kinetic studies of reactions 1 and 2, exploration of the range of metallo species capable of accomplishing reaction 3, and an evaluation of the potential role of metallo ketones as reactive intermediates.

Acknowledgment. This work was supported by the National Science Foundation and the Office of Basic Energy Sciences, DOE Grant No. DE-AC02-83-Er13133.

Registry No. $(RhOEP)_2$, 63439-10-1; $(RhOEP)_2(CO)$, 101403-89-8; OEPRh-C(O)-RhOEP, 101403-90-1.

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(19) (a) On the basis of the thermodynamic parameters obtained for the Pd A-frame system[19b] where ΔH is measured to be between −11 kcal and −15 kcal, we estimate[14] that the M–C bond energies must be at least 49 kcal: (M–M) − 2(M–C) = −83 kcal (−87 kcal). Assuming that (M–M) ≥ 15 kcal, or there would be appreciable dissociation: (M–C) ≥ 49 kcal (51 kcal). (b) Lee, C.; James, B. R.; Nelson, D. A.; Hallen, R. T. *Organometallics* **1984**, *3*, 1360.

Asymmetric Carbon–Carbon Bond Formation Using Optically Active (η-C_5H_5)Fe(CO)$_2$–Vinyl Ether Complexes. Asymmetric Control at Two Adjacent Carbon Centers

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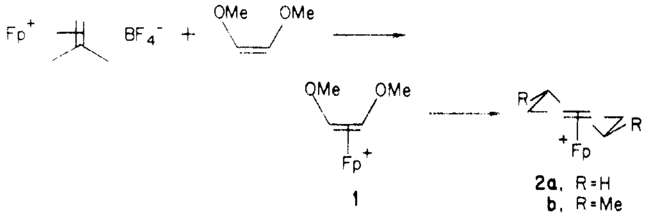
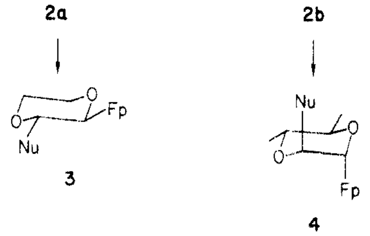
Summary: The dihydrodioxin–Fp complex **2b** (Fp = (η-C_5H_5)Fe(CO)$_2$) adds a broad range of nucleophiles to give optically active adducts **4** in which nucleophile and Fp group are diaxial. These may be converted to optically active Fp(η^2-vinyl ether) or Fp(η^2-alkene) cations of defined absolute configuration.

Optically active metal–olefin complexes, in which the olefin *itself* is a center of asymmetry, provide unique substrates for asymmetric carbon–carbon bond formation.[1] We wish now to report the preparation of optically active complex **2b**, which serves both as a unique platform for asymmetric C–C bond formation and for the preparation of optically active alkyl vinyl ether–iron complexes in which the *exclusive* locus of asymmetry is the olefin center. Both the achiral parent complex **2a** as well as **2b** are readily available from **1** by exchange etherification with ethylene glycol (CH_2Cl_2, 0 °C, 0.25 h; Et_2O, 94%) or with (*R*,*R*)-2,3-butanediol[2] (CH_2Cl_2, 0 °C, 1.5 h; Et_2O, 89%). Like **1**, which is available in multigram quanitities by exchange complexation of *cis*-1,2-dimethoxyethylene[3] with Fp(isobutylene)BF_4, **2a** and **2b** are moderately air stable, storable solids.



Complex **2b**, like the parent **2a** and its acylic analogue **1**, adds nucleophiles of a broad range of basicities, yielding a *single* optically active adduct (Table I). The structures of these products **4** are supported by their proton NMR spectra ($J_{2,3}$ = 1 Hz), which contrast with the spectra of all similar products **3** derived from the parent complex **2a** ($J_{2,3}$ = 8 Hz). Their ^{13}C spectra shows each of these to be a single diastereomer.[4] These structural assignments are further supported by a single-crystal X-ray structure determination of the cyano adduct **4e** shown in Figure 1.[5,6]



The high regioselectivity observed in the reaction of **2b** with nucleophiles may be due to stereoelectronic control, which would be expected to favor the chair transition state associated with nucleophile addition to C-3, but other factors may be operative.[7]

Complex **2b** serves as a valuable starting material for the synthesis of optically active Fp(alkyl vinyl ether) and Fp(alkene) cations of defined absolute configuration and high optical purity. Thus, **4a** is quantitatively converted to (*R*)-**5a** (ϵ_{480} = +1.34 $M^{-1}\cdot cm^{-1}$, 0°) on treatment with Me_3Si triflate and CH_2Cl_2–Et_2O at −78 °C for 10 min. ^{13}C NMR measurements at 0 °C show it to be a single diastereomer. Epimerization of the asymmetric olefin center in **5** occurs slowly at room temperature, through rotation about the putative double bond, to give a mixture of diastereomers.[8]

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(1) For the use of optically active tricarbonyl (η^5-cyclohexadienyl)iron complexes in asymmetric synthesis, see: Birch, A. J.; Kelly, L. F. *J. Organomet. Chem.* **1985**, *285*, 267 and references therein. Assymetric C–C bond formation has more commonly been achieved through addition to unsaturated ligands of transition-metal complexes in which either the metal or another ligand are optically active centers. See for example: Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893. Faller, J. W.; Chao, K.-H. *Organometallics* **1984**, *3*, 927. Trost, B. M.; Dietsche, T. *J. Am. Chem. Soc.* **1973**, *95*, 8200. Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1977**, *99*, 1649. Fiaud, J. C.; De Gournay, A. H.; Larcheveque, M.; Kagan, H. B. *J. Organomet. Chem.* **1978**, *154*, 175. Consiglio, G.; Botteghi, C. *Helv. Chim. Acta* **1973**, *56*, 460. Bosnich, B.; Mackenzie, P. B. *Pure Appl. Chem.* **1982**, *54*, 189.

(2) Strem Chemicals, Inc., Newburyport, MA.

(3) Marsi, M.; Rosenblum, M. *J. Am. Chem. Soc.* **1984**, *106*, 7264.

(4) Full ^1H and ^{13}C NMR data and elemental analyses are included in the supplementary material.

(5) Crystal data: monoclinic, space group $P2_1$; a = 7.859 (2) Å, b = 7.625 (2) Å, c = 12.212 (3) Å; β = 99.54 (3)°. Refinement by full-matrix least squares, with anisotropic temperature factors assigned to Fe, C, and O atoms and with H atoms in calculated positions led to R = 0.022 and R_w = 0.032 (using 2104 data) for which $|F_o| > 3.92\sigma(|F_o|)$. The absolute configuration was established by known stereochemistry at C-10 and C-11 as well as by using a Hamilton R factor test.

(6) The low conformation energy for an axial Fp group in **4**, despite the large size of this group, is no doubt due to the long Fe–C bond in Fp–R complexes (2.07 Å in **4e**, for example). The conformational energy for an axial Fp group in **4a** is estimated as no more than 0.1 kcal/mol, based on a minimum equilibrium value of 80% axial conformer in solution and a value of 0.9 kcal/mol for the conformational energy of an axial methyl group in **4a** and for the gauche methyl interaction in the corresponding diequatorial conformer.

(7) Electronic effects, associated with unsymmetrical coordination of the Fp cation to the olefin in **2b**, cannot be ruled out as contributing to the observed regioselectivity. The chemical shift for C-2,3 in **2a** is δ 102.7 (CD_3NO_2), but for **2b** these centers show resonance at δ 95.5 and 108.6, suggestive of unsymmetrical bonding and hence unsymmetrical charge distribution in this complex.

(8) At 25 °C, in CH_2Cl_2 solution, conversion of **5** to an equilibrium mixture of diasteromers may be followed in its CD spectrum. An equilibrium value of ϵ_{480} = +0.003 (±0.0006) $M^{-1}\cdot cm^{-1}$ is reached at the end of 19 h, at room temperature. For rotational barriers in Fp(vinyl ether)BF_4 complexes, see: Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361 and ref 3.

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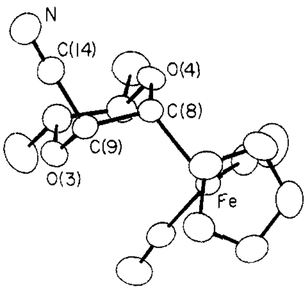
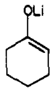
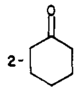
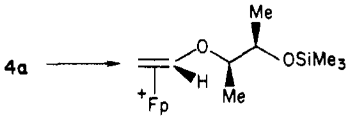


Figure 1. Ortep diagram of **4e** (50% probability ellipsoids are shown).

Table I. Adducts Derived from Nucleophilic Addition to 2b

reagent	product (**3**)	Nu	yield, % **3**	yield, % **4**
NaBH$_3$CN, NaOMe	**a**	H	60	49
LiMeCuCN	**b**	Me	36	40
PhMgBr	**c**	Ph		56
	**d**		90	60
Et$_4$NCN	**e**	CN	94	98
PhCH$_2$SNa	**f**	PhCh$_2$S	81	
CH$_2$CHMgBr	**g**	CH$_2$CH		65



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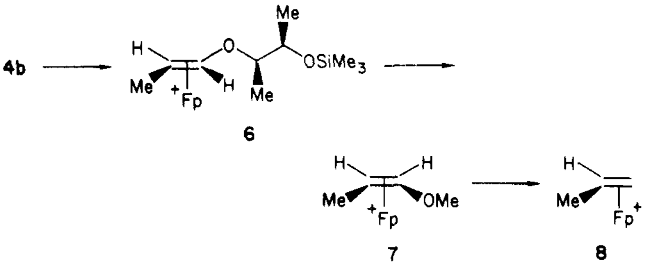
In a similar manner, **4b** is converted to the *trans*-propenyl ether complex (*R*,*S*)-**6** on treatment with Me$_3$Si triflate (Et$_2$O, –78 °C, 10 min). Dissolution of this material in methanol and immediate reprecipitation with ether gave the cis complex (*S*,*S*)-**7** in 78% overall yield from **4b** (ϵ_{480} = +0.15 M^{-1}·cm^{-1}).[9] This may be further transformed by reduction (NaBH$_4$, NaOMe, MeOH, –78 °C, 0.25 h, 82%) and treatment with HBF$_4$·Et$_2$O (Et$_2$O, –78 °C, 1 h, 84%) to the propene complex (*S*)-**8** (ϵ_{480} = –0.34 M^{-1}·cm^{-1}). To the best of our knowledge, **7** and **8** represent the first simple metal–olefin complexes which owe their optical activity entirely to asymmetry of olefin complexation.



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Further examiniation of **2b** and of vinyl ether–iron complexes derived from it, as substrates for asymmetric C–C bond formation is in progress.

Acknowledgment. This work was supported by the National Science Foundation (CHE 8117510) and in part by the National Institutes of Health (GM-16395), which is gratefully acknowledged. We are also indebted to Professor B. B. Snider for helpful discussions.

Registry No. **1**, 78251-22-6; **2a**, 101224-90-2; **2b**, 101224-91-3; **3a**, 101224-92-4; **3b**, 101224-93-5; **3d**, 101224-94-6; **3e**, 101224-95-7; **3f**, 101224-96-8; **4a**, 101224-97-9; **4b**, 101224-98-0; **4d**, 101224-99-1; **4e**, 101225-00-7; **4g**, 101225-01-8; (*R*,*S*)-**6**, 101225-02-9; (*S*,*S*)-**7**, 101313-00-2; (*S*)-**8**, 101313-01-3; (*R*,*R*)-2,3-butanediol, 24347-58-8; Me$_3$Si triflate, 27607-77-8; ethylene glycol, 107-21-1.

Supplementary Material Available: Tables of experimental procedure, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, observed and calculated structure amplitudes, and ^{1}H and ^{13}C NMR and combustion analyses and a complete figure with labels and thermal ellipsoid detail (18 pages). Ordering information is given on any current masthead page.

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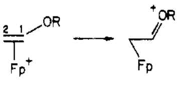
[9] The mechanism of isomerization has been shown to be unimolecular[3] and to proceed by rotation about the formal double bond in these complexes in such a way that only the configuration at C-1 is changed, as would be anticipated from canonical structure ii. Unpublished work with A. Bucheister and with C. Stockman.



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Book Reviews

Organic Reactions. Volume 34. Edited by Andrew S. Kende. Wiley, New York. 1985. xvii + 412 pages. $49.95.

This volume of *Organic Reactions* contains two chapters. The first chapter (317 pages) writted by Jaroslav Malek is entitled "Reductions by Metal Alkoxyaluminum Hydrides", and the second chapter (81 pages) is written by Chin-Lin J. Wang and is entitled "Fluorination by Sulfur Tetrafluoride". Both of these chapters are written in the conventional form of organic reactions (introduction, scope, mechanism, experimental procedures, and tables of examples) and are typical of the high quality of reporting and contribution selection that one has come to expect of *Organic Reactions*.

The first chapter entitled "Reductions by Metal Alkoxyaluminum Hydrides" is superb and is probably the most authoritative recent discussion of the area of metal hydride reduction of organic functional compounds. It is clear that the author has not only first hand knowledge of the area but also possesses a very detailed (1066 references) and mature understanding of a rather complicated and not completely understood, yet important area of chemistry. Chemists have published regularly and prolifically in this area not only reporting practical applications of metal hydride reductions, but also presenting new theories directed toward the understanding of mechanisms and stereochemistry. This chapter does an outstanding job of lucidly presenting many of the more accepted theories in a very organized way. I would recommend this chapter for anyone who would like to read the most recent attempt to bring understanding to an otherwise quite confused area.

Although this chapter is concerned mainly with metal alkoxyaluminum hydrides, there are also references to alkoxyaluminum hydrides, LiAlH$_4$, NaBH$_4$, etc. which are very helpful in putting the results of the metal alkoxyaluminum hydrides in perspective with respect to other hydride-reducing agents.

There are detailed presentations on the most important and best understood aspects of metal hydride reduction, such as composition of the reagents, disproportionation of the reagents, mechanisms (single electron transfer and polar), consideration