereochemical course to the reactions observed here. For example, Lambert[22] demonstrated by using specifically deuterated cyclopropane that bromination led to 1,3-dibromopropane with inversion of stereochemistry at both the sites of electrophilic and nucleophilic attack. Recently, Coxon[23] showed that cleavage of *endo*-tricyclo[3.2.1.$0^{2,4}$]octane with mercuric acetate in methanol led to only 4-*endo*-(acetoxymercurio)-2-*endo*-methoxybicyclo[3.2.1]octane (eq 1).



(1)

Experimental Section

General Methods. General procedures used were identical with those described in the preceding paper in this issue.[8] In addition, {^{1}H,^{1}H} COSY 2D NMR spectra were recorded on a Varian XL 400 NMR spectrometer, and mass spectrometric analysis was conducted on a VG70-250SEQ high resolution mass spectrometer. Bis(tributyltin) was obtained from Aldrich and used without purification.

$PhCH(OCH_3)SnBu_3$, 2. A solution of 19.1 g of bis(tributyltin) (32.9 mmol) in 70 mL of THF at 0 °C was treated with 13.2 mL (33.0 mmol) of a 2.5 M *N*-butyllithium solution (hexane) and was stirred at 0 °C for 20 min. The light yellow solution was cooled to −78 °C, and 6.0 g (38.3 mmol) of $PhCH(OCH_3)Cl$[24] was added. The solution was stirred at −78 °C for 1.5 h before workup. Petroleum ether (200 mL) and 50 mL of water were added to the −78 °C solution, and the mixture was warmed to 25 °C. The water layer was extracted twice with petroleum ether, and the organic layer was dried over anhydrous Na_2SO_4. The $PhCH(OCH_3)SnBu_3$, **2**, was separated by column chromatography (silica gel) by using petroleum ether (bp 35–60 °C) as eluent. The 8.6 g (64% yield) of $PhCH(OCH_3)SnBu_3$, **2**, was obtained after evaporating the solvent of the second band and was characterized by the following data: ^{1}H NMR (25 °C, $CDCl_3$) δ 4.59 ppm (−C*H*(OCH_3), s with ^{119}Sn sidebands, *J*(HSn) = 31.6 Hz), 3.29 (−OC*H*$_3$, s), 7.25 (H_m(−Ph), dd, $J(H_mH_o)$ = 8.0 Hz, $J(H_mH_p)$ = 7.2 Hz), 7.09 (H_o(−Ph), d, $J(H_mH_o)$ = 8.0 Hz), 7.04 (H_p(−Ph), t, $J(H_mH_p)$ = 7.2 Hz), 1.38, 1.24, and 0.84 (*n*-Bu−, multi-

(17) A concerted process cannot be distinguished from a mechanism involving a discrete γ carbocation with insufficient lifetime to allow C_γ–C_β bond rotation prior to C_α–C_γ bond formation.

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plets); ^{13}C NMR (25 °C, $CDCl_3$) δ 81.2 ppm (-*C*H(OMe)), 59.2 (-O-*C*H_3) (28.9, 27.4, 13.7, and 9.1 (*C*H_3*C*H_2*C*H_2*C*H_2-), 144.8 (C_{ipso} in C_6H_5), 128.3, 124.5, and 123.8 (-C_6H_5). Elemental anal. Calcd for $C_{20}H_{36}OSn$ (mw = 411.20): C, 58.42; H, 8.82. Found: C, 58.37; H, 8.99.

$C_6H_5CH(OCH_3)CH_2CH_2OH$, 3. A solution of 8.6 g (20.9 mmol) of $PhCH(OCH_3)SnBu_3$, **2**, in 50 mL of THF at -78 °C was treated with 8.4 mL (21.0 mmol) in 2.5 M *N*-butyllithium solution (hexane). An orange solution of $LiCH(OCH_3)Ph$, **1**, was formed and stirred for 10 min at -78 °C. Excess ethylene oxide (10 mL) was condensed into the orange solution of $LiCH(OCH_3)Ph$, **1**. After stirring 30 min at -78 °C, 30 mL of water was added to quench the reaction. THF was evaporated, and alcohol **3** was extracted into petroleum ether. The crude material was separated by column chromatography on silica gel. Tetrabutylstannane was eluted with petroleum ether (bp 35-60 °C) and alcohol **3** was collected by elution with acetone. After drying and solvent removal pure alcohol **3**, 2.2 g (63% yield), was obtained: ^1H NMR (25 °C, $CDCl_3$) δ 4.39 ppm (H_C(OMe), dd, $J(H_CH_E)$ = 4.2 Hz, $J(H_CH_D)$ = 8.8 Hz), 3.78 (C(H_B)$_2$OH, q, $J(H_BH_A)$ = $J(H_BH_E)$ = $J(H_BH_D)$ = 5.5 Hz), 3.23 (-OCH_3, s), 2.67 (-OH_A, t, $J(H_BH_A)$ = 5.4 Hz, this peak disappears upon addition of D_2O), 2.02 (CH_DH$_E$, multiplet, $J(H_DH_C)$ = 8.1 Hz, $J(H_DH_E)$ = 14.7 Hz, $J(H_DH_B)$ = 5.9 Hz), 1.83 (CH_EH$_D$, multiplet $J(H_EH_D)$ = 14.8 Hz, $J(H_EH_B)$ = 4.9 Hz, $J(H_EH_C)$ = 3.9 Hz), 7.31 (-C_6H_5, multiplet); ^1H NMR (25 °C, C_6D_6/D_2O) δ 4.15 ppm (H_AC-(OCH$_3$), dd, $J(H_AH_E)$ = 4.4 Hz, $J(H_AH_D)$ = 8.8 Hz), 3.65 (H_BC(OH), ddd, $J(H_BH_C)$ = 10.9 Hz, $J(H_BH_E)$ = 6.4 Hz, $J(H_BH_D)$ = 4.5 Hz), 3.54 (H_CC(OH), ddd, $J(H_CH_B)$ = 11.2 Hz, $J(H_CH_D)$ = 7.2 Hz, $J(H_CH_E)$ = 4.0 Hz), 1.97 (H_DCCH(OCH$_3$), multiplet, $J(H_DH_E)$ = 14.2 Hz, $J(H_DH_A)$ = 8.7 Hz, $J(H_DH_C)$ = 7.4 Hz, $J(H_DH_B)$ = 4.4 Hz), 1.64 (H_ECCH(OCH$_3$), multiplet, $J(H_EH_D)$ = 15.0 Hz, $J(H_EH_B)$ = 6.6 Hz, $J(H_EH_C)$ = 4.2 Hz, JH_EH_A) = 4.2 Hz), 2.93 (-OCH_3, s), 7.2 (-C_5H_5, multiplet); ^{13}C NMR (25 °C, $CDCl_3$) δ 83.9 ppm (-*C*H(OMe)), 61.2 (-O*C*H$_3$), 56.7 ppm (*C*H$_2$OH), 40.4 (-*C*H$_2$-), 141.5 (C_{ipso} in C_6H_5), 127.8, 128.5, and 126.5 ppm (C_p, C_m, and C_o in C_6H_5). Elemental anal. Calc for $C_{10}H_{14}O_2$ (mw = 166.22): C, 72.26; H, 8.49. Found: C, 72.29, H, 8.50. The {^1H,^1H} COSY 2D NMR spectrum was recorded.[14]

$C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)Ph$, 4. A 2.5 M *N*-butyllithium solution in hexane (2.6 mL, 6.5 mmol) was added to a solution of 1.06 g (6.38 mmol) of alcohol **3** in 15 mL of Et_2O at 0 °C. A dark yellow solution formed and was stirred at 0 °C for 15 min before addition of 1.63 g (6.38 mmol) of 4-bromobenzenesulfonyl chloride. The mixture was allowed to warm to 25 °C and further stirred for 1 h. The white solid of lithium chloride was separated by filtration through Celite and washed three times with diethyl ether (15 mL each). The ether solution was cooled to -78 °C and transferred into a solution of 1.35 g (6.37 mmol) of $C_5H_5(CO)_2Fe^-K^+$ in 100 mL of THF at -78 °C. The mixture was warmed to room temperature overnight. The solvent was evaporated, the product was dissolved in hexane, and the salt was separated by filtration through Celite. Complex **4** was further purified by column chromatography by using basic alumina of activity II-III and 10:1 hexane/ethyl acetate. The first yellow band was collected. After solvent was removed, compound **4** (1.42 g, 69% yield) was obtained as a yellow oil which solidified after standing in the freezer: ^1H NMR (C_6D_6, 25 °C) δ 3.96 ppm (C_5H_5, s), 3.16 (-OCH$_3$, s), 7.34 (H_o(C_6H_5), d, $JH(H_oH_m)$ = 7.2 Hz), 7.22 (H_m(C_6H_5), triplet, $J(H_mH_o)$ = 7.2 Hz, $J(H_mH_p)$ = 7.6 Hz), 7.11 (H_p(C_6H_5), triplet, $J(H_pH_m)$ = 7.6 Hz), 4.01 (H_E, dd, $J(H_EH_A)$ = 7.2 Hz, $J(H_EH_B)$ = 5.0 Hz), 2.15 ppm (H_A, dddd, $J(H_EH_A)$ = 7.2 Hz, $J(H_AH_D)$ = 13.2 Hz, $J(H_AH_B)$ = 13.1 Hz, $J(H_AH_C)$ = 4.4 Hz), 1.95 (H_B, dddd, $J(H_EH_B)$ = 5.0 Hz, $J(H_BH_D)$ = 5.0 Hz, $J(H_AH_B)$ = 13.1 Hz, $J(H_BH_C)$ = 13.1 Hz), 1.74 (H_C, ddd, $J(H_BH_C)$ = 13.1 Hz, $J(H_CH_D)$ = 8.9 Hz, $J(H_AH_C)$ = 4.0 Hz), 1.36 (H_D, ddd, $J(H_BH_D)$ = 4.4 Hz, $J(H_CH_D)$ = 8.9 Hz, $J(H_AH_D)$ = 13.2 Hz); ^{13}C{^1H} NMR (C_6D_6, 25 °C) δ 85.3 ppm (C_5H_5), 87.5 (-*C*H(OCH$_3$)C_6H_5), 56.6 (-O*C*H$_3$), 47.18 (-*C*H$_2$CH(OCH$_3$)C_6H_5), -1.45 (Fe*C*H$_2$), 218.02 and 217.98 ((*C*O)$_2$), 143.67 (C_{ipso} in C_6H_5), 127.5, 128.6, and 127.1 (C_p, C_m, C_o in -Ph); IR (CH_2Cl_2) ν_{CO} 2003, 1943 cm^{-1}. Elemental anal. Calcd for $C_{17}H_{18}O_3Fe$ (mw = 326.18): C, 62.60; H, 5.56. Found: C, 62.37; H, 5.67. The {^1H,^1H} COSY 2D NMR spectrum of compound **4** was recorded.[14]

***trans*-Dideuterioethylene.** A modified procedure similar to that of Nicholas and Carroll[16] was used. Eighty grams of zinc powder was washed with 100 mL of 1 M HCl for 10 min followed by three water washes. Three hundred and sixty grams of $KCr(SO_4)_2 \cdot 10H_2O$ was added to 500 mL of water together with the zinc powder and stirred overnight. A blue chromium(II) solution was formed. The blue chromium(II) solution was transferred to a flask containing 5.5 L of dideuterioacetylene (1 atm) and stirred overnight. The resulting green aqueous solution was replaced with a freshly made chromium(II) solution (500 mL, made from 140 g of $KCr(SO_4)_2 \cdot 10H_2O$ and zinc powder) and stirred for 6 h. *trans*-Dideuterioethylene was formed as shown by a strong absorbance in the gas-phase IR spectrum at 987 cm^{-1}. No absorbance was observed at 843 cm^{-1} for *cis*-dideuterioethylene.

Modified Procedure for Preparation of 2-Bromoethanol from Ethylene. The procedure for preparation of 2-bromoethanol was modified to improve yields. The reported procedure[15] involves addition of elemental Br_2 and ethylene to a large volume of water simultaneously. Since the solubility of Br_2 in water is low, a large amount of dibromoethane was formed. In the modified procedure, Br_2 was completely dissolved in a large volume of water. The aqueous bromine solution (40 g of Br_2 in about 2 L of water) was slowly transferred to the flask containing 5.5 L of dideuterioethylene (1 atm) (generated from 5.5 L of dideuterioacetylene). The resulting clear aqueous solution was saturated with KCl and extracted numerous times with 100 mL of methylene chloride (30×). The concentrated CH_2Cl_2 solution was dried over anhydrous Na_2SO_4, and 15.9 g (51% yield) of pure 2-bromoethanol was obtained by vacuum distillation.

Modified Procedure for Preparation of Dideuterioethylene Oxide from 2-Bromoethanol. A modified procedure similar to that of Price and Spector[15] was used. In a closed system connected to a series of three liquid nitrogen traps, *threo*-dideuteriobromohydrin (3.3 g) in 15 mL of water was added dropwise to 15 mL of water containing 5.5 g of NaOH and stirred for 10 min at 25 °C. Dideuterioethylene oxide was collected in the series of three liquid nitrogen traps by applying a vacuum at the end of the traps. The *cis*-dideuterioethylene oxide was purified by five successive vacuum transfers which eliminate water. By using this procedure, 1.2 mL (88% yield) of pure *cis*-dideuterioethylene oxide was obtained.

***erythro*-d_2-$C_6H_5CH(OCH_3)CHDCHDOH$, 5a,b.** In a procedure similar to the synthesis of compound **3**, 0.7 mL (13.4 mmol) of *trans*-dideuterioethylene oxide was condensed into a cold orange solution (-78 °C) of $LiCH(OCH_3)Ph$, **1**, generated in situ from 4.9 g (11.9 mmol) of **2** in 50 mL of THF and 4.8 mL (12.0 mmol) of 2.5 M *N*-butyllithium solution (hexane). Compounds **5a,b** (1.6 g, 80% yield) were obtained after separation by column chromatography. ^1H NMR of **5a,b** in C_6D_6/D_2O shows four broad peaks corresponding to H_A, H_B, H_C, and H_D in equal intensity establishing **5a** and **5b** as present in the expected 1:1 mixture. The {^1H,^1H} COSY 2D NMR spectrum demonstrated that compounds **5a,b** were stereospecifically labeled.[14] MS analysis shows **5a,b** to be more than 95% d_2-labeled. ^1H NMR (C_6D_6/D_2O, 25 °C) **5a**, δ 3.62 ppm (broad d, H_B), 1.94 (broad s, H_D), 4.15 (broad d overlapped with H_A of **5b**, H_A); **5b**, δ 3.51 (broad d, H_C), 1.62 (broad s, H_E), 4.15 (broad d overlapped with H_A of **5a**, H_A).

***threo*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)Ph$, 7a,b.** Similar to the synthesis of complex **4**, *erythro*-d_2 alcohols, **5a,b**, 1.10 g (6.54 mmol) in 15 mL of diethyl ether, was converted to brosylates by treatment with 2.7 mL (6.75 mmol) of a 2.5 butyllithium solution (hexane), followed by 1.73 g (6.77 mmol) of 4-bromobenzenesulfonyl chloride. **7a,b** were obtained by treatment of the brosylates with 1.45 g (6.84 mmol) of $C_5H_5(CO)_2Fe^-K^+$ in 100 mL of THF. Pure **7a,b**, 1.32 (61% yield), was obtained after separation by column chromatography. ^1H NMR of **7a,b** in C_6D_6 showed four broad peaks corresponding to H_A, H_B, H_C, and H_D in equal intensity (**7a**:**7b** = 1:1). The {^1H,^1H} COSY 2D NMR spectrum shown in Figure 1 verified that compounds **7a,b** were stereospecifically labeled as expected. ^{13}C NMR spectra of **7a,b** showed that C_α and C_β were deuterium labeled.[14] IR (CH_2Cl_2) ν_{CO} 2003 and 1943 cm^{-1}; ^1H NMR (C_6D_6, 25 °C) **7a**, δ 1.93 ppm (broad s, H_B), 1.33 (broad s, H_D), 4.00 (broad d overlapped with H_E of **7b**, H_E); **7b**, δ 2.13 ppm (broad s, H_A), 1.72 (broad s, H_C), 4.00 (broad d overlapped with H_E of **7a**, H_E). Other signals are the same as those reported for **4**. ^{13}C NMR (C_6D_6, 25 °C) δ -1.83 ppm (t, J_{DC} = 20.6 Hz, Fe*C*HD-), 46.69 t, J_{DC} = 19.3 Hz, Fe*C*H*D*C*H*D-). Other signals are the same as those reported for **4**.

***threo*-D_2-$C_6H_5CH(OCH_3)CHDCHDOH$, 6a,b.** In a procedure similar to the synthesis of compound **3**, 0.9 mL (17.2 mmol) of *cis*-dideuterioethylene oxide was condensed into the orange solution of $LiCH(OCH_3)Ph$, **1**, generated in situ from 4.7 g (11.4 mmol) of **2** in 50 mL of THF and 4.6 mL (11.5 mmol) of 2.5 M *n*-BuLi solution. Compounds **6a,b** (1.5 g, 77% yield) were obtained after separation by column chromatography. ^1H NMR of **6a,b** in C_6D_6/D_2O showed four broad peaks corresponding to H_A, H_B, H_C, and H_D in equal intensity (**6a**:**6b** = 1:1). The {^1H,^1H} COSY 2D NMR spectrum established that **6a,b** were stereospecifically labeled.[14] MS analysis shows **6a,b** to be more than 95% d_2-labeled. ^1H NMR (C_6D_6/D_2O, 25 °C) **6a**, δ 3.61 ppm (broad doublet, H_B), 1.61 (broad s, H_E), 5.15 (broad d overlapped with H_A of **6b**, H_A); **6b**, δ 3.51 ppm (broad doublet, H_C), 1.93 (broad triplet, H_D), 4.15 (broad d overlapped with H_A of **6b**, H_A). Other signals are the same as those reported for **3**.

***erythro*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)Ph$, 8a,b.** Similar to the synthesis of complex **4**, 0.98 g (5.83 mmol) of *threo*-d_2 alcohols, **6a,b**, in 15 mL of diethyl ether was converted to brosylates by treatment with 2.35 mL of 2.5 M *n*-BuLi solution followed by 1.51 g (5.92 mmol) of 4-bromobenzenesulfonyl chloride. **8a,b** were obtained by treatment of

the brosylates with 1.24 (5.85 mmol) of $C_5H_5(CO)_2Fe^-K^+$ in 100 mL of THF. Pure **8a,b**, 1.32 g (61% yield), was obtained after separation by column chromatography. ^1H NMR of **8a,b** in C_6D_6 shows four broad peaks corresponding to H_A, H_B, H_C, and H_D in equal intensity (**8a**:**8b** = 1:1). The $\{^1H,^1H\}$ COSY 2D NMR spectrum shown in Figure 2 demonstrated that **8a,b** were stereospecifically labeled as expected. ^{13}C NMR spectra of **8a,b** showed that C_α and C_β were deuterium-labeled.[14] IR (CH_2Cl_2) ν_{CO} 2001 and 1943 cm^{-1}; ^1H NMR (C_6D_6, 25 °C, decoupling at 4.05 ppm) **8b**, δ 2.18 ppm (d, $J(H_AH_D)$ = 12.7 Hz, FeCHDCH_AD), 1.39 (d, $J(H_DH_A)$ = 12.6 Hz, FeCH_DH–); **8a**, δ 1.99 ppm (d, $J(H_BH_C)$ = 12.9 Hz, FeCHDCH_BD), 1.76 (d, $J(H_CH_B)$ = 12.6 Hz, FeCH_CD–); ^{13}C NMR (C_6D_6, 25 °C) **8a,b**, δ −1.87 ppm (t, J_{DC} = 20.5 Hz, FeCHD–), −1.79 ppm (t, J_{DC} = 20.5 Hz, FeCHD–), 46.67 (t, J_{DC} = 19.4 Hz, FeCHDCHD–), 46.71 (t, J_{DC} = 19.2 Hz, FeCHDCHD–). Other signals are the same as those of **4**.

Generation of Phenylcyclopropane from $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, 4. Trimethylsilyl triflate (0.12 mL, 0.67 mmol), was added to a methylene chloride solution (10 mL, −78 °C) containing 0.20 g (0.61 mmol) of compound **4** and 10 μl (0.07 mmol) of triethylamine. The solution was allowed to warm to 25 °C overnight. The deep red solution was extracted with 50 mL of a saturated aqueous sodium bicarbonate solution and 75 mL of isopentane. The isopentane layer was dried over anhydrous potassium carbonate, and most of the isopentane was distilled off. Nonane (20 μL) was added to the residue. Phenylcyclopropane was isolated by preparative GC, and the yield (75%) was determined by using nonane as an internal standard: ^1H NMR ($CDCl_3$, 25 °C) 1.88 ppm (H_A, tt, $J(H_AH_B)$ = $J(H_AH_{B'})$ = 5.2 Hz, $J(H_AH_C)$ = $J(H_AH_{C'})$ = 7.9 Hz), 0.68 ppm (H_B, $H_{B'}$ (cis to phenyl), ddd, $J(H_BH_C, H_{B'}H_{C'})$ = −4.6 Hz, $J(H_BH_{C'}, H_{B'}H_C)$ = 6.4 Hz, $J(H_AH_B, H_AH_{B'})$ = 5.2 Hz), 0.94 ppm (H_C, $H_{C'}$ (trans to phenyl), ddd, $J(H_CH_A, H_{C'}H_A)$ = 8.4z, $J(H_BH_{C'}, H_{B'}H_C)$ = 6.4 Hz, $J(H_BH_C, H_{B'}H_{C'})$ = 4.5 Hz), 7.24 ppm (H_m(−Ph), dd, $J(H_mH_p)$ = 7.2 Hz, $J(H_mH_o)$ = 7.6 Hz), 7.13 ppm (H_p(−Ph), t, $J(H_mH_p)$ = 7.2 Hz), 7.06 ppm (H_o(−Ph), d, $J(H_mH_o)$ = 7.6 Hz). Experimental ^1H NMR data were confirmed by simulation.[14]

Generation of *cis*-2,*cis*-3-Dideutero and *trans*-2,*trans*-3-Dideuterio-*r*-1-Phenylcyclopropanes from *threo*-d_2-$C_5H_5(CO)_2FeCHDCHDCH(OCH_3)C_6H_5$, 7a,b. As in the ionization of unlabeled **4**, 0.15 mL (0.78 mmol) of trimethylsilyl triflate was added to 10 mL of a methylene chloride solution (−78 °C) containing 0.26 g (0.79 mmol) of **7a,b** and 11 mL (0.08 mmol) of triethylamine. Workup was carried out as previously described. Nonane (20 μL) was added to the residue. The dideuteriophenylcyclopropanes (75% yield) were separated by preparative GC: ^1H NMR ($CDCl_3$, 25 °C) *cis*-2,*cis*-3-dideuteriophenylcyclopropane, δ 0.90 ppm (d, J_{HH} = 8.4 Hz, H_C and $H_{C'}$), 1.88 (broad t, J_{HH} = 8.4 Hz, overlapped with H_A of *trans*-2,*trans*-3-D_2 isomer, H_A); *trans*-2,*trans*-3-dideuteriophenylcyclopropane, δ 0.64 ppm (d, J_{HH} = 4.8 Hz, H_B and $H_{B'}$), 1.88 (broad t, J_{HH} = 4.8 Hz, overlapped with H_A of *cis*-2,*cis*-3-D_2 isomer, H_A). ^1H NMR spectra together with decoupling experiments confirmed the structural assignments.[14]

Generation of *cis*-2,*trans*-3-*r*-1-Phenylcyclopropane from *erythro*-d_2-$C_5H_5(CO)_2FeCHDCHD(OCH_3)C_6H_5$, 8a,b. As in the ionization of unlabeled **4**, 0.15 mL (0.78 mmol) of TMSOTf was added to a 10 mL methylene chloride solution (−78 °C) containing 0.25 g (0.76 mmol) of **8a,b** and 10 μL (0.07 mmol) of triethylamine. Nonane (30 μL) was added to the residue. Dideuteriophenylcyclopropane (70% yield) was separated by preparative GC: ^1H NMR ($CDCl_3$, 25 °C) δ 1.88 ppm (broad d of d, J_{HH} = 8.4 Hz, J_{HH} = 4.4 Hz, H_A), 0.93 (broad d of d, J_{HH} = 8.0 Hz, J_{HH} = 6.4 Hz, H_C), 0.68 (broad d of d, J_{HH} = 4.8 Hz, J_{HH} = 6.4 Hz, $H_{B'}$). ^1H NMR spectra together with decoupling experiments confirmed the structural assignments.[14]

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Supplementary Material Available: Figures of $\{^1H,^1H\}$ COSY 2D NMR spectra for $C_6H_5CH(OCH_3)CH_2CH_2OH$, **3**, $C_5H_5(CO)_2FeCH_2CH_2CH(OCH_3)C_6H_5$, **4**, **5a,b**, and **6a,b**, ^{13}C NMR data for **7a,b** and **8a,b**, ^1H NMR and simulated ^1H NMR data for phenylcyclopropane, and ^1H NMR data and decoupling results for *cis*-2,*cis*-3-dideuterio-*r*-1-phenylcyclopropane, *trans*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropane, and *cis*-2,*trans*-3-dideuterio-*r*-1-phenylcyclopropane (9 pages). Ordering information is given on any current masthead page.

New Azasilatrane Cations: Quaternization of an Equatorial Nitrogen in Azasilatranes

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Abstract: Azasilatranes ($RSi(R'N_{eq}CH_2CH_2)_3N_{ax}$) possessing strong SiN_{ax} transannular interactions are regioselectively quaternized by Me^+ or Me_3Si^+ at an equatorial nitrogen, giving stable isolable salts. For the reaction of $Me_3SiO_3SCF_3$ with the azasilatrane in which R = R′ = Me, mixtures of the triflate salts of the cations $MeSi[Me_3SiN^+(Me)CH_2CH_2](MeNCH_2CH_2)_2N$ and $MeSi(MeNCH_2CH_2)_3N^+SiMe_3$ are present in solution and in the solid state. The stability of the latter cation is suggested to arise from delocalization of electron density and the N_{ax} positive charge in an elongated four-center four-electron MO system oriented along the molecular axis. The reaction of $MeSi(Me_3SiNCH_2CH_2)_3N$ with $Me_3SiO_3SCF_3$ is also unusual, giving the novel cation $MeSi(Me_3SiNCH_2CH_2)_2N^+CH_2CH_2N(SiMe_3)_2$, which may be in equilibrium with a dimer containing five-coordinate silicon. The ^1H ^{13}C, ^{29}Si, and ^{15}N NMR spectra of these compounds are discussed.

Introduction

Despite the analogy with the extensively studied silatranes **1a**,[1] the interest in azasilatrnaes **1b** has grown steadily during the past decade. A reason for this development is the wider scope of azasilatrane chemistry, owing to the availability of the option to vary the substitution pattern at both the silicon and the equatorial nitrogen ligands in their compounds.[2] With the use of this approach, a systematic variation in the strength of the transannular SiN_{ax} interaction to an extent unprecedented in silatrane chemistry has been achieved with azasilatranes.[2a,3] As a result of this

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