Huskey and Schowen,[9] Saunders,[10] and Limbach et al.[6] have all published calculations which confirm that coupled motion plus tunneling are required to explain effects similar to those in Table I. We have also modeled the glucose-6-phosphate hydrogenase reaction by use of the BEBOVID-IV program of Sims et al.[11] In order to predict the values of the deuterium isotope effects in Table I and maintain realistic bond orders in the $C\cdots H\cdots C$ system for hydride transfer, it was necessary to let the imaginary frequency be ~1000 cm^{-1} so that tunneling became appreciable. Such a model could predict the deuterium isotope effects seen in H_2O and D_2O but also predicted a different ^{13}C isotope effect in the latter solvent as the result of tunneling. Further theoretical work is clearly needed to determine the reasons why the hydrogen motions appear to involve tunneling, while that of carbon does not.

The data in Table I show one other striking effect, namely, an *increase* in the commitments in D_2O. Since one expects a solvent isotope effect on the proton transfer which accompanies the hydride migration, the commitments are predicted to *decrease* unless D_2O causes larger effects on the steps that set the stage for catalysis than on the proton-transfer step itself. These data emphasize the danger of assuming that D_2O solvent isotope effects will not be seen on conformation changes of enzymes![13]

Acknowledgment. This work was supported by NIH Grant GM 18938.

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[11] Sims, L. B.; Burton, G.; Lewis, D. E., BEBOVIB-IV, Program 337, Quantum Chemistry Exchange Program, Department of Chemistry, Indiana University, Bloomington, IN.

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[13] Actually it is not at all uncommon for D_2O to change the rates of conformation changes in proteins. See: Schowen, K. B. In "Transition States of Biochemical Processes"; Gandour, R. D., Schowen, R. L., Eds.; Plenum Press: New York, 1978; pp 225-283.

New Organoiron Synthons. *cis*- and *trans*-Vinylene Dication Equivalents

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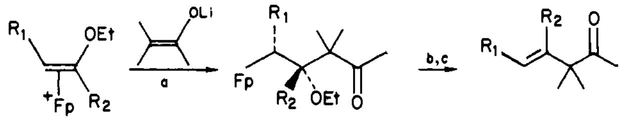
Received June 15, 1984

We have reported the use of vinyl ether–iron complexes (**1**) as synthetic surrogates for vinyl cations.[1] These reagents are easily prepared from α-halo acetals or ketals by successive metalation with NaFp (Fp = η^5-$C_5H_5Fe(CO)_2$) and acid-promoted elimination of alcohol[2] and may be stored without decomposition at 0 °C. They react rapidly with enolates at −78 °C to give adducts **2** resulting from stereospecific trans addition to the Fp–olefin bond. These are in turn transformed to vinyl, *trans*-propenyl, and isopropenyl ketones by successive acid-promoted elimination of ethanol and demetalation.

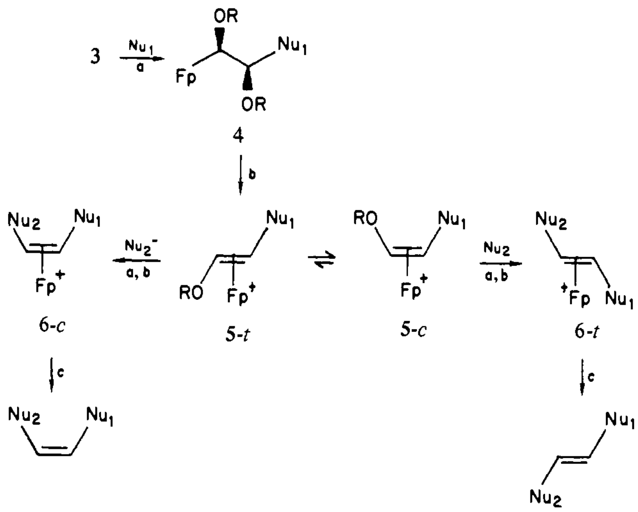


1 **2**

$R_1, R_2 = H; R_1 = H, R_2 = Me; R_1 = Me, R_2 = H$

(a) THF, −78 °C, 1 h; (b) $HBF_4 \cdot Et_2O$, CH_2Cl_2, −78 °C; (c) NaI, acetone, 25 °C, 0.5 h

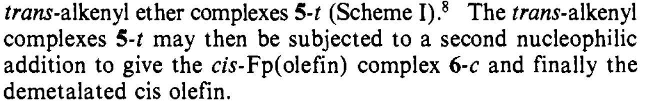
Scheme I[a]



[a] (a) THF, −78 °C, 0.5–1.0 h; (b) $HBF_4 \cdot Et_2O$, −78 °C then Et_2O; (c) CH_3CN, Δ, 2 h or NaI, acetone, 25 °C, 0.5 h.

We now find that the closely related (1,2-dialkoxyethylene)iron complexes **3** may be made to serve as either *cis*- or *trans*-vinylene dication equivalents, thus providing a new and more general route to *cis*- as well as *trans*-alkenyl cation equivalents.

Complex **3a**[3] may be prepared in multigram quantities by exchange complexation of *cis*-1,2-dimethoxyethylene[4] with Fp(isobutylene)BF_4 (CH_2Cl_2, 40 °C, 2 h, 95%).[5] This salt is transformed quantitatively to **3b** by briefly slurring in ethanol at room temperature and reprecipitating with ether.[6]



3a **3b**

Both **3a** and **3b** are yellow crystalline, nonhygroscopic, air-stable solids, which may be stored at 0 °C. They react rapidly in THF suspension or in solutions of CH_2Cl_2 at −78 °C with a broad range of carbon nucleophiles (Table I) to give neutral adducts **4**.[7] These, on exposure to HBF_4 etherate at −78 °C, are converted to *trans*-alkenyl ether complexes **5**-*t* (Scheme I).[8] The *trans*-alkenyl complexes **5**-*t* may then be subjected to a second nucleophilic addition to give the *cis*-Fp(olefin) complex **6**-*c* and finally the demetalated cis olefin.

Alternatively, since the barrier to rotation about the double bond in Fp(vinyl ether) cations is comparatively low[9] and since cis metal–olefin complexes are in general thermodynamically more stable than their trans isomers,[10] isomerization of **5**-*t* to **5**-*c* may be effected by allowing solutions of **5**-*t* to stand at room tem-

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[1] Rosenblum, M.; Bucheister, A.; Chang, T. C. T.; Cohen, M.; Marsi, M.; Samuels, S. B.; Scheck, D.; Sofen, N.; Watkins, J. C. *Pure Appl. Chem.* **1984**, *56*, 129 and references therein.

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[4] McElvain, S. M.; Stammer, C. H. *J. Am. Chem. Soc.* **1951**, *73*, 915.

[5] Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. Exchange complexation of *trans*-1,2-dimethoxyethylene is reported[3] to give **3a** but in low yield.

[6] This exchange is effected to avoid potential nucleophilic attack at the alkyl center. Complex **3b** cannot be obtained directly by exchange complexation of 1,2-diethoxyethylene.

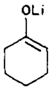
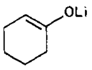
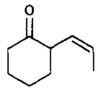
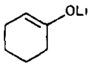
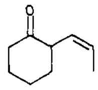
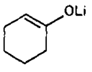
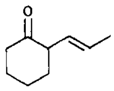
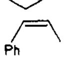
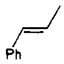
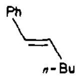
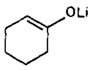
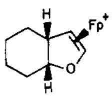
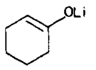
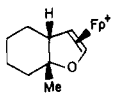
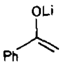
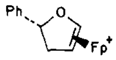
[7] The threo structure assigned to **4** is supported by the NMR spectra of the adducts derived from the addition of phenylmagnesium bromide or cyclohexanonelithium enolate to **3b**, which show J_{ab} = 3 Hz, in accord with the structure **4** (Nu_1 = Ph, 2-cyclohexanone).

[8] These all show J_{ab} = 11 Hz, while the cis isomers show J_{ab} = 6 Hz.

[9] Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361.

[10] Herberhold, M. "Metal π-Complexes"; Elsevier: Amsterdam, 1972; Vol. II. Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.

Table I. Sequential Reactions of Carbon Nucleophiles with 3[a]

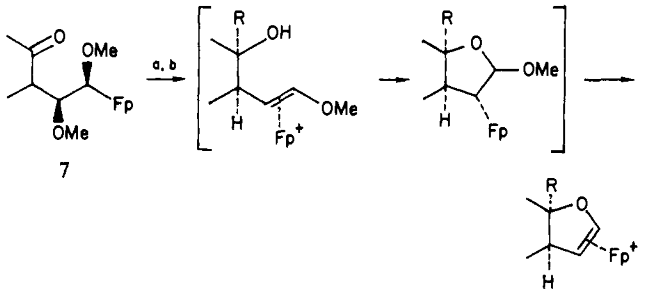
substrate	Nu_1	Nu_2	product	yield, %[b]
3a	Me_2CuLi		5-*t* (R = Me)	76
3b	Me_2CuLi		5-*t* (R = Et)	71
3b	$Me_2Cu(CN)Li_2$		5-*t* (R = Et)	74
3b	Me_2CuLi, Δ		5-*c* (R = Et)	83
3b	Me_2CuLi (EtOH)[f]		5-*c* (R = Et)	93
3b	$(n\text{-}Bu)_2Cu(CN)Li_2$		5-*t* (R = Et)	60
3b	$(n\text{-}Bu)_2Cu(CN)Li_2$, Δ[e]		5-*c* (R = Et)	45
3b			5-*t* (R = Et)	*c*
3b	Me_2CuLi	Me_2CuLi	6-*c*	37[d]
3b	Me_2CuLi, Δ[e]	Me_2CuLi	6-*t*	40[d]
3b	Me_2CuLi			52[d]
3b		Me_2CuLi		37[d]
3b	Me_2CuLi, Δ[e]			38[d]
3b	Me_2CuLi	PhMgBr		27[d]
3b	Me_2CuLi, Δ[e]	PhMgBr		19[d]
3b	$(n\text{-}Bu)_2Cu(CN)Li_2$	$(n\text{-}Bu)_2Cu(CN)Li_2$	6-*c*	34[d]
3b	PhMgBr	$(n\text{-}Bu)_2Cu(CN)Li_2$		28[d]
3b	$(n\text{-}Bu)_2Cu(CN)Li_2$	PhMgBr		24[d]
3a		internal RO^-		50
3a		internal RO^-		87
3a		internal RO^-		63

[a] Reactions of nucleophiles with 3a,b and with the intermediate akenyl ethyl ether complexes were carried out at −78 °C for 1 h in THF solution. [b] Yields given are of isolated materials. [c] The product was not isolated. [d] Overall yield from 3b. [e] The trans complex 5-*t* was isomerized thermally before treatment with Nu_2. [f] The trans complex 5-*t* was isomerized by slurrying in ethanol at 0 °C for several minutes.

perature for 30 min.[11] For those *trans*-vinyl ether complexes that decompose at ambient temperature (5-*t*, Nu_1 = 2-cyclohexanone),[12] trans to cis isomerization can be effected by carrying out the protonation of **4** in ethanol at −78 °C.

The *cis*-alkenyl ether complexes 5-*c* are likewise amenable to successive trans nucleophile addition and acid-promoted loss of ethanol to give the corresponding trans olefin complexes and ultimately the free trans-1,2-disubstituted olefin. Demetalation may be effected by either brief treatment of **6** with sodium iodide in acetone solution at room temperature or by heating briefly in acetonitrile.[13] A summary of preliminary results with a number of simple carbon nucleophiles is given in Table I.[14]

Scheme II[a]



7

8

[a] (a) L-Selectride or MeLi, THF, −78 °C, 0.5 h; (b) HBF_4, THF, −78 °C then Et_2O.

A final variant of this chemistry is shown in Scheme II. In this sequence, the adducts **7** derived from the reaction of lithium cyclohexanone or acetophenone enolate to **3a** were converted, without isolation of intermediates through successive treatment

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(11) At equilibrium less than 3% of *trans*-**5** complexes exist in equilibrium with *cis*-**5** isomers for all of those complexes examined (Nu_1 = Me, *n*-Bu, Ph, 2-cyclohexanone). A kinetic study of this process for the *trans*-propenyl ethyl ether complex 5-*t* (Nu_1 = Me), over a 30 °C temperature range in deuterioacetone, shows that the isomerization process is first order, with a calculated activation energy of 21.9 kcal/mol (log *A* = 12.7, 25 °C).

(12) These complexes undergo Fp transfer from carbon to oxygen above 0 °C.

(13) The latter procedure is especially convenient since the unwanted Fp group is easily removed as the Fp(acetonitrile)BF_4 salt by precipitation with ether or extraction into water.

(14) All new compounds have been fully characterized by the IR and proton NMR spectra and gave acceptable elemental analyses.

with L-Selectride (Aldrich) or methyllithium, followed by HBF_4 etherate, to dihydrofuran complexes **8**.[15] This was then precipitated from solution, washed free of impurities, and finally decomplexed by brief exposure to iodide in acetone solution.

Further synthetic applications of the chemistry of these organoiron complexes is being examined.

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE 8117510). We are indebted to J. C. Watkins for carrying out some of the initial exploratory experiments.

Registry No. 3a, 78251-22-6; **3b**, 92695-23-3; **4** (R = Et; Nu_1 = Ph), 92719-92-1; **4** (R = Et; Nu_1 = 2-cyclohexanone), 92695-24-4; **5**-*t* (R = Me; Nu_1 = Me), 92695-25-5; **5**-*t* (R = Et; Nu_1 = Me), 92761-54-1; **5**-*c* (R = Et; Nu_1 = Me), 55337-32-1; **5**-*t* (R = Et; Nu_1 = *n*-Bu), 92695-26-6; **5**-*c* (R = Et; Nu_1 = *n*-Bu), 92761-55-2; **5**-*t* (R = Et; Nu_1 = 2-cyclohexanone), 92695-27-7; **6**-*c* (Nu_1 = N_2 = Me), 56323-74-1; **6**-*t* (Nu_1 = Nu_2 = Me), 56323-76-3; **6**-*c* (Nu_1 = Nu_2 = *n*-Bu), 92719-93-2; Fp(isobutylene)BF_4, 41707-16-8; $Me_2Cu(CN)Li_2$, 80473-70-7; (*n*-Bu)$_2$Cu(CN)Li_2, 80473-69-4; Me_2CuLi, 15681-48-8; PhMgBr, 100-58-3; dicarbonyl(η^5-2,4-cyclopentadien-1-yl)[(4,5-η)-1-phenyl-1,2-dihydrofuran]iron(1+), 92695-28-8; dicarbonyl(η^5-2,4-cyclopentadien-1-yl)-[(2,3-η)-3a,4,5,6,7,7a-hexahydroindene]iron(1+), 92695-31-3; lithium cyclohexanone enolate, 56528-89-3; lithium acetophenone enolate, 55905-98-1; (*Z*)-2-propen-1-ylcyclohexanone, 92695-29-9; (*E*)-2-propen-1-ylcyclohexanone, 92695-30-2; (*Z*)-1-propenylbenzene, 766-90-5; (*E*)-1-propenylbenzene, 873-66-5; (*Z*)-1-hexenylbenzene, 15325-54-9; (*E*)-1-hexenylbenzene, 6111-82-6.

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[15] The stereochemistry shown for these complexes in Scheme II and Table I follows from the stereospecificity defined earlier for Fp driven reactions and from preferred trans addition of nucleophile to adduct **7**. The structural assignment for **8** is supported by greater shielding of H-4 and H-5 protons in the dihydrofuran complexes compared with the free dihydrofurans. These protons must consequently be in the shielding region of the Fp group (along the Cp ring-centroid iron axis)[5] and hence cis to these protons.

Preparation of *n*-Octadecaborane(22), *n*-$B_{18}H_{22}$, by Oxidative Fusion of Dodecahydrononaborane(1−) Clusters

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Oxidative fusion of small clusters has great potential as a synthetic route to larger cluster systems. Application to the synthesis of carborane and metallocarborane systems is well documented.[1] We now report the preparation of *n*-$B_{18}H_{22}$ by the oxidation of $Me_4NB_9H_{12}$ with metal halides including Hg(I), Hg(II), Sn(IV), and Fe(II) salts.

n-$B_{18}H_{22}$ was first observed in 1962 as one of the components in a mixture of isomers prepared by the hydrolysis of ethanolic solutions of $B_{20}H_{18}^{2-}$ [2] and has since been systhesized by several other methods with yields ranging from poor to moderate.[3] It's structure, see Figure 1, comprises two decarborane-like structural units fused along the common B(5)–B(6) edge.[4] *i*-$B_{18}H_{22}$ exhibits a very similar structure in which the cages are also edge fused but twisted relative to each other.[5]

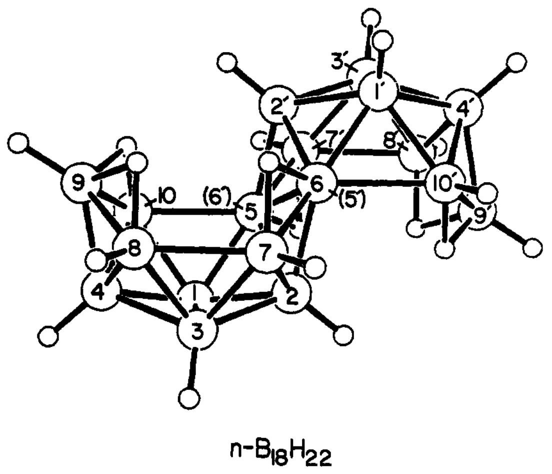

Figure 1. Structure and numbering scheme of *n*-$B_{18}H_{22}$.[4]

Table I. Yield of *n*-$B_{18}H_{22}$ as a Function of Salt

salt	% yield	salt	% yield
$HgCl_2$	47	Hg_2Cl_2	58
$HgBr_2$	68	$FeBr_2$	31
HgI_2	63	$SnCl_4$	low

In our optimized synthesis of *n*-$B_{18}H_{22}$, 0.70 g (1.9 mmol) of $HgBr_2$ was added with stirring to 0.34 g (1.8 mmol) of $Me_4NB_9H_{12}$,[6] which had been dissolved in 50 mL of freshly distilled CH_2Cl_2. A grey precipitate as well as minute droplets of elemental mercury began to appear within 5 min. Stirring was continued at room temperature overnight, after which the reaction mixture was filtered and the CH_2Cl_2 removed in vacuo. The resulting residue was extracted with toluene, and this solution was, in turn, filtered and the solvent removed to yield 0.13 g (0.60 mmol) *n*-$B_{18}H_{22}$, a 68% yield. All manipulations were performed under a nitrogen atmosphere using standard Schlenk line techniques. The light yellow product was identified by comparison of its ^{11}B NMR to that reported by Todd.[7]

The highest yield preparations of *n*-$B_{18}H_{22}$ have resulted from the use of $HgBr_2$ as in the synthesis described above. This reaction has been directly scaled up to yield 10 mmol of product without significant variation in yield. Analogous reactions using $HgCl_2$ and HgI_2 as well as salts of Hg(I), Sn(IV), and Fe(I) also resulted in the production of *n*-$B_{18}H_{22}$ but at significantly reduced yields, see Table I. Attempts to run the reaction in more basic solvents only resulted in reduced yields or the production of $B_9H_{13}{\cdot}L$ species.

Besides the *n*-$B_{18}H_{22}$, we find the only other boron-containing products of these reactions to be a mixture of two compounds we have tentatively identified as mono- and dihalogenated nonaboranes. We also observe the production of hydrogen gas but in a significantly smaller quantity than would be expected if the simplest view of this reaction is considered, see eq 1.

$$3HgBr_2 + 4Me_4NB_9H_{12} \rightarrow 2B_{18}H_{22} + Hg + Hg_2Br_2 + 2H_2 + 4Me_4NBr \quad (1)$$

The reaction we describe represents a straightforward synthesis of *n*-$B_{18}H_{22}$ in good yield with only the simplest precautions necessary to exclude gross amounts of air and water. We have not yet observed any metal-containing intermediates of the type suggested by the oxidative fusion work of Grimes.[1] Any serious

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