Organometallics 1987, *6*, 2394–2404

Vinylation of Cyclohexanone Enolates Using Vinyl Ether–Iron Complexes. Diastereoselectivity of Carbon–Carbon Bond Formation

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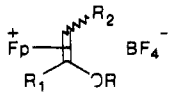
Received April 10, 1987

Cationic vinyl ether–iron complexes **1**, isolated as stable BF_4^- salts, are readily available from α-halo acetals and ketals. The olefin ligand in these complexes is unsymmetrically bound to the metal, which accounts for the relatively low barrier for rotation about the formal double bond, which is observed in these substances (15–23 kcal/mol), and for the high regioselectivity with which nucleophiles add to the activated olefinic center. The salts **1** serve as vinylating, isopropenylating, and cis-propenylating reagents with cyclohexanone enolates. Reaction of **1a** with cyclohexanone enolate gave a single diastereomeric product **5**. This has been converted to the lactone **10**, which establishes the relative configuration of the adjacent chiral centers in **5**. The relative configuration of analogous chiral centers in the major diastereomer **16a**, formed by the alkylation of 3-methylcyclohexanone enolate with **1a**, has been established by a single-crystal X-ray diffraction study and shown to be identical with that in **5**. Complex **1a** also gives a single diastereoisomeric adduct with 6-methylcyclohexanone enolate, and this has been shown by ^{13}C NMR studies to have the same relative configuration at the newly formed chiral centers as in **5** and **16a**. Alkylation of 5-methylcyclohexanone enolate with **1b** leads to a mixture of isopulegone and isoisopulegone, while alkylation of the kinetic enolate derived from 3-methyl-2-cyclohexenone with this complex yields isopiperitenone.

Introduction

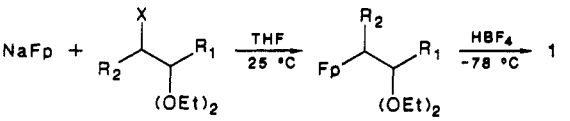
The lexicon of organic synthons abounds with vinyl anion reagents. By contrast, vinyl cations are known only as transient intermediates,[2] and the relatively few reagents which function as masked vinyl cations are of comparatively recent origin.[3] Among this latter class of reagent, the vinyl ether–iron complexes **1** are unique in possessing unit cationic charge, which confers on them exceptionally high reactivity toward a range of nucleophiles. We recently reported briefly on the use of these substances as vinyl cation equivalents in reactions with cyclohexanone enolates.[4,5] This paper provides a full account of this work and examines the diastereoselectivity of the reactions of **1a** with several cyclohexanone enolates.



1a: $R_1, R_2 = H$
b: $R_1 = Me; R_2 = H$
c: $R_1 = H; R_2 = Me$
Fp = η-$C_5H_5Fe(CO)_2$

Results and Discussion

Preparation of Complexes. The iron complexes **1a–c** were prepared from the α-halo acetals following procedures previously reported.[6] Notwithstanding the low reactivity of α-halo acetals toward common nucleophiles,[7] reaction with NaFp proceeds rapidly at moderate temperatures. It is possible that this metalation reaction does not involve direct nucleophilic displacement, but rather single electron transfer, followed by collapse of the radical pair. Precedent for such a reaction course is to be found in the reactions of cyclopropylmethyl halides with NaFp, which yield metalated products through radical intermediates.[8] The chloro acetal is well-suited to the preparation of **1a**, but **1b,c** are better prepared from the corresponding bromo acetals. Either methyl or ethyl acetals may be used in the preparation of vinyl ether complexes **1** since the alkyl group in these cations are readily exchanged. Thus, dissolution of the methyl vinyl ether complexes corresponding to **1a–c** (R = Me) in a small volume of ethanol at room temperature for several minutes, followed by reprecipitation with ether, affords a quantitative yield of trans-etherified products **1a–c** (R = Et). These changes, which reflect the very high reactivity of Fp–vinyl ether complexes toward nucleophiles, provide a general procedure for the preparation of primary and secondary alkyl vinyl ether complexes from the more readily available methyl or ethyl analogues. The ethyl ether complexes are in general preferred over the methyl analogues since, in them, the possibility for competitive nucleophilic attack at the alkyl group rather than at the vinyl center is reduced. The salts **1a–c** (R = Me, Et) are crystalline solids, which may be handled in air without decomposition and stored at 0 °C for extended periods of time without decomposition. They undergo rapid hydrolysis on exposure to moisture to give the corresponding σ-Fp–aldehyde or ketone. Treatment



(1) (a) Taken in part from: Chang, T. C. T. Ph.D. Thesis, Brandeis University, June, 1983. (b) Taken in part from: Stockman, C. Ph.D. Thesis, Brandeis University, June, 1986.
(2) Rappaport, Z. *Acc. Chem. Res.* **1976**, *9*, 265. Hanack, M. *Acc. Chem. Res.* **1976**, *9*, 364.
(3) A recent summary of these has been given by: Hudrlik, P. F.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6251. To these may be added: Kende, A. S.; Fludzinski, P. *Tetrahedron Lett.* **1982**, 2373. Clive, D. L. J.; Russell, C. G.; Suri, S. C. *J. Org. Chem.* **1982**, *47*, 1632.
(4) Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. *J. Am. Chem. Soc.* **1982**, *102*, 5930.
(5) Chang, T. C. T.; Rosenblum, M. *J. Org. Chem.* **1981**, *46*, 4103.
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(7) McElvain, S. M.; Stammer, C. J. *J. Am. Chem. Soc.* **1951**, *73*, 715.
(8) Krusic, P. J.; Fagan, P. J.; San Filippo, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 250.

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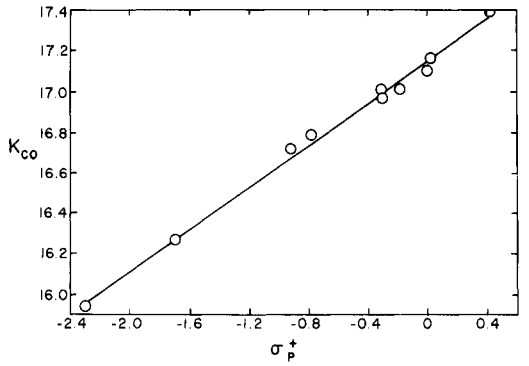
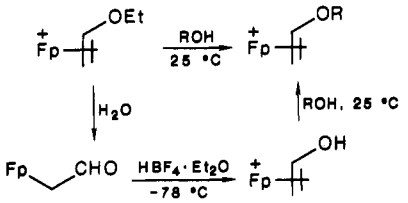
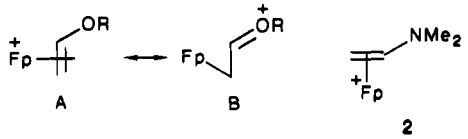


Figure 1. Correlation of carbonyl force constants with σ_p^+ for Fp(η-CH_2=CRX) cations.

of these with fluoroboric acid etherate yields the corresponding vinyl alcohol complex, which may in turn be converted to a vinyl ether complex by brief dissolution in alcohol at room temperature and reprecipitation with ether. These reactions are summarized below for **1a** (R = Et).



Structure and Properties. Although Fp(η^2-olefin) cations are in general excellent substrates for addition reactions by carbon[9] and heteroatomic[10] nucleophiles, complexes derived from monoalkylated olefins may yield mixtures of regioisomers with carbon nucleophiles.[9] By contrast, the reactions of Fp(η^2-vinyl ether) cations are regiospecific, due to partial localization of charge as indicated by canonical structure B shown below.



The unsymmetrical nature of Fe–C bonding in the cation, which is conveyed by this formalism, is well-supported by the crystal structure of **1a** (R = Me), in which the difference between Fe–C_α and Fe–C_β bond distances has been shown to be somewhat greater than 0.12 Å.[11] This distortion in metal–olefin bonding is brought to an extreme in the vinylamine complex **2** where the difference in these distances is 0.70 Å.[11]

The vinyl ether–Fp complexes lie about midway on a structural continuum which joins the symmetrically π-bonded Fp(ethylene) cation with the σ-bound neutral Fp(alkyl) complexes. This is illustrated by the position of these complexes on the plot (Figure 1), which correlates Cotton–Kraihanzel[12] CO stretching force constants for a series of Fp(olefin) cations (Table I) and Brown's σ_p^+ constants.[13] The first parameter has been shown to be an effective measure of charge on the metal,[14] while the second reflects the substituent's ability to transfer charge to the metal center from the ligand. Each of these provide a measure of the relative importance of canonical form B in contributing to the structure of the complex.

The unequal charge distribution in vinyl ether and vinylamine complexes, implicit in the large contribution of form B to their ground-state structures, is manifest in the ^{13}C chemical shifts of vinyl carbon centers in these complexes compared with those of the corresponding alkyl-substituted olefin complexes.[16] As can be seen from the data of Table II, the chemical shift difference between C_α and C_β is significantly enhanced in the vinyl ether and

Table I. Carbonyl Force Constants and σ^+ Substituent Constants For Fp(CH_2=CHX)BF_4 Complexes

substituent (X)	γ_{CO}, cm^{-1}	k_{CO},[a,b] mdyn/Å	σ_p^+[c]	γ_{CO} ref
1. CHO	2100, 2050	17.39	+0.42	15
2. $SiMe_3$	2043, 2080[e]	17.16	+0.02	*d*
3. H	2040, 2075	17.10	0	15
4. Ph	2035, 2070	17.01	−0.18	15
5. Et	2030, 2070	16.97	−0.30	15
6. Me	2035, 2070	17.01	−0.31	15
7. OMe	2020, 2058[e]	16.79	−0.78	*d*
8. OH	2010, 2060[f]	16.72	−0.92	6
9. NMe_2	1975, 2045	16.27	−1.70	*d*
10. O^-	1968, 2005[f]	15.94	−2.30	6

[a] See ref 12 for calculations. [b] All spectra were taken in nitromethane unless otherwise noted. [c] Taken from ref 13. [d] This work. [e] Taken in methylene chloride. [f] Taken in KBr.

Table II. ^{13}C Chemical Shifts for Fp(CH_2^α=$CR^\beta X$) Cations

substituents R	X	$\delta(C_\alpha)$[a]	$\delta(C_\beta)$[a]	$\Delta\delta$	ref
H	H	56.7	56.7	0	15
H	Ph	48.7	85.6	36.9	15
H	CMe_3	48.0	105.0	57.0	*b*
H	Et	53.9	90.3	36.4	*b*
H	Me	55.8	85.7	29.9	15
H	OMe	27.3	146.2	118.9	*b*
H	NMe_2	0.1	177.6	177.5	*b*
Me	Me	54.4	122.9	68.5	*b*
Me	OMe	17.6	199.5	181.9	*b*
OMe	OMe	−8.7	199.6	208.3	*b*
Me	NMe_2	4.5	197.0	192.5	*b*

[a] Taken in nitromethane; given in parts per million referenced to internal TMS. [b] This work.

Table III. Rotational Barriers about the C–C Bond in Fp(CHR_1=CZR_2)$^+BF_2^-$

complex	R_1	Z	R_2	solv[a]	$\Delta G^\ddagger$, kcal/mol	$\Delta\nu$, Hz	T_c, °C
1a	H	OMe	H	n	>18.9	3.0	>70
1b	H	OMe	Me	n	14.8	6.0	8
3a	H	CH_2Fp	H	n	13.4	49.5	0
3b	H	CH_2Fp	Me	a	11.2	6.4	−60
2	H	NMe_2	H	c	9.8	50.0	−70
1c	Me	OMe	H	a	21.9		
1b	H	OCH_2CMe_3	Me	n	14.5	7.3	−9

[a] Solvent: n, nitromethane; a, acetone; c, methylene chloride.

(9) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8427.
(10) Lennon, P.; Madhavarao, M.; Rosan, A. M.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93.
(11) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361.
(12) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.
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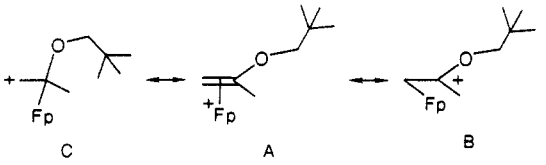
(15) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.
(16) For a discussion of the effect of electron density on ^{13}C chemical shifts, see: Wehrli, F. W.; Wirthlin, T. *Integration of Carbon-13 NMR Spectra*; Heyden: London, 1978. See also: Farnum, D. G. *Adv. Phys. Org. Chem.* **1975**, *11*, 123. Fliszár, S.; Cardinal, G.; Béraldin, M.-T. *J. Am. Chem. Soc.* **1982**, *104*, 5287.

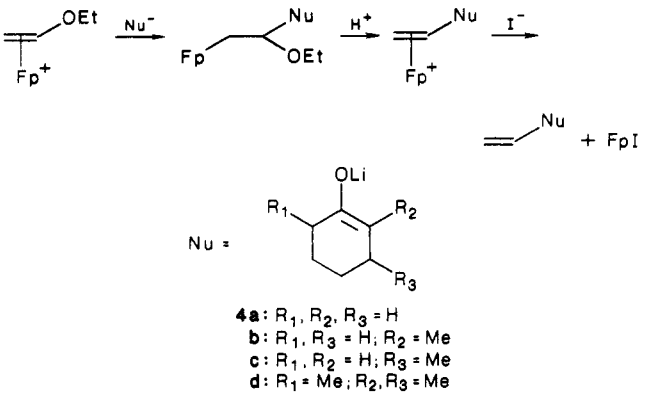
amine complexes compared with this difference in the less polarized alkyl- and phenyl-substituted olefin complexes. This chemical shift difference reaches a maximum in the vinyl and isopropenylamine complexes and is still larger in the ketene acetal complex where C_α is more highly shielded than it is in the uncharged Fp–ethyl complex (δ −2.41). Such changes are indicative of increasing charge concentration at C_β in the heterosubstituted Fp(olefin) cations.

The increased importance of canonical form B is also manifest in the rotational barrier about the C–C "double bond" in these complexes. Rotational barriers for a number of simple vinyl ether–Fp complexes and for the vinylamine complex **2** are summarized in Table III. With the exception of the last entry for the *trans*-propenyl complex **1c**, rotational barriers were determined from the coalescence temperature of vinyl proton resonances in the variable-temperature NMR spectra of these compounds.[17] The activation energy for the isomerization of (*E*)-**1c** to the *Z* isomer, through rotation about the C–C double bond, was determined kinetically.[18] In general, the rotational barriers in these complexes resembles those in β-acylenamines and related push–pull alkenes.[19] The rotational barrier in **1a** could not be determined by NMR spectroscopy since the compound decomposed at 70 °C before the onset of coalescence. The rotational barrier for this substance is estimated to lie between 19 and 22 kcal/mol, the higher limit being that associated with the isomerization of the propenyl complex **1c**. The coalescence temperature for **1b** was found to be independent of its concentration, and hence the exchange mechanism is intramolecular rather than dissociative. A similar mechanism has been assumed to apply to all of the other complexes shown in Table III. That rotation about the C–C bond takes place through contributions of canonical form B rather than high energy form C can be shown by examining the dynamic behavior of the neopentyl isopropenyl ether complex **1b** (R = neopentyl). Exchange of vinyl protons in this substance through form C would leave the diastereotopic methylene protons of the neopentyl group unchanged, while rotation of the C–C bond, as implied by resonance form B, provides a mechanism for simultaneous exchange of both pairs of protons. Variable-temperature NMR studies show that the latter circumstance obtains, with a calculated rotational barrier of 14.1 ± 0.5 (vinyl protons) or 14.9 ± 0.5 kcal/mol (methylene protons).[20] As would be anticipated, these values lie close to that found for **1b**.



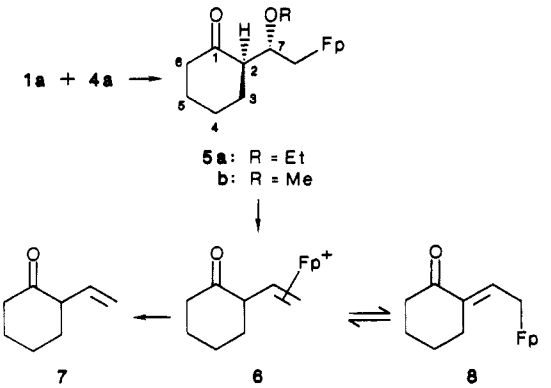
It is of interest to note that the $FpCH_2$ group, as reflected by the C–C rotational barrier in complex **3a**,[21] may be placed between a methoxy and a dimethylamino group in its capacity to release electrons to the metal through the unsaturated ligand. So great is this release in the dimethylamino complex **2**, that the diastereotopic methyl groups in this complex remain chemically shift nonidentical, without appreciable broadening, up to a temperature of 100 °C. The rotational barrier about the C–N bond in this complex is estimated to be greater than 19 kcal/mol, resembling that in amides.[22]

Vinylation Reactions. The generalized sequence by which Fp(η^2-vinyl ether)BF_4 complexes serve as vinyl cation equivalents is summarized below and has been examined for a number of cyclohexanone lithium enolates **4a–d**.



4a: R_1, R_2, R_3 = H
b: R_1, R_3 = H; R_2 = Me
c: R_1, R_2 = H; R_3 = Me
d: R_1 = Me; R_2, R_3 = Me

The reaction of cyclohexanone lithium enolate **4a** in THF solution with complex **1a** (R = Et, Me) to give **5** (R = Et, Me) (90%) takes place rapidly at −78 °C and is evidenced by the disappearance of infrared metal–carbonyl bands at 2060 and 2020 cm^{-1} of **1a** and their replacement by bands 2000 and 1940 cm^{-1} characteristic of the uncharged adduct. Brief treatment at −78 °C in methylene chloride solution with HBF_4 etherate gives the salt **6** (90%), which may be precipitated from solution by the addition of ether and freed from organic impurities by washing with ether. Decomplexation is readily achieved by either brief exposure of the salt to a solution of sodium iodide in acetone at room temperature or by heating a solution of the salt in acetonitrile (95%). The first procedure yields FpI, which can be separated from the ketone product by chromography, while the second gives the Fp(acetonitrile)BF_4 salt, which is readily separated from the organic product by precipitation from solution with ether.



In this and in all subsequent condensations of **1** with lithium enolates, it is important that the enolate be present in slight excess. If instead, the cationic complex is in slight excess, then the adduct formed at low temperature is rapidly transformed, on warming to room temperature, to

(17) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon: Oxford, 1969; p 55. Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.
(18) Marsi, M.; Rosenblum, M. *J. Am. Chem. Soc.* **1984**, *106*, 7264.
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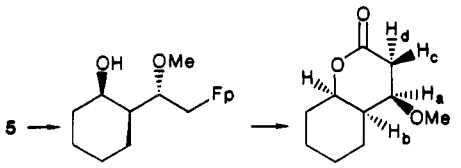
(20) Bucheister, A. A. Ph.D. Thesis, Brandeis University, 1983.
(21) Laing, M.; Moss, J. R.; Johnson, J. *J. Chem. Soc., Chem. Commun.* **1977**, 656. King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *7*, 311. Kerber, R. C.; Giering, W. P.; Bauch, T.; Waterman, P.; Chou, E. *J. Chem. Soc., Chem. Commun.* **1976**, *120*, C31.
(22) Jackman, L. M. In *Dynamic NMR Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; p 203.

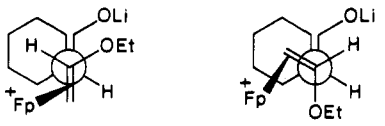
the α,β-unsaturated ketone **8**. The formation of this complex may be due to initial conversion of some of the adduct **5** to cation **6** in the presence of **1a**, and subsequent proton transfer from **6** to **5**, initiating further reaction. Since allylic deprotonation of Fp(olefin) cations may in general be carried out with as weak a base as triethylamine, it is not surprising that the tertiary proton in **6** is highly acidic due to activation by both the carbonyl and Fp(olefin)$^+$ functions. This acidity is further evidenced by the NMR spectrum of **6**, taken in acetone solution, which clearly shows a weak triplet resonance at δ 7.13 characteristic of the vinyl proton in the conjugated ketone **8**.

Both the proton and carbon-13 NMR spectra of **5** (R = Et, Me) show the adduct to be a single diastereomer. The structure of **5** (R = Me) was established by reduction with L-selectride to the hydroxy ester **9**, followed by conversion to the lactone **10** by oxidation with ceric ammonium nitrate, in 63% overall yield. The ^{1}H NMR spectrum of this product, taken at 300 MHz, shows J_{ab} = 4.5, J_{ac} = 10.5, and J_{ad} = 7.1 Hz in accord with a cis arrangement of H_a and H_b protons in **10**. Hence the adduct **5** must have the anti configuration at C-2,7 as shown.



9 **10**

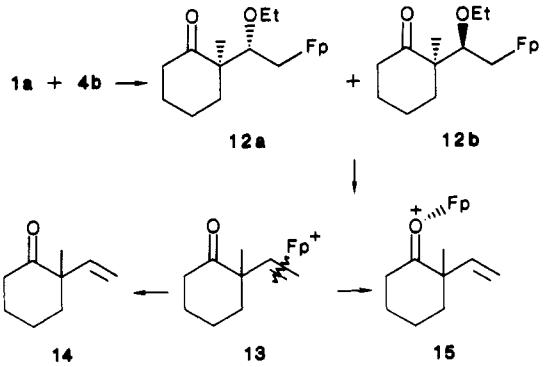
The stereochemical outcome may be accommodated by a transition state involving trans addition[9] of enolate to the olefin complex, with the orientation of interacting olefin centers being either antiperiplanar or synclinal to one another, as shown in structures **11a** and **11b**. Both



11a **11b**

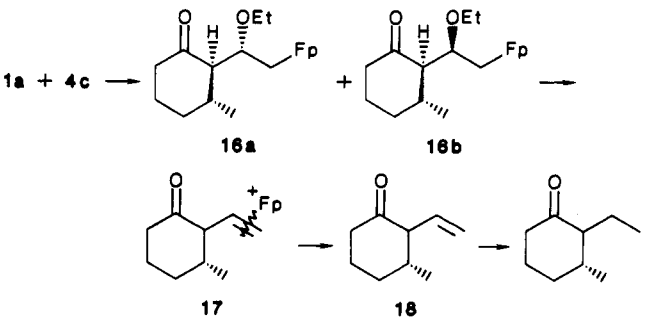
of these conformational forms have been invoked to account for diastereoselectivity in aldol and in allylmetal condensations.[23,24] The closed, or chelated transition state, commonly invoked in aldol-type reactions, requires a synclinal orientation of reacting centers, but the organometallic reactions considered here must proceed through an open transition state, and hence both antiperiplanar as well as synclinal orientations are possible. The antiperiplanar orientation **11a** would be expected to be preferred over its diastereoisomeric form, which would place the ethoxy group over the cyclohexane ring, while the transition state **11b** conforms to the topological rules of Seebach and Golinski[25] for donor–acceptor interactions. Here the synclinal orientation of reacting centers is favored and the Burgi, Shefter, and Dunitz[26] preferred trajectory of nucleophilic attack, with the hydrogen of the donor component antiperiplanar to the acceptor center, is invoked.

Alkylation of 2-methylcyclohexanone lithium enolate (**4b**) with cation **1a** (R = Et) also takes place rapidly at low temperatures to give the adduct **12** in 90% yield. No products of competing proton-transfer reactions are observed, but the product, in contrast to that formed from cyclohexanone enolate, is a 4:3 mixture of diastereomers. The diastereomeric products are readily separated by preparative TLC on alumina, and these were converted by protonation and subsequent demetalation, either individually or together, in high yield, to 2-methyl-2-vinylcyclohexanone (**14**). The sterically crowded nature of the intermediate olefin complex **13** is suggested by its rapid rearrangement to **15** on standing briefly at room temperature.



12a **12b** **14** **13** **15**

The very high reactivity of **1a** also ensures regiospecific alkylation of the enolate **4c**, obtained either from addition of lithium dimethylcuprate to cyclohexenone[27] or through hydrosilylation of 3-methylcyclohexenone followed by desilylation.[28] The adduct was obtained as a 3:1 mixture of diastereomers **16a**/**16b** which were separated chromatographically. Their ^{13}C NMR spectra, compared with that of the parent adduct **5**, show each to be a trans-2,3-disubstituted cyclohexanone, and hence each must be epimeric at C-7. This assignment is confirmed by conversion of the mixture of diastereomers, through successive low-temperature protonation, followed by sodium iodide demetalation of the intermediate cation **17** to *trans*-2-vinyl-3-methylcyclohexanone (**18**) in 90% yield. Hydrogenation of **18** in the presence of 10% palladium on carbon gave the known *trans*-2-ethyl-3-methylcyclohexanone[29] as the sole product.



16a **16b** **17** **18**

In order to establish the structure of the major diastereomer **16a** derived from the condensation of **1a** with **4c**, a single-crystal X-ray structure determination was carried out. Crystal data and experimental detail appear in Table IV, while atomic coordinates for non-hydrogen atoms are presented in Table V. A perspective view of the molecule is shown in Figure 2. It is evident that the molecular

(23) Heathcock, C. H. In *Asymmetric Synthesis*; Academic: New York, 1984; Vol. 3, Chapter 2. Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970 and references therein.

(24) The former has been invoked in the reactions of allylsilanes with aldehydes. Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963.

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Table IV. Data for the X-ray Diffraction Study of $(C_5H_5)Fe(CO)_2(C_{11}H_{19}O_2)$

(A) Crystal Data at 21 (1) °C

crystal system: triclinic[a]	$Z = 2$
space group: $P\bar{1}$ [C_i^1; No. 2]	$V = 903.4$ Å^3
$a = 7.831$ (2) Å	crystal size: 0.16 × 0.20 × 0.40 mm
$b = 10.183$ (3) Å	fw 360.24
$c = 12.322$ (4) Å	$\rho_{calcd} = 1.32$ g cm^{-3}
$\alpha = 102.42$ (3)°	$\rho_{obsd} = 1.33$ (1) g cm^{-3}
$\beta = 90.34$ (3)°	$\mu = 8.7$ cm^{-1} (Mo K$\bar{\alpha}$)
$\gamma = 109.15$ (3)°	

cell constant determination: 12 pairs of $\pm(hkl)$ and refined 2θ, ω, and χ values in the range $20 \leq 2\theta \leq 22°$ (λ Mo K$\bar{\alpha}$) = 0.71073 Å)

(B) Measurement of Intensity Data

radiatn: Mo K$\bar{\alpha}$, graphite monochromator
reflctns measd: $+h,\pm k,\pm l$ (to $2\theta = 47°$)
scan type, speed: θ–2θ, 1.95–3.91°/min
scan range: unsymmetrical, from 0.8° below Kα_1 peak to 0.9° above Kα_2 peak
no. of reflctns measd: 2909; 2681 in unique set
std reflctns: 026, 430, 004 measd after each 60 reflctns; variatn $<\pm 3\sigma(I)$ for each
absn correctn: empirical, using 012, 024, 035, and 137 reflctns, normalized transmission factors 0.834–1.000
statistical informatn: $R_s = 0.033$; $R_{av} = 0.017$ ($0kl$ reflctns)
automatic recentering after every 800 reflctns

(C) Solution and Refinement, with 1858 Data for Which $F > 3.92\sigma(F)$

weighting of reflctns: *as* before,[b] $p = 0.035$
soln: Patterson, difference-Fourier, routine
refinement:[c] full-matrix least squares, with anisotropic temperature factors for Fe, C, and O atoms; isotropic temperature factors for fixed H atoms; $R = 0.044$; $R_w = 0.053$; SDU = 1.08; R, R_w (str factor calcn with all 2681 reflctns) = 0.079, 0.060
final difference map: 3 peaks 0.24–0.28 e/Å^3 near (C17), C(3), and O(1); other peaks random and ≤0.23 e/Å^3
weighting scheme anal.: no systematic dependence on magnitude of $|F_o|$, (sin θ)/λ, sequence number, or indices

[a] The corresponding primitive TRACER II reduced cell is isodimensional with this cell but has constants b, c, a, β, γ, and α. (TRACER II Cell Reduction Program, S. L. Lawton, Mobil Oil Corp., April, 1967.) [b] Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113 and references there in. [c] $R_s = \sum(\sigma(|F_o|)/\sum|F_o|$; $R_{av} = \sum|I - I_{av}|/\sum I$. $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$. SDU = $\{\sum w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$, where m (= 1858) is the number of observations and n (= 208) is the number of parameters.

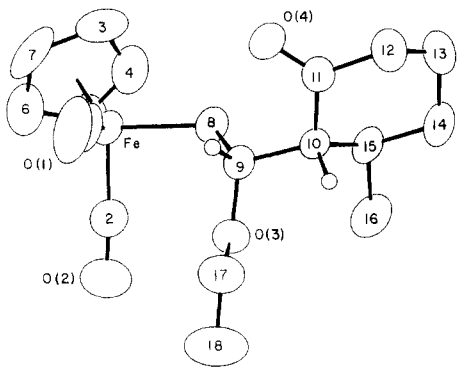


Figure 2. Molecular structure of **16a**, showing 50% boundary ellipses for atoms refined by using anisotropic temperature factors. For clarity, all H atoms except H(9) and H(10), bonded to C(9) and C(10), respectively, have been omitted. H(9) and H(10) have been assigned arbitrary temperature factors in the drawing.

structure corresponds to a preferred orientation of reacting components in the transition state analogous to that depicted by either **11a** or **11b**. Bond lengths and angles (Table VI) lie within normal ranges.

Finally, the condensation of **1a** (R = Et) with 6-methylcyclohexanone lithium enolate gave the adduct **19** as a single diastereomer. The stereochemistry assigned to the product at C-6 is supported by its ^{13}C NMR spectrum, which shows increased shielding at C-2 and C-4 typical of the γ-effect for an axial methyl group.[30] Thus, alkylation of this enolate must take place through axial attack of the cation **1a**. Furthermore, the relative stereochemistry at the C-2 and C-7 centers may be deduced from a comparison of the chemical shifts of the methylene carbon center adjacent to the Fp group. This resonance, which is at δ 3.1 in **19**, is close to that observed in **5** and **16a** (δ 3.7 and 3.2 respectively) but is significantly different from that

Table V. Atomic Coordinates for $(C_5H_5)Fe(CO)_2(C_{11}H_{19}O_2)$[a]

atom	x	y	z
Fe	0.02973 (10)	0.03627 (7)	0.26019 (5)
O(1)	0.2866 (7)	−0.0294 (4)	0.1110 (4)
O(2)	0.2442 (8)	0.0498 (5)	0.4554 (4)
O(3)	0.0994 (4)	−0.2612 (3)	0.3248 (3)
O(4)	−0.1444 (5)	−0.4028 (4)	0.0059 (3)
C(1)	0.1813 (8)	−0.0044 (5)	0.1691 (5)
C(2)	0.1574 (9)	0.0378 (5)	0.3761 (5)
C(3)	−0.1685 (12)	0.0800 (8)	0.1753 (6)
C(4)	−0.2160 (8)	0.0729 (7)	0.2828 (8)
C(5)	−0.0878 (12)	0.1748 (8)	0.3559 (6)
C(6)	0.0408 (10)	0.2498 (6)	0.3018 (8)
C(7)	0.0015 (12)	0.1991 (9)	0.1898 (7)
C(8)	−0.1124 (7)	−0.1784 (5)	0.2419 (4)
C(9)	−0.0125 (6)	−0.2853 (4)	0.2253 (4)
C(10)	−0.1396 (6)	−0.4418 (4)	0.1907 (3)
C(11)	−0.1979 (6)	−0.4840 (5)	0.0661 (4)
C(12)	−0.3218 (8)	−0.6335 (6)	0.0223 (4)
C(13)	−0.4816 (8)	−0.6733 (5)	0.0912 (5)
C(14)	−0.4187 (7)	−0.6424 (5)	0.2136 (5)
C(15)	−0.3048 (7)	−0.4864 (5)	0.2588 (4)
C(16)	−0.2516 (8)	−0.4606 (6)	0.3819 (5)
C(17)	0.2573 (8)	−0.2992 (6)	0.3054 (5)
C(18)	0.3601 (10)	−0.2771 (9)	0.4080 (6)

[a] Numbers in parentheses in this and subsequent tables indicate estimated standard deviations in the least significant digit.

Table VI. Selected Bond Lengths (Å) and Angles (deg) in $(C_5H_5)Fe(CO)_2(C_{11}H_{19}O_2)$

Bond Lengths

Fe–C(1)	1.725 (6)	C(3)–C(7)	1.456 (13)
Fe–C(2)	1.732 (6)	C(4)–C(5)	1.342 (11)
Fe–C(3)	2.083 (9)	C(5)–C(6)	1.328 (11)
Fe–C(4)	2.087 (7)	C(6)–C(7)	1.360 (13)
Fe–C(5)	2.092 (9)	C(8)–C(9)	1.518 (7)
Fe–C(6)	2.096 (7)	C(9)–C(10)	1.541 (6)
Fe–C(7)	2.099 (9)	C(10)–C(11)	1.525 (6)
Fe–C(8)	2.063 (5)	C(10)–C(15)	1.541 (7)
O(3)–C(9)	1.432 (6)	C(11)–C(12)	1.491 (7)
O(3)–C(17)	1.419 (8)	C(12)–C(13)	1.510 (9)
O(4)–C(11)	1.205 (6)	C(13)–C(14)	1.516 (9)
C(1)–O(1)	1.151 (8)	C(14)–C(15)	1.521 (7)
C(2)–O(2)	1.149 (8)	C(15)–C(16)	1.514 (7)
C(3)–C(4)	1.388 (12)	C(17)–C(18)	1.429 (10)

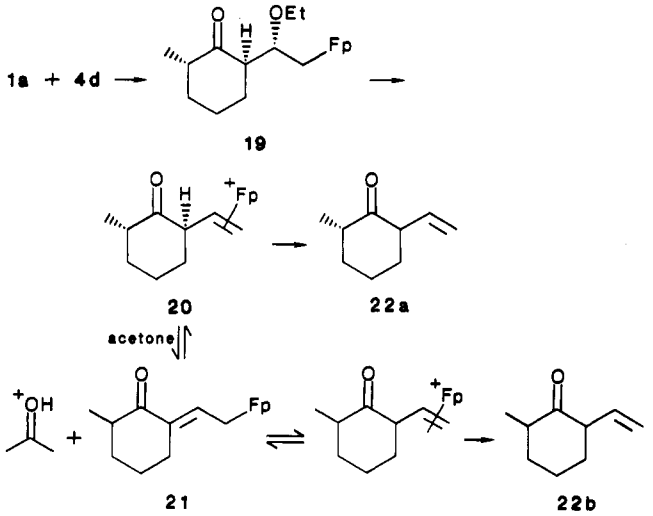
Bond Angles

Fe–C(1)–O(1)	177.9 (5)	O(3)–C(9)–C(8)	109.1 (4)
Fe–C(2)–O(2)	174.8 (6)	C(11)–C(10)–C(15)	110.8 (4)
Fe–C(8)–C(9)	120.1 (3)	C(11)–C(10)–C(9)	110.9 (4)
C(1)–Fe–C(2)	93.2 (3)	C(15)–C(10)–C(9)	117.0 (4)
C(1)–Fe–C(8)	90.3 (2)	C(12)–C(11)–O(4)	121.6 (5)
C(2)–Fe–C(8)	91.0 (2)	C(12)–C(11)–C(10)	116.1 (4)
C(9)–O(3)–C(17)	113.6 (4)	O(4)–C(11)–C(10)	122.3 (4)
C(4)–C(3)–C(7)	104.9 (7)	C(13)–C(12)–C(11)	112.2 (5)
C(5)–C(4)–C(3)	109.1 (7)	C(14)–C(13)–C(12)	110.8 (5)
C(6)–C(5)–C(4)	109.9 (8)	C(15)–C(14)–C(13)	112.1 (5)
C(7)–C(6)–C(5)	110.2 (8)	C(16)–C(15)–C(10)	112.7 (4)
C(3)–C(7)–C(6)	105.9 (8)	C(16)–C(15)–C(14)	109.8 (4)
C(10)–C(9)–O(3)	111.1 (4)	C(10)–C(15)–C(14)	110.8 (4)
C(10)–C(9)–C(8)	113.4 (4)	C(18)–C(17)–O(3)	110.9 (5)

(30) Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1974**, *52*, 308.

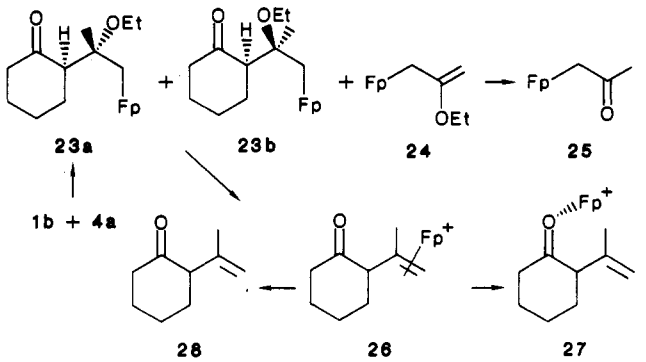
observed in **16b** (δ 5.5). Again, the preferred product appears to be that formed through transition states analogous to states **11a** or **11b**.

In view of the apparent homogeneity of the condensation product, we were surprised to observe that its transformation through successive protonation and demetalation with NaI in acetone gave a 1:1 mixture of *cis*- and *trans*-2-methyl-6-vinylcyclohexanone (**22a** and **22b**, respectively). It seems likely that epimerization of **19** takes place in the demetalation step as a result of competition between (a) proton transfer from the olefin complex **20** to solvent and (b) displacement of the Fp group. As with the cation **6**, a ^{1}H NMR spectrum of **20** in acetone solution shows the presence of enone complex **21** in equilibrium with **20**. However, demetalation of **20** can readily be effected without epimerization, by simply heating the salt briefly in acetonitrile solution. Under these conditions, the product is exclusively **22a**.



Isopropenylation. Since the isopropenyl group is a common structural feature among terpenes, it was of interest to extend the vinylation sequence to include isopropenylation of enolates as well. The requisite isopropenyl complex **1b**, like the parent cation **1a**, is a yellow crystalline, air-stable salt, which may be prepared on a large scale and stored indefinitely at 0 °C without decomposition.[6,31] The reaction of this salt with cyclohexanone lithium enolate in THF solution takes place rapidly at −78 °C to give the adduct **23** in 77% yield together with 15% of the acetone complex **25**, derived by competitive proton transfer from **1b** and subsequent hydrolysis of the resulting (ethoxyallyl)Fp complex **24**. The adduct **23** is formed as an 84:16 mixture of diastereomers. The major diastereomer is tentatively assigned structure **23a**, based on the assumption of larger steric interactions for the ethoxy function than for the methyl group in transition states corresponding to **11a** or **11b**. While this order is the reverse of the relative conformational energies for these substituents in cyclohexane, resonance interactions of the oxygen long pair with the cationic center in the vinyl ether complex forces the alkoxyl group to be coplanar with the remainder of the ligand[11] and consequently should increase its effective size. Some further evidence in support of this structural assignment is provided by the observation that alkylation of cyclohexanone lithium enolate with **1b** (R = neopentyl) yields diastereomeric adducts in a 96:4 ratio. Both of the major diastereomers show very similar chemical shifts for the methylene carbon bonded to the iron center (δ 9.5 and 8.6), which correlate with the calculated chemical shift for these centers based on a configuration analogous to that found in **5**, **16a**, and **19a**.[32] We were, however, unable to detect this ^{13}C resonance for the minor diastereomer corresponding to these adducts.

Low-temperature protonation of the mixture of diastereomeric adducts **23** gave the unstable olefin complex **26** (95%) as a yellow solid, which isomerized to the carbonyl-coordinated complex **27** on standing briefly at room temperature. Both **26** and **27** are smoothly demetalated by brief exposure to sodium iodide in acetone solution to give 2-isopropenylcyclohexanone **28** in essentially quantitative yield.



Proton transfer from **1b** (R = Et), which is a minor side reaction with **4a**, becomes a dominant mode of reaction with more hindered enolates. Thus, with enolate **4b**, the sole reaction product is the acetone complex **25**. The same result is obtained with the less hindered enolate **4c**. Attempts to avoid this outcome by changing the solvent to DMF, adding TMEDA, or running the condensation reaction at higher temperatures did not change the reaction with either enolates **4b** or **4c**.

Some advantage may, however, be taken of these observations in the circumstance in which a mixture of enolates, derived by kinetic deprotonation of a ketone, is to be isopropenylated. Thus, of the two enolates **29** and **30**, derived from 3-methylcyclohexanone by treatment with either lithium 2,2,6,6-tetramethylpiperidide[33] or tritylithium[34] at −78 °C, **29** reacts with **1b** by proton transfer, while **30** is alkylated to give **31** in 50% yield after chromatographic purification. Alternatively, **30**, prepared by hydrosilylation[28] of 5-methyl-2-cyclohexenone[35] and desilylation, was converted in 60% yield to **31**. This product, obtained as a mixture of three diastereomers, was converted by protonation to a mixture of unstable olefin complexes **32** and, thence, by sodium iodide decomplexation, to a 2:1 mixture of isopulegone (**33**) and isoisopulegone (**34**)[36] (94%). Hydrogenation of this product gave a mixture of menthone **35** and isomenthone **36**, identified by comparison of their ^{13}C NMR spectra with the literature.[36b] Finally, it may be noted that a mixture of **33** and **34** can be obtained in 40% overall yield from 3-methylcyclohexanone on a 50 mM scale, without purification of reaction intermediates.

Isopiperitenone (**38**), previously obtained in low yield along with carvone by oxidation of limonene,[37] may sim-

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(32) Pretsch, E.; Seibl, J.; Simon, W. *Spectral Data For Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, 1983; p 10.

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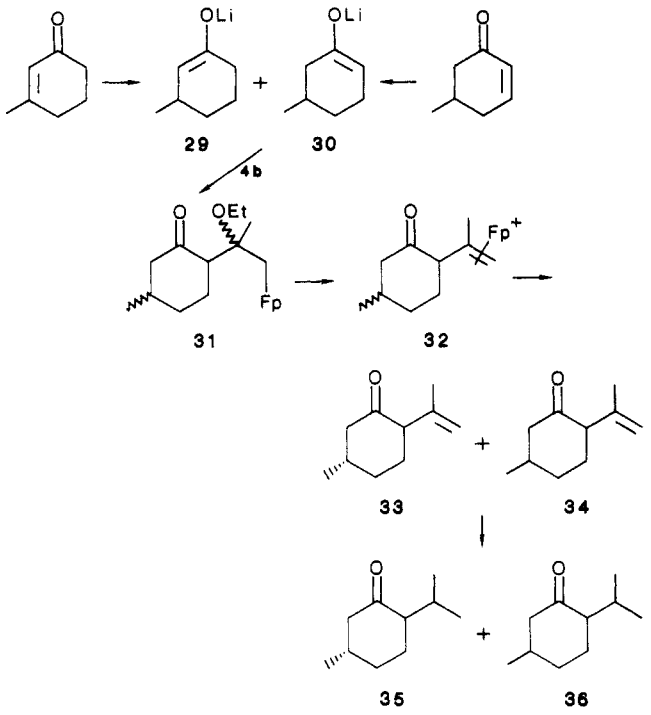
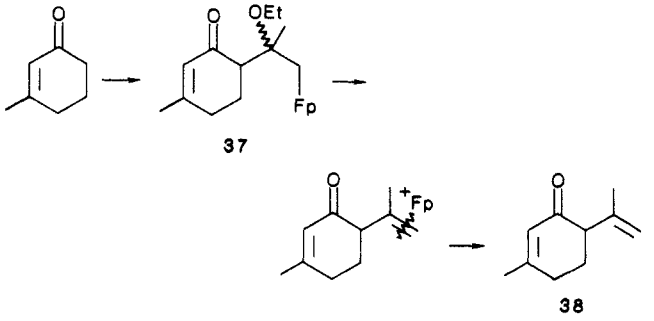
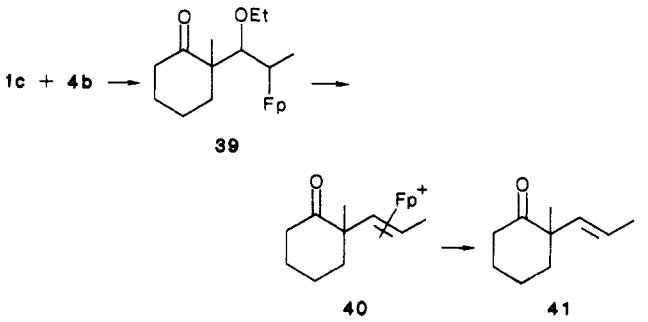


ilarly be prepared from 3-methyl-2-cyclohexenone. The kinetic enolate, derived from this ketone with LDA in THF, reacts with **4b** to give the adduct **37**, with little interference from competing proton-transfer reactions. Low-temperature protonation, followed by demetalation and Kugelrohr distillation, gave isopiperitenone **38**, identified by proton NMR spectral comparison with literature data,[38] in 88% overall yield.



Trans Propenylation. The propenyl ether complex **1c** (R = Et) exists as the cis isomer since the barrier to interconversion of cis and trans isomers is relatively low (Table III) and the cis isomer is expected to be thermodynamically favored.[39] Since both enolate addition to **1c** and Fp assisted elimination of ethanol from the adduct are trans stereoselective processed,[40] the net stereochemical result is inversion. Hence **1c** functions as a *trans*-propenyl cation equivalent.

The cation reacts rapidly with 2-methylcyclohexanone enolate **4b** to give the adduct **39** that could not be isolated, due to its instability at room temperature. Instead this was converted directly, at −78 °C, to the olefin complex **40** with fluoroboric acid etherate. The yellow crystalline salt, obtained in 80% yield, was also found to be thermally unstable at room temperature. Demetalation with sodium iodide and distillation gave **41** in 72% yield.



Experimental Section

Solvents were routinely dried by standard procedures and stored under nitrogen. All reactions and subsequent operations were performed under a nitrogen atmosphere. Infrared spectra were recorded on Perkin-Elmer spectrophotometers Models 457, 567, and 683. ^{1}H nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R-32 spectrometer (NSF GU 3852). ^{13}C nuclear magnetic resonance spectra were determined at 22.64 MHz on a Bruker WH-90 spectrometer (NSF GU 3852, GP 37156) and were collected with broad-band proton decoupling for determination of chemical shifts and with single-frequency off-resonance proton decoupling for the determination of multiplicities. Melting points were determined under a nitrogen atmosphere on a Kofler hot stage and are uncorrected. Elemental analyses were determined by either Galbraith Laboratories, Inc., Knoxville, TN, or Microlytics, South Deerfield, MA.

Preparation of Fp(η^2-vinyltrimethylsilane)BF_4. Fp(η^2-isobutylene)BF_4 (5 g, 15.6 mmol) was taken up in 35 mL of dry methylene chloride in a round-bottom flask, and then vinyl trimethylsilane (4.5 mL, 31 mmol) was added by syringe. The reaction was allowed to run to room temperature for 2 days until all of the isobutylene salt was consumed (^{1}H NMR). The solution was then filtered through Celite to remove $FpCO^+BF_4^-$ and cooled to −78 °C, and anhydrous ether was added to precipitate the product as a yellow solid. This was collected, washed with anhydrous ether, and recrystallized at −30 °C from methylene chloride–ether to give 4.0 g (70%) of product: IR (CH_2Cl_2) 2043, 2080 (C≡O) cm^{-1}; NMR (CD_3NO_2) δ 5.72 (s, 5 H, Cp), 4.62 (dd, 1 H, J = 12, 3 Hz, =CH_2 trans to $SiMe_3$), 3.84 (dd, 1 H, J = 17, 12 Hz, =CH($SiMe_3$)), 3.65 (dd, 1 H, J = 17, 3 Hz, =CH_2 cis to $SiMe_3$). Anal. Calcd for $C_{12}H_{17}O_2SiFeBF_4$: C, 39.59; H, 4.71. Found: C, 39.51; H, 4.71.

Preparation of Complex 2. Dimethylamine was bubbled through a 10-mL ether suspension of **1a** (R = Me) (322 mg, 1 mmol) at −30 °C for 10 min. The reaction was then allowed to warm to room temperature, stirred for an additional 10 min, and then filtered. The collected product was recrystallized from methylene chloride to give 315 mg (94%) of **2** as yellow crystals: mp 158 °C dec; IR (KBr) 2020, 1975 cm^{-1} (C≡O), 1645 (C=N^+Me_2); ^{1}H NMR (CD_3NO_2) δ 8.0 (t, 1 H, CH=NMe_2), 5.25 (s, 5 H, Cp), 3.50 (s, 3 H, NMe), 3.10 (s, 3 H, NMe), 2.05 (d, 2 H, J = 9 Hz, $FpCH_2$); ^{13}C (CD_3NO_2) δ 214.8 (C≡O), 177.5 (C=N), 87.0 (Cp), 47.6, 38.3 (Me), 0.1 ($FpCH_2$). Anal. Calcd for $C_{11}H_{14}O_2BF_4FeN$: C, 39.40; H, 4.19; H, 4.18. Found: C, 39.26; H, 4.23; N, 4.12.

Preparation of Complex 5 (R = Et). *n*-Butyllithium (0.71 mL, 1.6 mmol) was added dropwise to cyclohexanone silyl enol ether[27] (0.27 g, 1.59 mmol) dissolved in 5 mL of dry THF, at 15 °C. After the solution was stirred for 45 min, it was cooled to −78 °C and transferred by stainless-steel cannula to a slurry of complex **1a** (R = Et) (0.45 g, 1.34 mmol) in 5 mL of dry THF. The mixture was stirred for 1 h at −78 °C and then allowed to warm to room temperature. Solvent was removed, and the residue was chromatographed on 50 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.42 g (90%) of product as a yellow oil identified by both ^{1}H and ^{13}C NMR spectral analysis

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as a single isomer: IR (CH_2Cl_2) 2000, 1940 (MCO), 1700 (C≡O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.88 (s, 5 H, Cp), 3.50 (m, 3 H, OCH_2, OCH), 2.80–1.50 (m, 11 H, CH, CH_2), 1.06 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 217.5, 217.0 (MCO), 213.3 (C=O), 85.2 (Cp), 83.8 (C-7), 64.4 (CH_2O), 54.2 (C-2), 42.3 (C-6), 26.7 (C-5), 25.2 (C-3), 24.6 (C-4), 15.4 (CH_3), 3.7 (FpC).

Preparation of Complex 6. Tetrafluoroboric acid etherate (0.22 mL, 1.32 mmol) was added dropwise to a solution of complex **5** (0.42 g, 1.15 mmol) in 10 mL of methylene chloride and cooled to −78 °C. After 0.5 h, ether was added dropwise and the yellow crystals that precipitated from solution were transferred by cannula to a Schlenk tube and collected to give 0.4 g (90%) of **6** identified by ^1H NMR spectral analysis as a 2:1 mixture of two diastereomers: IR (CH_2Cl_2) 2080, 2040 (C≡O), 1705 (C=O) cm^{-1}; NMR (acetone-d_6) δ 5.88 and 5.87 (2s, 5 H, 2Cp), 5.40 (m, 1 H, CH=), 4.24 and 4.02 (2d (1:2), 1 H, J = 9 Hz, $=CH_2$), 3.60 and 3.51 (2d (1:2), 1 H, J = 15 Hz, $=CH_2$), 2.60–1.50 (m, 9 H, CH, CH_2).

Preparation of 7. Sodium iodide (0.2 g, 1.33 mmol) was added to a solution of complex **6** (0.4 g, 1 mmol) in 20 mL of acetone, at room temperature. After the mixture was stirred for 0.5 h, solvent was removed and the residue was extracted with petroleum ether. Removal of the solvent gave a dark green oil which was purified by Kugelrohr distillation to give 0.12 g (95%) of **7** as a colorless oil identified by comparison of NMR spectra data with the data reported by Marvell:[42] IR (neat) 1710 (C=O), 1640, 995, 925 ($RCH=CH_2$) cm^{-1}; NMR ($CDCl_3$) δ 6.41–5.90 (m, 1 H, CH=), 5.32–5.01 (m, 2 H, $=CH_2$), 3.10 (m, 1 H, CH), 2.70–1.60 (m, 8 H, CH_2) [lit.[43] NMR (CCl_4) δ 6.0–5.1 (m, 3 H, $CH=CH_2$), 2.9 (m, 1 H), 2.5–2.2 (m, 2 H), 2.1–1.5 (br m, 6 H)]. Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.32; H, 9.74.

Preparation of Alkyliron Complex 8. n-Butyllithium (1.3 mL, 2.94 mmol) was added to cyclohexanone silyl enol ether (0.5 g, 2.94 mmol) dissolved in 5 mL of THF, at 15 °C. After the solution was stirred for 45 min, it was cooled to −78 °C and transferred by stainless-steel cannula to a slurry of complex **1a** (R = Et) (1.07 g, 3.2 mmol) in 5 mL of THF at −78 °C. The mixture was stirred for 1 h at −78 °C and allowed to warm to room temperature. Evaporation of solvent gave a yellow oil that became red upon standing at room temperature for 0.5 h. This oil was chromatographed on 80 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.92 g (86%) of product as a deep yellow oil: IR (CH_2Cl_2) 2000, 1940 (C≡O), 1660 (conjugated C=O) cm^{-1}; NMR ($CDCl_3$) δ 7.20 (t, 1 H, J = 10 Hz, =CH), 2.05 (d, 2 H, J = 10 Hz, $FpCH_2$), 2.50–1.50 (m, 8 H, CH_2).

Preparation of 9. To 1.05 g (3.2 mmol) of complex **5** (R = Me) dissolved in 5 mL of THF, under argon at −78 °C, was added 1.2 equiv of L-selectride. The mixture was stirred at −78 °C for 2 h, then 2 mL of methanol was added, and stirring was continued for 2 h. The mixture was then warmed to room temperature, solvent was removed in vacuo, and the residue was extracted with ether. The combined ether extracts were filtered through alumina, and solvent was removed in vacuo. After the solution was left standing at 0 °C overnight, the material had crystallized. This was washed twice at −78 °C with hexane and dried in vacuo, leaving the product (447 mg, 42%) as an amber crystalline solid: ^{13}C ($CDCl_3$) δ 217.3 (MCO), 93.5 (CHOMe), 66.1 (COH), 58.3 (CH), 45.7 (CH_3), 32.6, 26.6, 26.0, 20.1 (CH_2), 1.1 (CH_2Fp).

Preparation of Lactone 10. The hydroxy ether **9** (447 mg, 1.3 mmol) was dissolved in 5 mL of THF. The solution was cooled to 0 °C and saturated with CO, then ceric ammonium nitrate (2 equiv, 1.4 g), dissolved in 8 mL of THF, was added, and the mixture was stirred for 5 min. A blue-green color developed immediately and then faded rapidly to orange. The mixture was allowed to warm to room temperature and added to 40 mL of aqueous sodium bicarbonate (5%), and this was extracted four times with 50 mL of ether. The combined extracts were dried over magnesium sulfate and passed through a small amount of activity IV alumina, and solvent was removed in vacuo, leaving 142 mg (63%) of product: IR (neat) 1730 cm^{-1}; NMR ($CDCl_3$) δ 4.33 (m, 1 H, CHOCO), 3.70–3.62 (8-line mult, 1 H, J = 10.5, 7.1, 4.5 Hz, CHOHe), 3.32 (s, 1 H, OCH_3), 2.88 (q, 1 H, J = 7.1, 19.0 Hz, eq CHCO), 2.43 (q, 1 H, J = 10.5, 19.0 Hz, ax CHCO), 2.1–1.2 (m, J = 9 Hz, CH, CH_2); ^{13}C NMR ($CDCl_3$) δ 170.96 (CO), 75.93, 75.37 (OCH), 55.85 (OCH_3), 36.60 (CH), 33.10, 30.44, 24.18, 19.72, 18.07 (CH_2). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.68; H, 8.83.

Preparation of Adduct 12. n-Butyllithium (2.4 mL, 5.7 mmol) was added dropwise to 2-methylcyclohexanone silyl enol ether[43] (1 g, 5.46 mmol) dissolved in 5 mL of THF, at 15 °C. After the solution was stirred for 45 min, it was cooled to −78 °C and transferred by stainless-steel cannula to a slurry of complex **1a** (R = Et) (1.8 g, 5.4 mmol) in 5 mL of dry THF. The mixture was stirred for 1 h at −78 °C and allowed to warm to room temperature. Solvent was removed, and the residue was chromatographed on 80 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 1.75 g (90%) of the desired product as a yellow oil identified by its ^1H NMR spectrum as a 4:3 mixture of two diastereomers. Preparative thin-layer chromatography on alumina (1000 μm) yielded two fractions on elution with 40% ether–Skelly B. The major fraction (R_f 0.63) was obtained as a yellow oil: IR (CH_2Cl_2) 2000, 1950 (M≡CO), 1710 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 4.80 (s, 5 H, Cp), 3.65 (m, 3 H, OCH, OCH_2), 2.38 (dd, 2 H, $FpCH_2$), 2.20–1.40 (m, 8 H, CH_2), 1.24 (t, 3 H, CH_3), 1.06 (s, 3 H, CH_3). The minor fraction (R_f 0.69) was obtained as a yellow oil: IR (CH_2Cl_2) 2000, 1950 (M≡CO), 1710 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 4.90 (s, 5 H, Cp), 3.60 (m, 3 H, OCH, OCH_2), 2.45 (dd, 2 H, $FpCH_2$), 2.30–1.40 (m, 8 H, CH_2), 1.24 (t, 3 H, CH_3), 1.18 (s, 3 H, CH_3).

Preparation of Complex 13. Tetrafluoroboric acid etherate (0.83 mL, 5 mmol) was added dropwise to a solution of complex **12** (1.75 g, 4.87 mmol) dissolved in 10 mL of methylene chloride and cooled to −78 °C. After 0.5 h, ether was added dropwise and the yellow crystals that precipitated from solution were transferred by cannula to a Schlenk tube and collected to give 1.76 g (90%) of complex **13** that isomerizes readily to carbonyl-coordinated complex **15** (red oil) on standing briefly at room temperature. IR (CH_2Cl_2) of complex **13**: 2080, 2040 (C≡O), 1710 (C=O) cm^{-1}. IR (CH_2Cl_2) of complex **15**: 2080, 2030 (C≡O), 1655 (MO=C) cm^{-1}.

Preparation of 14. Sodium iodide (0.75 g, 5 mmol) was added to a solution of complexes **13** and **15** (1.76 g, 4.4 mmol) in 30 mL of acetone, at room temperature. After the mixture was stirred for 0.5 h, solvent was removed and the residue was extracted with petroleum ether. Removal of the solvent gave a dark green oil that was purified by Kugelrohr distillation to give 0.59 g (98%) of **14** as a colorless oil identified by comparison of its IR and NMR data with the data reported by Marvell:[42] IR (CH_2Cl_2) 1705 (C=O), 1630, 990, 925 ($RCH=CH_2$) cm^{-1}; NMR ($CDCl_3$) δ 6.02 (dd, 1 H, J = 10 and 18 Hz, CH=), 5.16 (d, 1 H, J = 10 Hz, $=CH_2$), 5.00 (d, 1 H, J = 18 Hz, $=CH_2$), 2.50–1.40 (m, 8 H, CH_2), 1.19 (s, 3 H, CH_3) [lit.[42] IR (CCl_4) 1705, 1000, 910 cm^{-1}; NMR (CCl_4) δ 5.95–5.00 (m, 3 H, $CH=CH_2$), 2.32 (m, 2 H), 2.1–1.5 (m, 6 H), 1.09 (s, 3 H)]. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.39; H, 10.23.

Preparation of 3-Methylcyclohexanone Silyl Enol Ether by Hydrosilation of 3-Methyl-2-cyclohexen-1-one. Trimethylsilane (1.6 g, 22 mol) was condensed in a small flask and transferred by cannula to a mixture of 3-methyl-2-cyclohexen-1-one (2.0 g, 18.2 mmol) and tris(triphenylphosphine)rhodium chloride (0.084 g, 0.091 mmol) in 20 mL of benzene. The color of the solution changed from deep red to light yellow after the addition of trimethylsilane and changed back to deep red after the solution was heated under nitrogen for 6 h at 65 °C. The NMR spectrum indicated that 3-methyl-2-cyclohexen-1-one was consumed completely. Solvent was removed, the residue was extracted with 50 mL of hexane, the catalyst was filtered off, and the filtrate was concentrated in vacuo to give 3 g of light yellow oil. The oil was distilled at reduced pressure to give 2.5 g (75%; bp 48 °C (7.5 mm)) of 3-methylcyclohexanone silyl enol ether as a colorless liquid: IR (CH_2Cl_2) 1655 (C=COSi) cm^{-1}; NMR (CCl_4) δ 4.78 (m, 1 H, =CH), 2.40–1.35 (m, 7 H, CH, CH_2), 0.95 (d, 3 H, J = 7 Hz, CH_3), 0.30 (s, 9 H, $Si(CH_3)_3$).

Preparation of 16a and 16b from Cyclohexenone. 2-Cyclohexen-1-one (0.15 g, 1.6 mmol) was added dropwise to a cold (0 °C) solution of lithium dimethylcuprate(I) [from cuprous iodide (0.3 g, 1.6 mmol), methyllithium (2 mL, 1.6 M in ether, 3.2 mmol), and 5 mL of ether].[27] After the solution had been stirred for 15

(42) Marvell, E. N.; Rusay, R. *J. Org. Chem.* **1977**, *42*, 3336.
(43) Rubottom, G. M.; Mott, R. C.; Krueger, D. S. *Synth. Commun.* **1977**, *7*, 327.

min, it was cooled to −78 °C and treated with complex **1a** (R = Et) (0.47 g, 1.2 mmol). The resulting mixture was stirred for 1 h, allowed to warm to room temperature, and then filtered through a bed of activity IV, neutral alumina. Solvent was removed, and the residue was chromatographed on 80 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave a first fraction (0.26 g, 60%) of product as a yellow oil: IR (CH_2Cl_2) 2000, 1940 (C≡O), 1700 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.84 (s, 5 H, Cp), 3.74 (td, 1 H, J = 3, 9 Hz, OCH), 3.41 (m, 2 H, OCH_2), 2.60–1.60 (m, 10 H, CH, CH_2), 1.25 (t, 3 H, J = 7 Hz, CH_3), 1.12 (d, 3 H, J = 8 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 217.1 (M═CO), 216.9 (C≡O), 213.1 (CO), 84.9 (Cp), 84.3 (C-7), 63.5 1 (CH_2O), 59.5 (C-2), 41.5 (C-6), 33.5 (C-4), 33.1 (C-3), 23.9 (C-5), 21.1 (C-3 Me), 15.1 (Me), 3.2 (FpC). Elution with 10% ether–Skelly B gave a second fraction (0.15 g, 35%) of product as a yellow oil: IR (CH_2Cl_2) 2000, 1940 (C≡O), 1700 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.79 (s, 5 H, Cp), 3.75 (m, 1 H, O-CH), 3.46 (m, 2 H, OCH_2), 2.50–1.30 (m, 10 H, CH, CH_2), 1.27 (t, 3 H, J = 7 Hz, CH_3), 1.14 (d, 3 H, J = 7.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 217.3, (C≡O), 213.5 (C≡O), 85.3 (Cp), 83.0 (C-7), 64.0 (CH_2O), 63.8 (C-2), 41.1 (C-5), 33.2 (CH), 30.5 (C-3), 23.4 (C-5), 20.8 (C-3 Me), 15.4 (Me), 5.2 (FpC). The first and second fractions of product were combined and protonated with HBF_4·Et_2O and then demetalated with sodium iodide to give 0.15 g (95%) of **18** identified by comparison of IR and NMR spectra.

Preparation of Alkyliron Complex 16 from 3-Methylcyclohexanone Silyl Enol Ether. *n*-Butyllithium (0.64 mL, 1.6 mmol) dissolved in 5 mL of dry THF, at 15 °C, was added dropwise to 3-methylcyclohexanone silyl enol ether (0.3 g, 1.6 mmol). After the solution was stirred for 45 min, it was cooled to −78 °C and transferred by stainless-steel cannula to a slurry of complex **1a** (R = Et) (0.6 g, 1.5 mmol) in 5 mL of THF at −78 °C. The mixture was stirred for 1 h at −78 °C and allowed to warm to room temperature. Solvent was removed, and the residue was chromatographed on 40 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.35 g (65%) of **16** as a yellow oil identified by ^1H NMR spectral analysis as a 3:1 mixture of two diastereomers: IR (CH_2Cl_2) 1995, 1940 (C≡O), 1700 (C═O) cm^{-1}; NMR ($CDCl_3$) δ 4.84, 4.79 (2s (3:1), 5 H, 2Cp), 3.92–3.25 (m, 3 H, OCH, OCH_2), 2.32 (dd, 1 H, J = 4, 10 Hz, CH), 2.00–0.90 (m, 9 H, CH, CH_2), 1.21–1.10 (m, 6 H, CH_3).

Preparation of 18. Tetrafluoroboric acid (0.16 mL, 0.97 mmol) was added dropwise to a solution of **16** (0.35 g, 0.97 mmol) dissolved in 10 mL of methylene chloride and cooled to −78 °C. After 0.5 h, ether was added dropwise and the yellow crystals that precipitated from solution were transferred by cannula to a Schlenk tube and collected. These were dissolved in 20 mL of acetone and treated with sodium iodide (0.15 g, 1 mmol). The mixture was stirred for 0.5 h at room temperature. Solvent was removed, and the residue was extracted with petroleum ether. Removal of the solvent gave a dark green oil that was purified by Kugelrohr distillation to give 0.12 g (90%) of **18** as a colorless oil identified by its ^1H NMR spectrum as a single trans isomer: IR (neat) 1710 (C═O), 1645, 998, 925 (RCH═CH_2) cm^{-1}; NMR ($CDCl_3$) δ 5.98–5.57 (m, 1 H, CH═), 5.20 (dd, 1 H, J = 2, 11 Hz, RCH═CH_{cis}) 4.98 (dd, 1 H, J = 2, 17 Hz, RCH═CH_{trans}), 2.70–1.40 (m, 8 H, CH, CH_2), 1.00 (d, 3 H, J = 6 Hz, CH_3).

Hydrogenation of 18. To a 25-mL round-bottom flask was added **17** (0.05 g, 0.36 mmol), catalyst (10% palladium on carbon, 0.01 g), and methanol (5 mL). The apparatus was purged and filled with hydrogen at 1 atm. After 1 equiv of hydrogen was absorbed (1 atm/room temperature overnight), the catalyst was removed by careful vacuum filtration on Celite. Removal of methanol gave 0.045 g (90%) of *trans*-3-methyl-2-ethylcyclohexanone as a colorless oil: IR (CCl_4) 1710 cm^{-1}; NMR ($CDCl_3$) δ 2.48–2.20 (m, 2 H), 2.10–1.50 (m, 8 H), 1.05 (d, 3 H, J = 6 Hz, CH_3), 0.88 (t, 3 H, J = 7 Hz, CH_3), [lit.[29] IR (CCl_4) 1710 cm^{-1}; NMR ($CDCl_3$) δ 2.42–2.21 (m, 2 H), 2.05–1.38 (m, 8 H), 1.04 (d, 3 H, J = 7 Hz, CH_3), 0.87 (t, 3 H, J = 7 Hz, CH_3).

Preparation of Alkyliron Complex 19. *n*-Butyllithium (1.4 mL, 3.1 mmol) was added dropwise to 6-methylcyclohexanone silyl enol ether[44] (0.55 g, 3 mmol) dissolved in 8 mL of dry THF, at 15 °C. After the solution was stirred for 45 min, it was cooled to −78 °C and transferred by stainless-steel cannula to a slurry of complex **1a** (R = Et) (1 g, 3 mmol) in 5 mL of THF at −78 °C. The mixture was stirred for 1 h at −78 °C, allowed to warm to room temperature, and then filtered through a bed of 10 g of activity IV, neutral alumina. Solvent was removed, and the residue was chromatographed on 80 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.97 g (90%) of product as a yellow oil identified by both ^1H and ^{13}C NMR spectral analysis as a single diasteromer: IR (CH_2Cl_2) 2000, 1950 (C≡O), 1700 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80 (s, 5 H, Cp), 3.67 (m, 1 H, OCH), 3.50 (q, 2 H, J = 7 Hz, OCH_2), 2.60 (m, 1 H, CH), 1.16 (t, 3 H, J = 7 Hz, CH_3), 1.09 (d, 3 H, J = 6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 217.3, 216.9 (MCO), 216.3 (C═O), 85.3 (Cp), 84.6 (CO), 63.4 (CH_2O), 53.0 (C-2), 43.8 (C-6), 33.3 (C-5), 26.0 (C-3), 20.5 (C-4), 16.2 (CH_3), 15.4 (CH_3), 3.1 ($FpCH_2$).

Preparation of Complex 20. Tetrafluoroboric acid etherate (0.5 mL, 3 mmol) was added dropwise to complex **19** (0.97 g, 2.7 mmol) in 10 mL of methylene chloride and cooled to −78 °C. After 0.5 h, ether was added dropwise and the yellow crystals that precipitated from solution were transferred by cannula to a Schlenk tube and collected to give 0.97 g (90%) of complex **20**: IR (CH_2Cl_2) 2080, 2040 (MCO), 1710 (C═O); NMR ($CDCl_3$) δ 5.90 and 5.92 (2s, 5 H, 2Cp), 5.45 (m, 1 H, CH═), 4.16 and 4.06 (2d, 1 H, J = 9 Hz, ═CH_2), 3.20–1.50 (m, 8 H, CH, CH_2), 1.17 (m, CH_3).

Preparation of Complex 21. Triethylamine (0.5 mL, 3.6 mmol) was added dropwise to complex **20** (0.97 g, 2.43 mmol) dissolved in 30 mL of methylene chloride in room temperature. After 2 h, solvent was removed and the residue was extracted with ether. The ether solution was filtered through a bed of 10 g of activity IV, neutral alumina. Removal of ether gave 0.61 g (80%) of complex **21** as a deep yellow oil: IR (CH_2Cl_2) 2005, 1960 (C≡O), 1650 (conjugated C═O) cm^{-1}; NMR ($CDCl_3$) δ 7.15 (t, 1 H, J = 10 Hz, CH═), 4.85 (s, 5 H, Cp), 2.05 (d, 2 H, J = 9 Hz, $FpCH_2$), 2.50–1.50 (m, 7 H, CH, CH_2), 1.14 (d, 3 H, J = 8 Hz, CH_3).

Preparation of 22a and 22b. Sodium iodide (0.4 g, 2.7 mmol) was added to a solution of complex **20** (1 g, 2.5 mmol) in 30 mL of acetone at room temperature. After 0.5 h, solvent was removed and the residue was extracted with petroleum ether. Removal of the solvent gave a drak green oil that was purified by Kugelrohr distillation to give 0.34 g (98%) of **22** as a colorless oil identified by ^1H NMR spectral analysis as a 1:1 mixture of trans and cis isomers:[45] IR (neat) 1705 (C═O), 1640, 995, 920 (RCH═CH_2) cm^{-1}; NMR ($CDCl_3$) δ 6.30–5.80 (m, 1 H, CH═), 5.20–4.90 (m, 2 H, ═CH_2), 3.35–3.00 (m, 1 H, CH), 3.00–1.40 (m, 7 H, CH, CH_2), 1.06, 1.01 (2d (1:1), 3 H, J = 7 Hz, 6.5 Hz, $2CH_3$). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.46; H, 10.47.

Preparation of 22a. Freshly precipitated **20** was taken up in a small volume of acetonitrile, and the solution was filtered and then heated to reflux for 10 min. Some solvent was removed, and the remaining solution was then added slowly to ether. The yellow Fp(acetonitrile)BF_4 complex, which precipitated, was removed by filtration. Solvent was removed in vacuo, and Kugelrohr distillation of the product gave *trans*-2-methyl-6-vinylcyclohexanone (**22a**) as a colorless oil. An NMR spectrum of this product shows only the one methyl doublet at δ 1.06 of the trans isomer.

Preparation of 23 from Cyclohexanone. A solution of LDA (5 mL, 3.3 mmol) in THF was prepared by the method of House[27] and cooled to −78 °C. To this solution was added dropwise cyclohexanone (0.3 g, 3.1 mmol). The resulting solution was stirred for 20 min at −78 °C and transferred by stainless-steel cannula to a slurry of complex **1b** (R = Et) (0.7 g, 2 mmol) in 10 mL of THF at −78 °C. The mixture was stirred for 3 h at −78 °C and allowed to warm to room temperature. Solvent was removed, and the residue was chromatographed on 80 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.46 g (65%) of **23** as a yellow oil identified by ^{13}C NMR spectral analysis as a 84:16 mixture of two diastereomers: IR (CH_2Cl_2) 1998, 1948 (C≡O), 1705 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.78 (s, 5 H, Cp), 3.25 (q, 2 H, J = 8 Hz, OCH_2), 2.80–1.50 (m, 11 H, CH, CH_2), 1.2 (s, 3 H, CH_3), 1.15 (t, 3 H, J = 8 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 218.0 (C≡O), 212.6 (C═O), 85.7, 85.4 (2Cp (84:16)), 80.1, 59.5, 54.6, 44.4, 29.9, 28.3, 25.6, 24.0, 16.2, 9.5 (FpC). Elution with 40% ether–Skelly B gave 0.16 g (34%) of **25** as a yellow oil.

(44) House, H. O.; Czuba, L. J.; Gall, M. J.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(45) For assignments of axial and equatorial methyl resonances in 2-methylcyclohexanones, see: Johnson, F.; Starkovsky, N. A.; Gorowitz, W. D. *J. Am. Chem. Soc.* **1965**, *87*, 3492.

Preparation of 23 from Cyclohexanone Silyl Enol Ether. *n*-Butyllithium (0.52 mL, 1.18 mmol) was added dropwise to cyclohexanone silyl enol ether (0.2 g, 1.17 mmol) dissolved in 5 mL of THF, at 15 °C. After the solution was stirred for 45 min, it was cooled to −78 °C and transferred by stainless-steel cannula to a slurry of complex **1b** (0.4 g, 1.16 mmol) in 5 mL of dry THF. The mixture was stirred for 1 h at −78 °C and allowed to warm to room temperature. Solvent was removed, and the residue was chromatographed on 60 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.32 g (77%) of **23** as a yellow oil identified by comparison of IR and NMR spectra. Elution with 40% ether–Skelly B gave 0.04 g (15%) of **25** as a yellow oil identified by comparison of IR and NMR spectra.

Alkylation of Cyclohexanone Lithium Enolate with Fp(neopentyl η^2-isopropenyl ether)BF_4. *n*-Butyllithium (0.52 mL, 1.18 mmol) was added dropwise to cyclohexanone silyl enol ether (0.20 g, 1.17 mmol) dissolved in 5 mL of THF, at 15 °C. After the solution was stirred for 45 min, it was cooled to −78 °C and transferred by stainless-steel cannula to a slurry of the vinyl ether complex (0.44 g, 1.12 mmol) in 5 mL of dry THF. The mixture was stirred for 1 h at −78 °C and allowed to warm to room temperature. Solvent was removed, and the residue was chromatographed on 60 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.28 g (63%) of product as a yellow oil identified by ^{13}C NMR spectra analysis as a 96:4 mixture of two diastereomers: IR (CH_2Cl_2) 1998, 1948 (C≡O), 1705 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.76 (s, 5 H, Cp), 2.92 (s, 2 H, OCH_2), 2.80–1.50 (m, 11 H, CH, CH_2), 1.22 (s, 3 H, CH_3), 0.90 (s, 9 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 220.7, 220.3 (C≡O), 215.4 (C═O), 85.6, 85.3 (2Cp (96:4)), 79.5, 69.3, 59.9, 44.0, 31.8, 29.7, 28.8, 27.2, 25.6, 22.0, 8.6 (FpC). Elution with 40% ether–Skelly B gave 0.06 g (23%) of **25** as a yellow oil identified by comparison of IR and NMR spectra.

Preparation of Complexes 26 and 27. Tetrafluoroboric acid etherate (0.25 mL of 1.5 mmol) was added dropwise to a solution of complex **23** (0.46 g, 1.3 mmol) dissolved in 10 mL of methylene chloride and cooled to −78 °C. After 0.5 h, ether was added dropwise and the yellow crystals that precipitated from solution were transferred by cannula to a Schlenk tube and collected to give 0.5 g (95%) of **26** that isomerizes readily to complex **27** (red oil) on standing briefly at room temperature. **27**: IR (CH_2Cl_2) 2080, 2040 (C≡O), 1640 (M^+···O═C) cm^{-1}; NMR (CD_3NO_2) δ 5.53 (s, 5 H, Cp), 4.88 (m, 1 H, ═CH_2), 4.71 (m, 1 H, ═CH_2), 3.12 (m, 1 H, CH), 2.6–1.5 (m, 8 H, CH_2), 1.70 (s, 3 H, CH_3).

Preparation of 28. Sodium iodide (0.23 g, 1.5 mmol) was added to a solution of complex **27** (0.5 g, 1.2 mmol) dissolved in 30 mL of acetone at room temperature. After the mixture was stirred for 0.5 h, solvent was removed and the residue was extracted with petroleum ether. Removal of the solvent gave a dark green oil that was purified by Kugelrohr distillation to give 0.16 g (97%) of **28** as a colorless oil: IR (neat) 1705 (C═O), 1645, 896 (R_2CCH_2) cm^{-1}; NMR ($CDCl_3$) δ 4.95 (m, 1 H, ═CH_2), 4.76 (m, 1 H, ═CH_2), 3.00 (m, 1 H, CH), 2.50–1.50 (m, 8 H, CH_2), 1.75 (s, 3 H, CH_3).

Preparation of 5-Methylcyclohexenyl Trimethylsilyl Ether from 5-Methyl-2-cyclohexen-1-one. Trimethylsilane (1.6 g, 22 mol) was condensed in a small flask and transferred by cannula to a mixture of 5-methyl-2-cyclohexen-1-one[35] (2.0 g, 18.2 mmol) and tris(triphenylphosphine)rhodium chloride (0.084 g, 0.091 mmol) in 20 mL of benzene. The color of the solution changed from deep red to light yellow after the addition of trimethylsilane and changed back to deep red after the solution was heated for 6 h at 65 °C. The NMR spectrum indicated that 5-methyl-2-cyclohexen-1-one was consumed completely. Solvent was removed, the residue was extracted with 50 mL of hexane, the catalyst was filtered off, and the filtrate was concentrated in vacuo to give 3 g of light yellow oil. The oil was distilled at reduced pressure to give 2.67 g (80%) of product (bp 48–50 °C (2.2 mm)) as a colorless liquid: IR (CH_2Cl_2) 1665 (C═COSi) cm^{-1}; NMR (CCl_4) δ 4.72 (t, 1 H, J = 4 Hz, CH═), 2.20–0.90 (m, 7 H, CH, CH_2), 0.95 (d, 3 H, J = 5 Hz, CH_3), 0.15 (s, 9 H, $Si(CH_3)_3$).

Preparation of Adduct 31. *n*-Butyllithium (0.67 mL, 2.38 M in hexane, 1.6 mmol) was added dropwise to the silyl enol ether prepared above (0.276 g, 1.5 mmol) dissolved in 5 mL of THF at 15 °C. After the solution was stirred for 45 min, it was cooled to −78 °C and transferred by stainless-steel cannula to a slurry of complex **1b** (0.5 g, 1.43 mmol) in 5 mL of THF. The mixture was stirred for 3 h at −78 °C and allowed to warm to room temperature. Solvent was removed, and the residue was chromatographed on 80 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.32 g (60%) of **31** as a yellow oil identified by ^{13}C NMR spectral analysis as a 63:11:26 mixture of three diastereomers: IR (CH_2Cl_2) 1990, 1940 (C≡O), 1710 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.80 (s, 5 H, Cp), 3.30 (m, 2 H, OCH_2), 2.80–1.50 (m, 10 H, CH, CH_2), 1.20 (s, 3 H, CH_3), 1.3–1.0 (m, 6 H, $2CH_3$); ^{13}C NMR ($CDCl_3$) δ 217.5, 217.1 (C≡O), 215.2 (C═O), 85.55, 85.36, 85.23 (3Cp (63:11:26)), 79.8, 58.4, 54.4, 52.5, 36.3, 34.7, 28.8, 22.9, 22.3, 14.1, 9.0 (FpC). Elution with 40% ether–Skelly B gave 0.13 g (38%) of **31** as a yellow oil identified by comparison of IR and NMR spectra with the sample as prepared below.

Preparation of 31 from 3-Methylcyclohexanone. To a THF solution (5 mL, 3 mmol) of trityllithium that was prepared by the method of Antony and Maloney[34] cooled to −78 °C was added dropwise 3-methylcyclohexanone (0.34 g, 2.6 mmol) in 5 mL of THF at −78 °C. The mixture was stirred for 3 h at −78 °C and then was transferred by cannula to a slurry of **1b** (0.9 g, 2.6 mmol) in 5 mL of THF at −78 °C. The mixture was stirred for 3 h at −78 °C and then allowed to warm to room temperature. Solvent was removed, and the residue was chromatographed on 80 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.51 g (53%) of **31** as a yellow oil identified by comparison of IR and NMR spectra. Elution with 40% ether–Skelly B gave 0.21 g (38%) of **25** as a yellow oil identified by comparison of IR and NMR spectra.

Preparation of 33 and 34. Tetrafluoroboric acid etherate (0.12 mL, 0.72 mmol) was added dropwise to a solution of complex **31** (0.25 g, 0.67 mmol) dissolved in 10 mL of methylene chloride and cooled to −78 °C. After 0.5 h, ether was added dropwise and the yellow crystals that precipitated from solution were transferred by cannula to a Schlenk tube and collected. This yellow crystal complex **32** was dissolved in 30 mL of acetone and treated with sodium iodide (0.11 g, 0.73 mmol) at room temperature. After the mixture was stirred for 0.5 h, solvent was removed and the residue was extracted with petroleum ether. Removal of the solvent gave a dark green oil that was purified by Kugelrohr distillation to give 0.096 g (94%) of product as a colorless oil identified by ^1H NMR spectral analysis as a 5:2 mixture of **33** and **34**: IR (neat) 1710, 1720 (C═O of **33** and **34**), 1644, 900 (R_2C═CH_2) cm^{-1}. ^1H NMR ($CDCl_3$) of **34**: δ 4.96 (1m, 1 H, ═CH_2), 4.84 (m, 1 H, ═CH_2), 3.00 (m, 1 H, CH), 2.50–1.60 (m, 7 H, CH, CH_2), 1.75 (s, 3 H, CH_3), 0.98 (d, 3 H, J = 8 Hz, CH_3). ^1H NMR ($CDCl_3$) of **33**: δ 4.96 (m, 1 H, ═CH_2), 4.75 (m, 1 H, ═CH_2), 3.00 (m, 1 H, CH), 2.50–1.60 (br m, 7 H, CH, CH_2), 1.75 (s, 3 H, CH_3), 1.02 (d, 3 H, J = 5 Hz, CH_3).

Preparation of 35 and 36. To a 50-mL round-bottom flask was added a mixture of **33** and **34** (0.18 g, 1.18 mmol), catalyst (10% palladium on carbon, 0.04 g), and methanol (25 mL). The apparatus was purged and filled with hydrogen to 1 atm. After 1 equiv of hydrogen was absorbed (1 atm/room temperature overnight), the catalyst was removed by careful vacuum filtration on Celite. Removal of methanol gave a colorless oil. Preparative thin-layer chromatography on silica gel (1000 μm) yielded two fractions on elution with 40% ether–Skelly B. The trans isomer **35** (0.13 g, 72%; R_f 0.7) was obtained as a colorless oil identified by comparison of ^{13}C NMR spectral data with the data reported by Roberts:[36b] ^{13}C NMR ($CDCl_3$) δ 212.1 (C═O), 78.5, 77.1, 75.7, 55.9, 50.9, 35.5, 34.0, 27.9, 26.0, 22.3, 21.2, 18.8, [lit.[36b] ^{13}C NMR ($CDCl_3$) δ 212.0, 56.1, 51.0, 35.6, 34.1, 28.4, 26.0, 22.3, 21.3, 18.8]. The cis isomer **36** (0.05 g, 27.5%; R_f 0.58) was obtained as a colorless oil identified by comparison of ^{13}C NMR spectral data with the data reported by Roberts: ^{13}C NMR ($CDCl_3$) δ 214.2 (C═O), 78.5, 77.0, 75.6, 57.2, 48.1, 34.4, 29.5, 27.0, 21.4, 20.9, 19.9 [lit.[36b] ^{13}C NMR ($CDCl_3$) δ 214.1, 57.2, 48.2, 34.4, 29.6, 27.0, 21.4, 21.0, 19.9].

Preparation of 33 and 34 from 3-Methylcyclohexanone without Isolation of Intermediates. A solution of lithium 2,2,6,6-tetramethylpiperidide,[33] prepared from 2,2,6,6-tetramethylpiperidine (7.2 g, 50 mmol) and *n*-butyllithium (25 mL, 2 M in hexane, 50 mmol) in 100 mL of THF, was cooled to −78 °C, and 3-methylcyclohexanone (5.6 g, 50 mmol) was added dropwise. The enolate solution was transferred by cannula to a slurry of **1b** (17.2 g, 50 mmol) in 100 mL of THF cooled to −78 °C. After 3–5 h, the solution was allowed to warm to 25 °C, THF

was removed, and the residue was taken up in 50 mL of methylene chloride. This was cooled to 0 °C and treated with 48% aqueous tetrafluoroboric acid (7 mL, 50 mmol) dissolved in 40 mL of acetic anhydride. Reaction was continued for 0.5 h at 0 °C, and then 50 mL of ether was added. The red oily product, which separated, was washed with ether and then taken up in 100 mL of acetone and treated with sodium iodide (7.5 g, 50 mmol) at room temperature for 0.5 h. Acetone was removed in vacuo, and the residue was extracted with ether. The ether solution was concentrated in 10 mL, petroleum ether (200 mL) was added, and the solution was filtered. Removal of solvent and Kugelrohr distillation of the residue (0.1 mm, 25–60 °C) gave 3.5 g (46%) of a mixture of **33** and **34** (2:1) as a pale yellow oil identified by comparison of IR and NMR spectra.

Preparation of Complex 37. A solution of LDA (5 mL, 1.5 mmol) was prepared in THF and cooled to −78 °C. To this solution was added dropwise 3-methyl-2-cyclohexen-1-one (0.176 g, 1.6 mmol). The resulting solution was stirred for 20 min and transferred by stainless-steel cannula to a slurry of complex **1b** (0.5 g, 1.43 mmol) in 5 mL of dry THF at −78 °C. The mixture was stirred for 1 h and allowed to warm to room temperature. Solvent was removed, and the residue was chromatographed on 60 g of activity IV, neutral alumina. Elution with 5% ether–Skelly B gave 0.5 g (93%) of the desired product as a yellow oil: IR (CH_2Cl_2) 1995, 1940 (C≡O), 1655 (conjugated C=O) cm^{-1}; NMR ($CDCl_3$) δ 5.80 (m, 1 H, CH=), 4.80 (s, 5 H, Cp), 3.26 (m, 2 H, OCH_2), 2.70–1.70 (m, 7 H, CH, CH_2, Fp–CH_2), 1.90 (s, 3 H, CH_3), 1.15 (t, 3 H, J = 7 Hz, CH_3), 1.10 (s, 3 H, CH_3).

Preparation of Isopiperitenone (38). Tetrafluoroboric acid etherate (0.25 mL, 1.5 mmol) was added dropwise to a solution of complex **37** (0.48 g, 1.29 mmol) dissolved in 10 mL of methylene chloride and cooled to −78 °C. After 0.5 h, ether was added dropwise and the yellow crystals that precipitated from solution were transferred by cannula to a Schlenk tube and collected. This yellow crystalline solid is thermally unstable and isomerizes readily to the carbonyl-coordinated complex (red solid; IR (CH_2Cl_2) 1580 cm^{-1} (conjugated C=O···M^+)) on standing briefly at room temperature. Sodium iodide (0.375 g, 2.5 mmol) was added to the solution of this cationic complex dissolved in 30 mL of acetone at room temperature. After the mixture was stirred for 0.5 h, solvent was removed and the residue was extracted with petroleum ether. Removal of the solvent gave a dark green oil that was purified by Kugelrohr distillation to give 0.168 g (87%) of **38** as a colorless oil identified by comparison of IR and NMR spectral data with the data reported by Tori:[38] IR (neat) 1655 (conjugated C=O), 900 (R_2C=CH_2) cm^{-1}; NMR ($CDCl_3$) δ 5.92 (m, 1 H, CH=), 4.96 (m, 1 H, =CH_2), 4.77 (m, 1 H, =CH_2), 2.97 (t, J = 8 Hz, CH), 2.50–1.90 (m, 4 H, CH_2), 1.95 (br s, 3 H, CH_3), 1.76 (br s, 3 H, CH_3) [lit.[38] NMR ($CDCl_3$) δ 5.88, 4.93, 4.75, 1.95, 1.75; IR (CH_2Cl_2) 1655, 895 cm^{-1}].

Preparation of 2-Methyl-*trans*-2-propenylcyclohexanone (41). *n*-Butyllithium (2.8 mL, 6.2 mmol) was added dropwise to 2-methylcyclohexanone silyl enol ether (1.1 g, 6 mmol) dissolved in 5 mL of dry THF, at 15 °C. After the solution was stirred for 45 min, it was cooled to −78 °C and transferred by stainless-steel cannula to a slurry of complex **1c** (2 g, 5.7 mmol) in 5 mL of dry THF. The mixture became clear yellow solution after it was stirred for 1 h at −78 °C: IR (THF) 2000, 1950 (C≡O), 1705 (C=O) cm^{-1}. Tetrafluoroboric acid etherate (1 mL, 6 mmol) was added dropwise to this clear yellow solution at −78 °C. After 0.5 h, ether was added dropwise and the yellow crystals that precipitated from solution were transferred by cannula to a Schlenk tube and collected to give 1.9 g (80%) of **40** (IR (CH_2Cl_2) 1710 (C=O) cm^{-1}) which isomerizes readily to the carbonyl-coordinated complex (IR (CH_2Cl_2) 1655 (M^+—O=) cm^{-1} on standing briefly at room temperature. This mixture was dissolved in 30 mL of acetone and treated with sodium iodide (0.6 g, 4 mmol). After the mixture was stirred for 0.5 h, solvent was removed and the residue was extracted with petroleum ether. Removal of the solvent gave a dark green oil that was purified by Kugelrohr distillation to give 0.62 g (72%, based on complex **1c** used) of **41** as a colorless oil identified by ^1H NMR spectral analysis as the trans isomer: IR (CH_2Cl_2) 1705 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 5.75–5.20 (m, 2 H, CH=CH (the multiplet changed to two doublets at δ 5.70 and 5.37 (2d, J = 16 Hz) on spin decoupling of the vinylic methyl group), 2.70–1.50 (m, 8 H, CH_2), 1.70 (d, 3 H, J = 6 Hz, CH_3), 1.15 (s, 3 H, CH_3). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.79; H, 10.71.

Structure Determination of 16a. Single crystals were grown by cooling a hexane solution of the compound to 0 °C. Laue photographs and a preliminary X-ray photographic study indicated the crystal to be of excellent quality. The crystal was then transferred to a Supper No. 455 goniometer and optically centered on a Syntex $P2_1$ diffractometer. Operations were performed as described previously.[46] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Fe were included in the calculations.[47] Details of the structure analysis, in outline form, are presented in Table IV. Atomic coordinates for all atoms appear in Table V, while bond lengths and bond angles are collected in Table VI.

Acknowledgment. This research was supported by grants from the National Institutes of Health (GM-16395) and the National Science Foundation (MPS-75-09590) which are gratefully acknowledged. We also thank Professor B. B. Snider for helpful discussions relating to ^{13}C spectral data and Ms. Xiao-Ya Zhu for technical assistance.

Registry No. **1a** (R = Me), 36222-36-3; **1a** (R = Et), 75182-42-2; **1b** (R = Me), 71844-57-0; **1b** (R = Et), 78782-37-3; **1b** (R = CH_2CMe_3), 110205-19-1; **1c** (R = Me), 110269-14-2; **1c** (R = Et), 75197-50-1; **2**, 110205-11-3; **3a**, 62259-73-8; **3b**, 81161-08-2; **4a**, 56528-89-3; **4b**, 72059-91-7; **4c**, 57524-90-0; **4d**, 75222-37-6; **5a**, 110205-12-4; **5b**, 110205-13-5; **6**, 75182-46-6; **7**, 1122-24-3; **8**, 75192-36-8; **9**, 110205-14-6; **10**, 110193-13-0; **12a**, 110269-08-4; **12b**, 110269-09-5; **13**, 75182-50-2; **15**, 63196-62-3; **16a**, 110205-15-7; **16b**, 110205-16-8; **17**, 110269-10-8; **18**, 110205-17-9; **19**, 110222-94-1; **20**, 110269-11-9; **21**, 75182-48-8; **22a**, 75182-41-1; **22b**, 75222-38-7; **23a**, 75222-39-8; **23a** (neopentyl ester), 78853-56-2; **23b**, 110269-15-3; **23b** (neopentyl ester), 78791-20-5; **25**, 110205-21-5; **26**, 42065-40-7; **27**, 110205-08-8; **28**, 110205-09-9; **31**, 58070-37-4; **32**, 78782-41-9; **33**, 110205-10-2; **34**, 29606-79-9; **35**, 52152-10-0; **36**, 89-80-5; **37**, 491-07-6; **38**, 78782-38-4; **40**, 529-01-1; **41**, 110269-12-0; Fp(η^2-vinyltrimethylsilane)BF_4, 110205-05-5; Fp(η^2-isobutylene)BF_4, 110205-07-7; Fp(OC_6H_8-2-Me-2-(*E*)-CH=$CHCH_3$), 41707-16-8; Fp(OC_6H_8-3-Me-6-C(OEt)=CH_2), 110205-20-4; Fp-(CH_2=$CHCMe_3$)$^+$, 110205-22-6; Fp(CH_2=$CHEt$)$^+$, 110205-23-7; Fp(CH_2=CMe_2)$^+$, 38817-11-7; Fp(CH_2=C(OMe)$_2$)(BF_4), 46238-51-1; Fp(CH_2=C(NMe_2)Me)$^+$, 110205-25-9; vinyltrimethylsilane, 110205-26-0; 3-methylcyclohexanone, 754-05-2; cyclohexanone silyl enol ether, 591-24-2; 2-methylcyclohexanone silyl enol ether, 6651-36-1; trimethylsilane, 19980-35-9; methyl-2-cyclohexen-1-one, 993-07-7; tris(triphenylphosphine)rhodium chloride, 1193-18-6; 2-cyclohexen-1-one, 14694-95-2; 5-methyl-2-cyclohexen-1-one, 930-68-7; 5-methylcyclohexeneyl trimethylsilyl ether, 7214-50-8; lithium 2,2,6,6-tetramethylpiperidide, 110193-14-1; 2,2,6,6-tetramethylpiperidine, 38227-87-1; 2,2,6,6-tetramethylpiperidine, 768-66-1; (−)-menthol, 2216-51-5; (+)-menthol, 15356-60-2; (−)-borneol, 464-45-9; (−)-isoborneol, 10334-13-1; (−)-myrtanol, 53369-17-8; (+)-2-butanol, 4221-99-2; (+)-methyl-β-hydroxyisobutyrate, 80657-57-4; *trans*-3-methyl-2-ethylcyclohexanone, 75731-83-8; 6-methylcyclohexanone silyl enol ether, 19980-33-7; cyclohexanone, 108-94-1.

Supplementary Material Available: Table SI and SII, listing thermal parameters and atomic coordinates for hydrogen atoms (2 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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