The reductive elimination of vinyl(1,2-phenylenedioxy)borane from the vinyliridium complexes suggested that this might be a true catalytic hydroboration system. We have found that this is indeed the case, following the system through greater than 6 turnovers.[13] The "resting state" of the catalyst under these conditions appears to be the vinyliridium complex. When the (1,2-phenylenedioxy)borane and alkyne have been depleted, the $Ir(PMe_3)_3Cl$ presumably formed reacts with chloroform solvent to form as an as-yet uncharacterized iridium(III) complex.

While this manuscript was in review, Evans reported on the mechanism of the rhodium-catalyzed hydroboration of olefins where the investigation involved careful deuterium labeling studies for a number of olefins.[14] Our isolation of complexes 1 and 2 and the observation of catalytic (albeit slow) hydroboration show that this is a useful system for modeling catalytic hydroboration. Through a combination of studies such as those of Evans and those contained in this report, the details of the mechanism(s) of metal-catalyzed hydroboration will be unraveled. We plan to continue our investigations into this system to further understand the nature of the unsaturate/metal interaction step and the role that ligand dissociation (both Cl^- and PMe_3) play in this system.

Acknowledgment. We acknowlege support for this work from the Jeffress Trust, Exxon Education Foundation, and the Corporation for Innovative Technology, as well as a generous loan of iridium from Engelhard and Johnson-Matthey. We also thank Drs. T. B. Marder and R. T. K. Baker for sharing of data prior to publication.

Supplementary Material Available: Tables I–IV, listings of final atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients for 1 (2 pages); a table of observed and calculated structure factors for 1 (11 pages). Ordering information is given on any current masthead page.

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[12] **2b**, ^1H NMR ($CDCl_3$): δ −0.04 (s, 9 H, $SiMe_3$), 1.49 (t, J_{P-H} = 3.7 Hz, 18 H, *trans*-PMe_3), 1.57 (d, J_{P-H} = 8.1 Hz, 9 H, *cis*-PMe_3), 6.72 (ddt, J_{H-H} = 20.2, J_{P-H} = 11.2, 3 Hz, IrC(H)=C(*H*)), 6.99 (AA′BB′, 4 H, $BO_2C_6H_4$), 8.23 ppm (ddt, J_{H-H} = 20.2, J_{P-H} = 5.9, 3.8 Hz, 1 H, IrC(*H*)=C(H)). **2c**; ^1H NMR ($CDCl_3$): δ 1.51 (t, J_{P-H} = 3.7 Hz, 18 H, PMe_3), 1.63 (d, J_{P-H} = 8.2 Hz, 9 H, PMe_3), 7.03 (AA′BB′, 4 H, $BO_2C_6H_4$) 7.19–7.36 (m, 5 H, phenyl), 8.17 ppm (ddt, J_{H-H} = 17.4, J_{P-H} = 3.0, 3.5 Hz, IrC(*H*)=C(H)). IrC(H)=C(*H*) obscured. **2d**, ^1H NMR ($CDCl_3$): δ 0.94 (s, 9 H, CMe_3), 1.50 (t, J_{P-H} = 3.7 Hz, 18 H, PMe_3), 1.57 (d, J_{P-H} = 8.2 Hz, 9 H, PMe_3), 5.84 (ddt, J_{H-H} = 17.0, J_{P-H} = 7.0, 3 Hz, 1 H, IrC(H)=C(*H*)), 6.66 (ddt, J_{H-H} = 17.0, J_{P-H} = 3.5, 3.5 Hz, 1 H, IrC(*H*)=C(H)), 6.96 ppm (AA′BB′, 4 H, $BO_2C_6H_4$).

[13] At room temperature, 6 turnovers require approximately 2 days. Control experiments show that this is faster than the rate of uncatalyzed hydroboration with (1,2-phenylenedioxy)borane under these conditions.

[14] Evans, D. A.; Fu, G. C. *J. Org. Chem.* **1990**, *55*, 2280.

Dyotropic Rearrangement in Homochiral Organoiron Complexes Resulting in Inversion at Two Adjacent Carbon Centers

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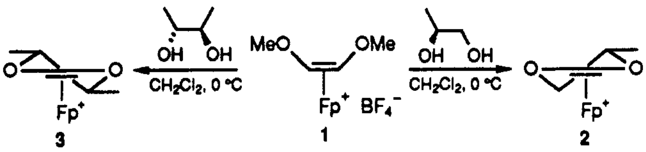
Summary: The kinetic products derived from addition of phthalimide, *N*-methyltoluenesulfonamide, or benzenethiol to homochiral Fp(dioxene)BF_4 salts **2** and **3** [Fp = $CpFe(CO)_2$] undergo unimolecular dyotropic rearrangement, resulting in inversion of the two initially formed asymmetric centers.

Transition-metal complexes are now widely used in organic synthesis, and many of these have in recent years found increasing use in asymmetric synthesis as reagents, catalysts, or auxiliaries.[1] As part of a program directed toward the use of the homochiral $Fp(\eta^2\text{-olefin})^+BF_4^-$ complexes in organic synthesis [Fp = $CpFe(CO)_2$], we have prepared a number of these salts, among them **2** and **3**, by exchange etherification of **1**[2] with (*S*)-(+)-1,2-propanediol[3] and (*R*,*R*)-butane-2,3-diol, respectively (absolute configurations are shown throughout). These cations undergo regioselective nucleophilic addition with both carbon and heteroatomic nucleophiles to give the neutral complexes **4** and **5**,[2] respectively, which may be further transformed to optically active α,β-disubstituted carboxylic acids.[4]



We wish now to report that several of these neutral homochiral organoiron complexes undergo facile rear-

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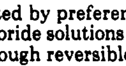
[1] *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5. Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187. Noyori, R.; Suga, S.; Kawai, K.; Okads, S.; Kitamura, M. *Pure Appl. Chem.* **1988**, *60*, 1597. Faller, J. W.; Linebarrier, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937 and references therein. Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 463. Davies, S. G. *Pure Appl. Chem.* **1988**, *60*, 13. Hayashi, T. *Ibid.* **1988**, *60*, 7. Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. Bandara, M. M. R.; Birch, A. J.; Kelley, L. F. *J. Org. Chem.* **1984**, *49*, 2496. Tamao, K.; Kumada, M. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Ed.; Wiley: New York, 1987; p 820. *J. Organomet. Chem.* **1989**, *370*, 1–407 (Brunner, H., Ed.).

[2] Turnbull, M. M.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1988**, *7*, 200.

[3] Complex **2** is obtained as a mixture with its diastereomer **2′**



but these are readily separated by preferential precipitation of the less soluble **2** from methylene chloride solutions of the mixtures. Since **2** and **2′** equilibrate in solution through reversible complexation, ratios of **2**:**2′** as high as 3:1 can be achieved. In practice, it is unnecessary to separate these diastereomers, since the adducts derived by nucleophilic addition have the same absolute configurations at all centers on the dioxane ring.

[4] Unpublished work with K.-H. Chu.

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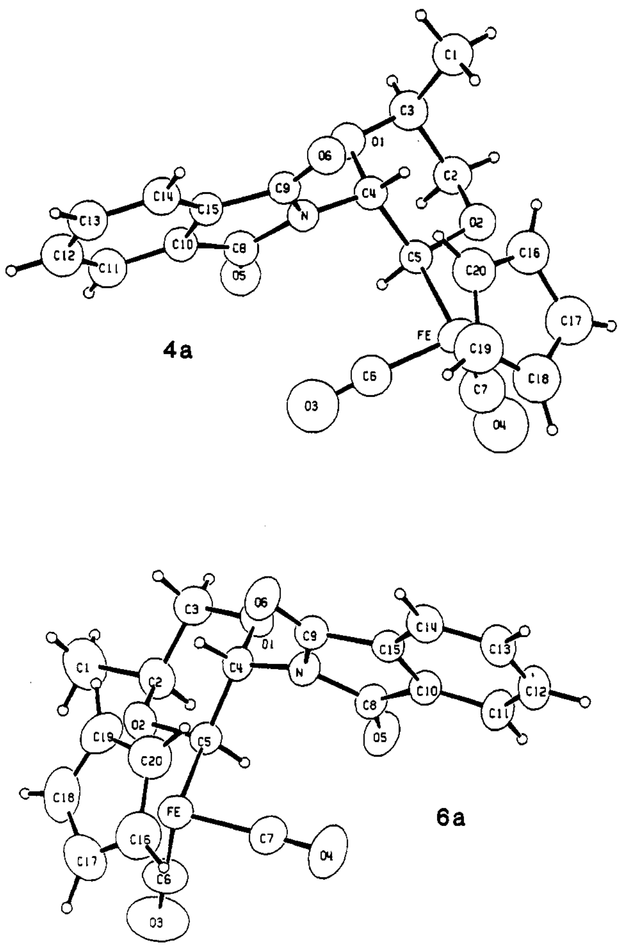


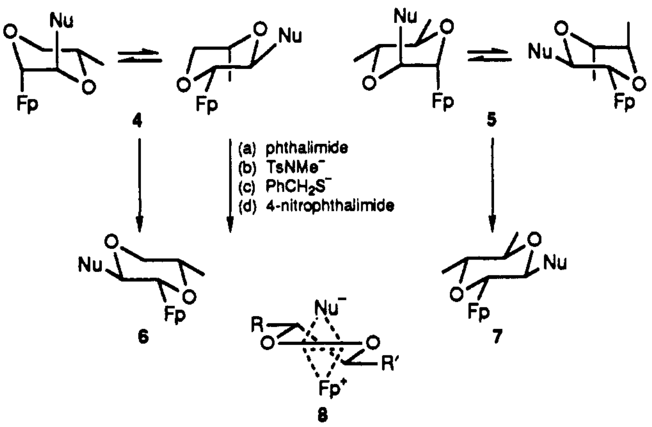
4a

6a

Figure 1. Molecular structure of complexes **4a** and **6a**, showing the atom numbering scheme. Complex **6a** is one of two symmetry-independent molecules in the unit cell. The two molecules of **6a** are identical within experimental error.

rangement to isomeric complexes, in which the configurations at the C-2 and C-3 centers of the dioxane ring are cleanly inverted.

Complex **4a**, prepared from **2** (phthalimide, Et_3N, THF, 0 °C, 1 h, quantitative), exists in solution as the diequatorial conformer ($J_{2,3}$ = 10 Hz; δ 1.51 (CH_3)). This compound is smoothly converted, in THF solution at room temperature, to **6a** ($J_{2,3}$ = 10 Hz; δ 1.05 (CH_3)). Kinetic studies show that the reaction follows first-order kinetics, with activation parameters ΔH = 19.37 kcal/mol and ΔS = −12.9 eu at 25 °C. The molecular structures of **4a** and **6a**, inferred from their NMR spectra and now confirmed by X-ray crystal structure determinations, are shown in Figure 1.[5] This clearly shows the interchanged positions of Fp and phthalimido substituents on the dioxane ring, the pseudoenantiomeric relationship of the asymmetric carbon centers, and the conformational change of the methyl substituent in the starting material and rearranged product.



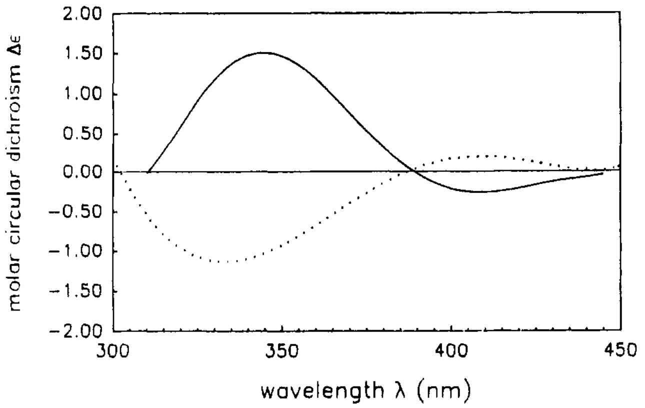


Figure 2. Circular dichroism spectra of compounds **4a** (—) and **6a** (- - -) taken in methylene chloride solution, on a JASCO J-20 recording spectrophotometer.

In accord with these results, the CD spectra of **4a** and **6a** (Figure 2), which are dominated by Cotton effects derived from induced asymmetry at the iron center,[6] reflect the essential mirror image relationship at the two carbon centers bound to the iron atom.

Similar reactions are observed for **4b** and **4c**, derived from the addition of *N*-methyltoluenesulfonamide and benzyl mercaptan to **2**. The addend substituents in these products exist preferentially in the diequatorial and diaxial conformations, respectively.[7] Complex **4c** rearranges rapidly at room temperature to give, at equilibrium, a 3:1 mixture of **4c** and **6c**, while **4b** undergoes slower transformation on heating in acetone solution to **6b**.

Parallel transformations are observed for **5a**–**5c**, derived from nucleophile addition to **3**. The phthalimide complex **5a** exists preferentially with the addend substituents in the equatorial conformation, while **5b** and **5c** exist principally with these in an axial conformation. Each of these compounds undergoes rearrangement to their isomers **7**, but at a rate significantly greater than is observed for the conversion of their respective analogues **4** to **6**.[8] As before, **5a** and **5b** are transformed to their corresponding isomers **7**, while **5c** is converted only partially to **7c**.

The rearrangements observed here appear to be closely related to neighboring group reactions,[9] best exemplified by the rearrangement of steroidal diaxial 1,2-dibromides

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[5] (a) Crystals of **4a** are monoclinic, space group $P2_1$ (No. 4), a = 14.278 (3) Å, b = 9.160 (2) Å, c = 14.597 (3) Å, β = 97.73 (3)°, Z = 4, V = 1898.4 Å^3. Data were collected to a maximum 2θ ($\lambda_{\mathrm{MoK}\alpha}$) = 48°. Full matrix least-squares refinement of positional and anisotropic thermal parameters for Fe atoms (isotropic thermal parameters for light atoms, H atoms fixed, total parameters = 234) led to R = 0.0584 and R_w = 0.0587, using 2541 data for which $I > 1.96\sigma(I)$. (b) Crystals of **6a** are orthorhombic, space group $P2_12_12_1$ (No. 19), a = 7.531 (2) Å, b = 15.146 (3) Å, c = 16.890 (3) Å, Z = 4, V = 1926.5 Å^3. Data were collected to a maximum 2θ ($\lambda_{\mathrm{MoK}\alpha}$) = 55°. Full matrix least-squares refinement of positional and anisotropic thermal parameters for all atoms (isotropic for fixed H, total parameters = 254) led to R = 0.0315 and R_w = 0.0354, using 2197 data for which $I > 1.96\sigma(I)$. The absolute configurations of **4a** and **6a** were established by reference to the (*S*)-(+)-1,2-propanediol moiety. Hamilton R-factor tests for **4a** (R = 0.0591; R_w = 0.0599) and **6a** (R = 0.0424; R_w = 0.0502) confirmed the choices of absolute configuration.

[6] Begum, M. K.; Chu, K.-H.; Coolbaugh, T. S.; Rosenblum, M.; Zhu, X.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 5252.

[7] For **4b**: $J_{2,3}$ = 9.0 Hz; δ 1.35 (CH_3). **4c**: $J_{2,3} \leq$ 0.1 Hz; δ 1.09 (CH_3).

[8] The approximate half-lives for these are: **4a**, 3.4 h; **5a**, 0.3 h (25 °C); **4b**, 7.5 h; **5b**, 1.0 h (40 °C); **4c**, 50 min; **5c**, 10 min (−40 to 25 °C).

[9] Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum: New York, 1976.

to their diequatorial isomers.[10] However, these latter reactions proceed through a tight ion pair, while the rearrangements reported here appear to proceed through either a relatively loose ion pair intermediate 8 or by reversion of the product to its ionic reactants. The results of experiments summarized below do not at present allow a clear choice to be made between these alternatives.

The relative rates of addition of phthalimide and of 4-nitrophthalimide to 2 were determined by competition experiments and found to be 2.0:1.0.[11] When the rearrangement of **4a** was allowed to proceed at room temperature in the presence of 2 M equiv of lithium 4-nitrophthalimide, the product was found to be a 4.0:3.0 mixture of the rearranged complexes **6a** and **6d**, consistent with incomplete exchange of anions in an ion pair such as 8. However, rearrangement of **4a** in the presence of a 2:1 molar ratio of 4-nitrophthalimide to **4a** led to the exclusive formation of **6d**, suggesting that, if an ion pair intermediate is involved in the rearrangement, proton exchange between the migrating phthalimide anion and the more acidic 4-nitrophthalimide must be faster than rearrangement of the ion pair.[12]

Regardless of the precise nature of the intermediate in these reactions, stereoelectronic factors would be expected to require that the rearrangement proceed through that conformer in which the addend substituents are axial. The faster rates of rearrangement of **5a**–**5c**, compared with the corresponding **4a**–**4c** adducts, are in accord with that expectation.[13]

Finally, it is of interest to note that adducts 4, derived from the addition of acetyl acetonate and dimethyl malonate anions to 2, do not undergo dyotropic rearrangement even on prolonged heating at 40 °C in THF and even though these adducts exist predominantly in the diaxial form. Anion stability alone cannot therefore be a determining factor in promoting dyotropic rearrangement. Instead, these observations find a plausible explanation in terms of an anomeric effect,[14] which promotes adduct reversion through a weakening of the carbon–heteroatom bond in 4 and 5.

Further work in progress is designed to apply these reactions to the synthesis of either of two enantiomeric 3-hydroxy esters starting from a single homochiral dioxene complex.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (GM-37067). We thank K. Wheeler for assistance with the X-ray structure determination.

Supplementary Material Available: Experimental procedure and tables of unimolecular rate constants, crystallographic data, atomic coordinates, bond lengths and angles, and thermal parameters for **4a** and **6a** (31 pages); tables listing calculated and observed structure factors for **4a** and **6a** (22 pages). Ordering information is given on any current masthead page.

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(10) Barton, D. H. R.; Head, A. J. *J. Chem. Soc.* **1956**, 932. Grob, C. A.; Winstein, S. *Helv. Chim. Acta* **1952**, *35*, 782.

(11) An equimolar mixture of the two salts, generated at low temperature by treatment of the imides with *n*-butyllithium, were allowed to react with a half molar equivalent of **2** in THF solution. The initial product, a mixture of **4a**, **6a**, and **6d**, was allowed to equilibrate further at room temperature to yield a mixture of **6a** and **6d** in a ratio of 2.0 ± 0.1:1.0, determined by separated integration of proton resonances at the three methine center in **6a** and **6d**.

(12) The pK_a's of phthalimide and 4-nitrophthalimide in 30% aqueous ethanol at 25 °C are 10.02 and 8.55, respectively. Guérillot, C. R. *C. R. Hebd. Seances Acad. Sci.* **1955**, *240*, 1107.

(13) The difference in populations of the diaxial addend conformations in 5 and 4 and the corresponding rearrangement rate differences are due to the higher energy of the diequatorial addend conformation in **5** compared with this conformer in **4**. These should differ by approximately 0.64 kcal/mol, the energy of an axial methyl group in a 1,4-dioxane. Ayras, P.; Nikkila, A.; Nurmi, T.; Pihlaja, K. *Finn. Chem. Lett.* **1974**, 237.

(14) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects At Oxygen*; Springer Verlag: Berlin, 1983.

Metal–Vinyl vs Metal–Alkyl Insertion Reactions of Titanacyclobutenes with Nitriles

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Summary: Disubstituted titanacyclobutenes, $\mathrm{Cp_2\overline{TiCR{=}CRC}H_2}$ (**1a**, R = CH_3; **1b**, R = CH_2CH_3), react with 2 equiv of nitriles under mild conditions to afford diazatitanacyclooctatrienes, resulting from nitrile insertion into both the titanium–alkyl and titanium–vinyl bonds of the titanacyclobutene. Hydrochlorination of these metallacyclic products affords tetrasubstituted pyridines. Significant steric bulk in either the nitrile or the metallacyclobutene leads to exclusive formation of single-insertion products.

Insertion reactions of transition-metal–alkyl bonds are well established.[1] In contrast, insertions into transition-metal–vinyl bonds are rather scarce, being found predominantly for strained metallacyclopropenes[2,3] (alkyne complexes) with the early transition metals, though also occasionally appearing for early and later metal vinyl complexes.[4] In our continuing survey of the reactivity of titanacyclobutenes with unsaturated organic substrates, we have found that insertion into the titanium–vinyl bond is apparently intrinsically favored over the anticipated insertion into the titanium–alkyl bond of the metallacycle,

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 6. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Interscience: New York, 1988; Chapter 27.

(2) Reviews: (a) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296–1320. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047–1058. (c) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189–202 and references therein.

(3) (a) Vaughan, G. A.; Hillhouse, G. L.; Lum, R. T.; Buchwald, S. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 7215–7217. (b) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *Ibid.* **1986**, *108*, 7441–7442. (c) Buchwald, S. L.; Wannamaker, M. W.; Watson, B. T. *Ibid.* **1989**, *111*, 776–767. (d) Jordan, R. F.; Taylor, D. F. *Ibid.* **1989**, *111*, 778–779.

(4) See, e.g.: Cassar, L.; Giarrusso, A. *Gazz. Chim. Ital.* **1973**, *103*, 793–795; *Chem. Abstr.* **1974**, *81*, 63045 m. Tohda, Y.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1975**, 54. Roe, D. M.; Calvo, C.; Krishnamachari, N.; Moseley, K.; Maitlis, P. M. *Ibid.* **1973**, 436. Dema, A. C.; Lukehart, C. M.; McPhail, A. T.; McPhail, D. R. *J. Am. Chem. Soc.* **1989**, *111*, 7615–7616. Erker, G.; Schlund, R.; Kruger, C. *Organometallics* **1989**, *8*, 2349–2355.

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