Stereochemistry of Reactions at Carbon–Transition Metal σ Bonds. $(CH_3)_3CCHDCHDFe(CO)_2C_5H_5$[1]

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Abstract: Convenient, stereoselective syntheses of *threo-* and *erythro-*3,3-dimethylbutan-1-ol-*1,2-d_2* (**1**) are described. Reaction of the *p*-bromobenzenesulfonate esters of **1** with $C_5H_5Fe(CO)_2MgBr$, -Li, or -Na yields π-cyclopentadienyldicarbonyliron *erythro-* and *threo-*3,3-dimethylbutyl-*1,2-d_2* (*erythro-* and *threo-***2**) with >95% inversion of configuration at carbon. Bromination of **2** in pentane, chloroform, carbon disulfide, and dimethylformamide, and iodination in carbon disulfide, all take place with >90% inversion of configuration at carbon. Reaction of **2** with triphenylphosphine, *tert*-butyl isocyanide, bromine (in methanol), oxygen, cerium(IV) ion, or chlorine (in chloroform) leads to derivatives of 4,4-dimethylpentanoic-*2,3-d_2* acid with >90% retention of configuration at carbon. Reaction of **2** with sulfur dioxide in a variety of solvents yields the product of sulfur dioxide insertion, $(CH_3)_3CCHDCHDSO_2Fe(CO)_2Cp$, with >95% inversion of configuration at carbon. Insertion of dimethyl acetylenedicarboxylate into the carbon–iron bond of **2** takes place with >80% retention of configuration at carbon. Thermal decomposition of **2** produces a range of isotopically substituted derivatives of 3,3-dimethyl-1-butene. The mechanistic significance of the results is discussed.

The most valuable single type of information to have in characterizing the mechanism of a reaction that makes or breaks bonds at a tetrahedral carbon atom is the stereochemistry of the transformation at that carbon. With this information it is possible to judge whether a reaction involves intermediate free carbon radicals or ions or occurs by SN2 or SE2 transition states. It is experimentally difficult to obtain stereochemical information about reactions involving transition metal alkyls. Traditional experimental procedures based on the preparation and reaction of enantiomeric organometallic compounds suffer from serious shortcomings. Enantiomerically pure organolithium and magnesium reagents are not generally available,[5] and nucleophilic displacements by metallate anions and decarbonylation reactions are complicated by side reactions[6] and by thermal instability of the products.[12] Further, it is presently difficult to relate the stereochemistry of the starting materials and products in organometallic reactions, since reactions of "known" and reliable stereochemistry have not been established.[13–15]

Examination of diastereomeric organometallic compounds provides approaches to organometallic stereochemistry that are more practical than those based on enantiomeric substances.[16–20] We have developed an nmr technique, based on determination of the relative configurations at the CHD centers of the $(CH_3)_3$-CCHDCHD moiety, that is particularly convenient.[21] The usefulness of this alkyl group rests in the fact that threo and erythro diastereomers of most compounds having the composition $(CH_3)_3CCHDCHDX$ are readily identified using spectroscopy. These diastereomers exist in solution as a rapidly interconverting mixture of one trans and two gauche conformers. The vicinal coupling constant characterizing the CHDCHD fragment is a weighted average of the couplings in each conformer. For most groups X, the trans conformation is sufficiently favored energetically that the vicinal coupling constants for erythro and threo diastereomers are easily distinguishable experimentally.[22] Analysis of the AA′XX′ or (AA′BB′) spectra of the CH_2CH_2

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[2] National Science Foundation Predoctoral Fellow, 1967–1968 and 1971–1973.

[3] National Institutes of Health Predoctoral Fellow, 1967–1970.

[4] M.I.T. UROP Participant.

[5] H. L. Goering and F. H. McCarron, *J. Amer. Chem. Soc.*, **80**, 2287 (1958); O. A. Reutov, *Bull. Soc. Chim. Fr.*, 1383 (1963); H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964); R. H. Letsinger, *ibid.*, 72, 4842 (1950).

[6] Cobaloxime anion,[7] and to a lesser extent other strongly nucleophilic metallate anions[8] such as $Fe(CO)_4^{2-}$ [9] and $CpFe(CO)_2^-$,[10,11] are exceptional in the ability to yield secondary alkyls by alkylation.

[7] G. N. Schrauzer, E. Deutsch, and R. J. Windgassen, *J. Amer. Chem. Soc.*, **90**, 2441 (1968); G. N. Schrauzer and E. Deutsch, *ibid.*, **91**, 3341 (1969); J. M. Pratt and P. J. Craig, *Advan. Organometal. Chem.*, **11**, 331 (1973).

[8] R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, **88**, 5121 (1966); R. B. King, *Advan. Organometal. Chem.*, 2, 157 (1964).

[9] W. O. Siegl and J. P. Collman, *J. Amer. Chem. Soc.*, **94**, 2516 (1972); J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972).

[10] K. M. Nicholas and M. Rosenblum, *J. Amer. Chem. Soc.*, **95**, 4449 (1973).

[11] M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

[12] Review: P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 271 (1973).

[13] Carbonylation and decarbonylation may prove to be one such reaction; *vide infra.*

[14] The difficulties encountered in working with enantiomerically enriched organometallic are illustrated by F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966); (b) J. J. Alexander and A. Wojcicki, *Inorg. Chim. Acta*, **5**, 655 (1971); (c) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970); (d) R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970).

[15] D. Dodd and M. D. Johnson, *Chem. Commun.*, 571 (1971).

[16] F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966); J. K. Stille and L. F. Hines, *ibid.*, **92**, 1798 (1970).

[17] D. R. Coulson, *J. Amer. Chem. Soc.*, **91**, 200 (1969).

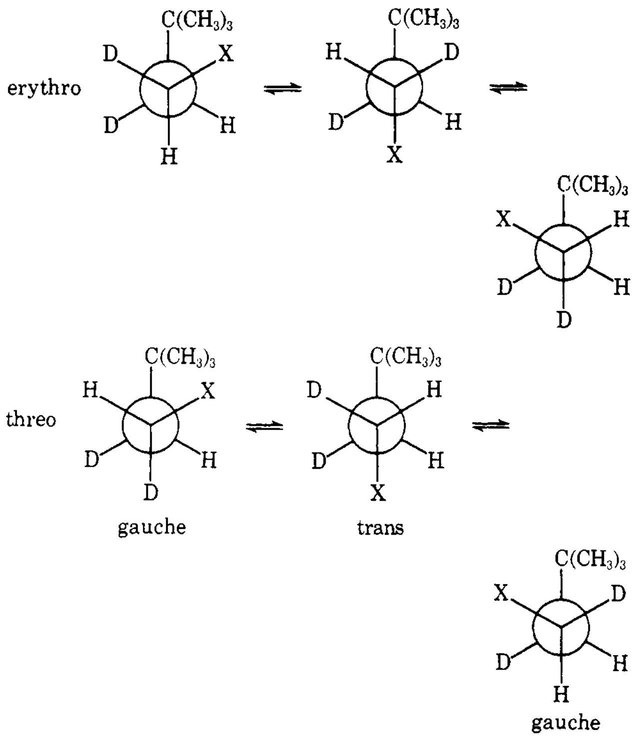
[18] F. R. Jensen and K. L. Nakamaye, *J. Amer. Chem. Soc.*, **90**, 3248 (1968); W. H. Glaze and C. H. Freeman, *ibid.*, **91**, 7198 (1969).

[19] W. H. Glaze and C. M. Selman, *J. Org. Chem.*, **33**, 1987 (1968); *J. Organometal. Chem.*, **11**, P3 (1968); W. H. Glaze, C. M. Selman, A. L. Ball, Jr., and E. E. Bray, *J. Org. Chem.*, **34**, 641 (1969).

[20] J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, **94**, 4043 (1972); J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970). The diasteriomeric π-cyclopentadienyldicarbonyliron 4-methylcyclohexanes have been prepared.[10]

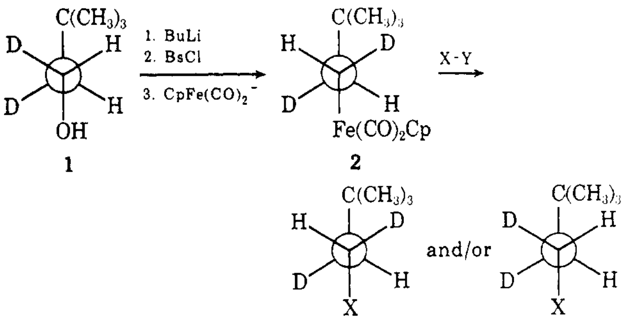
[21] G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971); *ibid.*, **91**, 4313 (1969).

[22] G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Amer. Chem. Soc.*, **89**, 1135 (1967). The uncertainties listed for ΔE in the third column of Table IV of this paper are in error; each should be *ca.* 10% of the value of ΔE. Thus, the first entry in this column should read $\Delta E = 2.33 \pm 0.28$ kcal/mol.



moieties of a number of 1-substituted derivatives of nondeuterated 3,3-dimethylbutane had previously established that values of the vicinal coupling constant greater than *ca.* 8 Hz were characteristic of the pairs of protons present in erythro diasteriomers, and values smaller than *ca.* 7 Hz were characteristic of threo diasteriomers. Thus, in principle, it is only necessary to read the value of the vicinal coupling constant from the deuterium-decoupled nmr spectrum of a composition $(CH_3)_3CCHDCHDX$ to establish whether it belongs to the erythro or threo series.[22,23]

The ability to differentiate spectroscopically between the erythro and threo diastereomers of $(CH_3)_3CCHD$-$CHDX$ provides the basis for a convenient and convincing method of determining the stereochemistry of a reaction involving a carbon–metal σ bond. Nucleophilic displacement of the leaving group of, *e.g.*, *threo*-$(CH_3)_3CCHDCHDOBs$ by cyclopentadienyldicarbonyliron anion yields an organoiron compound, **2**, which can be established to be an erythro diasteriomer by nmr spectroscopy. Reacting this material with a reagent that cleaves the C–Fe bond and determining



whether the product belongs to the erythro or threo series using the same technique immediately establishes the stereochemistry at carbon that characterizes the reaction.[25]

This technique has a number of practical advantages over other available methods for examining the stereochemistry of reactions of transition metal alkyls: first, the organometallic compounds involved are primary alkyls, and relatively stable thermally; second, E2 elimination seems to be a less important side reaction for SN2 displacement at C-1 of the 3,3-dimethylbutyl group than for similar reactions at secondary centers; third, since there is no significant steric difference between *threo*- and *erythro*-$(CH_3)_3CCHDCHDX$, it is only necessary to examine one diastereomer; finally, since many impurities do not hinder the identification of the diastereomeric composition of the sample, the standard of purity required for accurate analysis of these substances is less rigorous than that required for, *e.g.*, measurement of optical rotation.

Certain restrictions characteristic of this use of the 3,3-dimethylbutyl system deserve mention. First, organometallic derivatives of this alkyl moiety must be synthesized by nucleophilic displacements using metallate anions or by other less direct routes such as decarbonylation or transmetallation; 3,3-dimethylbutylmagnesium and lithium reagents are not configurationally stable.[26] The rate of SN2 displacement at C-1 of this alkyl group is relatively slow.[27,28] Second, since nmr spectroscopy is the only practical method of distinguishing between diastereomeric derivates in this series, the organometallic substances being examined must be diamagnetic. Finally, conclusions derived from studies of 3,3-dimethylbutylmetal compounds cannot necessarily be generalized to other types of alkylmetal systems, since the mechanisms of organometallic reactions seem particularly sensitive to changes in the structures of the alkyl moieties involved.

These restrictions notwithstanding, the study of 3,3-dimethylbutyl-*1,2-d*$_2$-metal compounds offers the most convenient method presently available for studying the stereochemistry of reactions of transition metal

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(23) The only ambiguity in this method would arise in the unlikely event that the gauche conformation were lower in energy than the trans for some group X. In this event, the spectrum of the CH_2CH_2 spin system could still have AA′XX′ character, and the erythro and threo diasteriomers of the dideuterated substances could still have different vicinal coupling constants; however, J_{threo} would be *greater* than $J_{erythro}$. We have not investigated a substituted derivative of 3,3-dimethylbutane that shows any indication of a low-energy gauche conformation. More importantly, previous analyses of the temperature dependence of the coupling constants in these compounds had established that the vicinal coupling constants that would characterize a molecule in a pure trans conformation would be *ca.* 14 and 4 Hz, while the vicinal coupling constants for a molecule existing entirely as an equilibrating mixture of gauche conformers would be *ca.* 9 and 4 Hz.[24] Most of the organometallic compounds examined in the present work belong to the erythro series and have coupling constants of 11–14 Hz. The magnitudes of these couplings require that the trans conformer be lower in energy than the gauche.

(24) These values are those expected from previous experimental and theoretical work: *cf.* E. B. Whipple, *J. Magn. Resonance*, **5**, 163 (1971). Recent papers discussing conformational analyses of acyclic molecules are summarized in E. F. Mooney, Ed., *Annu. Rep. NMR (Nucl. Magn. Resonance) Spectrosc.*, **1–5** (1967–1973).

(25) A closely related technique has been developed by Snyder: R. J. Jablonski and E. I. Snyder, *Tetrahedron Lett.*, 1103 (1968); R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968). The influence of steric effects on rates has also been used to infer the stereochemistry of SE2 reactions: *cf.* M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans. 2*, 1132 (1973).

(26) G. M. Whitesides, M. Witanowski, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 2854 (1965); M. Witanowski and J. D. Roberts, *ibid.*, **88**, 737 (1966).

(27) The relative rates of reaction of neopentyl bromide, 3,3-dimethylbutyl bromide, and *n*-butyl bromide with potassium iodide in acetone are 0.0064:4.15:100 (E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 79).

(28) P. L. Bock and G. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 2826 (1974).

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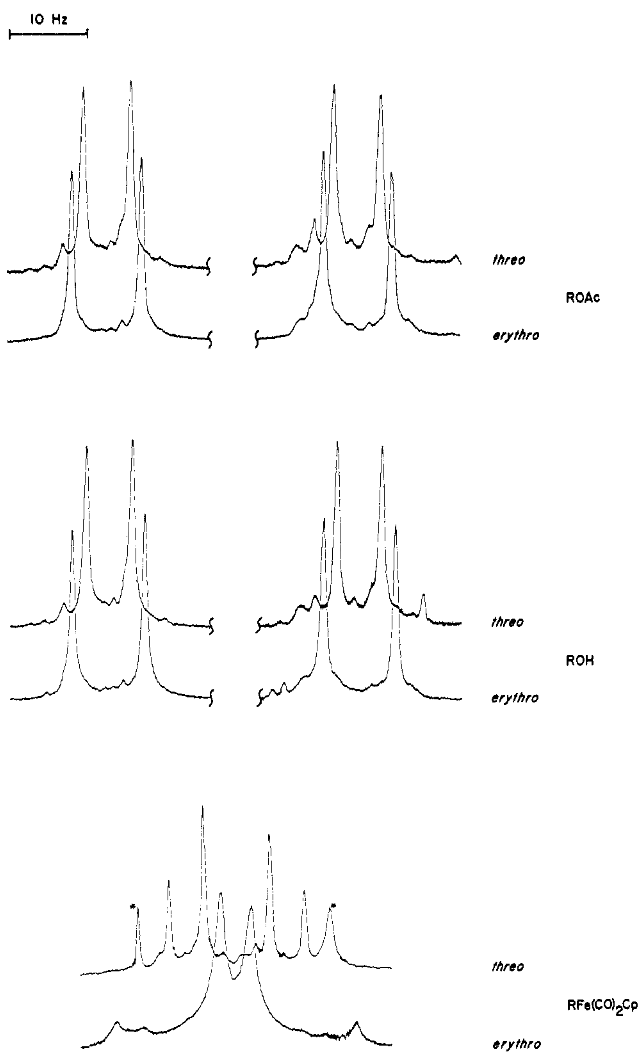


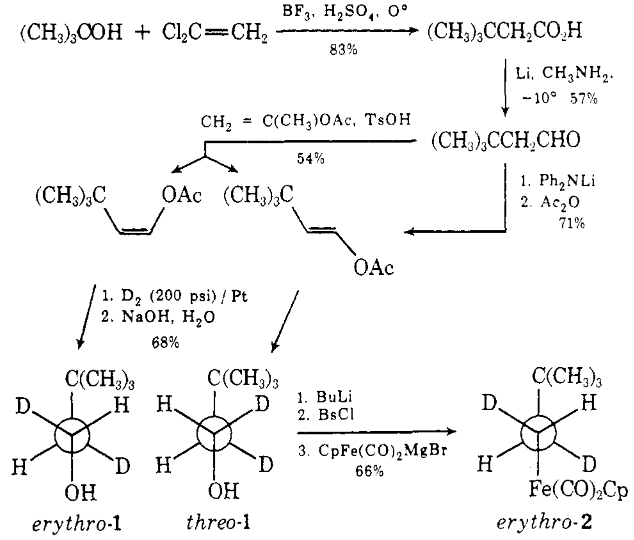
Figure 1. Deuterium-decoupled 100-MHz nmr spectra of the C*H*DC*H*D protons of *threo*- and *erythro*-$(CH_3)_3CCHDCHDOAc$, -$(CH_3)_3CCHDCHDOH$ (**1**), and -$(CH_3)_3CCHDCHDFe(CO)_2Cp$ (**2**). The peaks marked with asterisks in the spectrum of **2** are due to impurities.

alkyls. In this paper we detail procedures for the synthesis of the deuterated starting materials and the results of studies of a number of reactions of one transition metal compound, cyclopentadienyldicarbonyliron 3,3-dimethylbutyl-*1,2*-d_2 (**2**).

Results

Synthesis of *erythro*- and *threo*-$(CH_3)_3CCHDCHDFe(CO)_2Cp$. The parent compounds *threo*- and *erythro*-3,3-dimethylbutan-1-ol-*1,2*-d_2 (*threo*-**1** and *erythro*-**1**, respectively) were synthesized using the procedure outlined in Scheme I.[29] Reaction of *tert*-butyl alcohol and 1,1-dichloroethylene in concentrated sulfuric acid[30] yielded 3,3-dimethylbutyric acid, which was in turn reduced to 3,3-dimethylbutanal with lithium in methylamine.[31] The 2 : 3 mixture of *cis*- and *trans*-1-acetoxy-3,3-dimethylbut-1-ene produced by acid-catalyzed reaction of this aldehyde with isopropenyl acetate[32] was separated by distillation using an annular Teflon spinning band column; the trans isomer was produced directly by reaction of the enolate derived from 3,3-dimethylbutanal and lithium diphenylamide with acetic anhydride. Deuterogenation of the trans enol acetate over Platinum Black catalyst using 98% *d* deuterium gas produced *threo*-1-acetoxy-3,3-dimethylbutane-*1,2*-d_2 which was converted to *threo*-3,3-dimethylbutan-1-ol-*1,2*-d_2 (*threo*-**1**) by hydrolysis in 20% aqueous sodium hydroxide solution. Deuterogenation and hydrolysis of the cis enol acetate yielded *erythro*-**1**.

Scheme I. Synthesis of *threo*- and *erythro*-3,3-Dimethylbutan-1-ol-*1,2*-d_2 (Only One Enantiomer of Each Compound is Shown)



The deuterium-decoupled 100-MHz nmr spectra of the C*H*DC*H*D protons of chloroform solutions of *erythro*- and *threo*-**1** and the analogous acetates (Figure 1) consist of AX patterns in which the separation between erythro and threo resonances is sufficient to permit diastereomeric compositions to be analyzed *ca.* ±5%. These spectra establish that the synthesis outlined in Scheme I leads to deuterated alcohols with excellent stereoselectivity and also that the presence of the isotopic impurities present in the samples does not interfere with diastereomeric analysis.[33]

To prepare the organoiron compounds that form the subject of this work, these deuterated alcohols are converted to the corresponding brosylates and allowed to react with cyclopentadienyldicarbonyliron anion in tetrahydrofuran solution. Recent communications by Traylor and Kuivila have shown that the stereochemistry of the reaction between several alkyl bromides and trimethyltin anion depends, among other factors, on the nature of the counterion present in the system;[34,35]

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[29] The synthesis of *erythro*-**1** used in the early stages of the project was based on *trans*-ethylene-*1,2*-d_2 oxide.[21] The synthesis of this substance requires the manipulation of large volumes of acetylene-d_2 and ethylene-d_2 and has been discarded in favor of the more convenient synthesis reported here. Details of the earlier procedure are contained in the Ph.D. Thesis of D. J. Boschetto, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1971.

[30] K. Bott and H. Hellman, *Angew. Chem., Int. Ed. Engl.*, **5**, 870 (1966).

[31] A. O. Bedenbaugh, J. H. Bedenbaugh, W. A. Bergin, and J. D. Adkins, *J. Amer. Chem. Soc.*, **92**, 5774 (1970).

[32] H. O. House and V. Kramer, *J. Org. Chem.*, **28**, 3362 (1963).

[33] Treatment of *threo*-**1** with triphenylphosphine dibromide in DMF and mass spectroscopic analysis of the resulting deuterated 3,3-dimethylbutyl bromide establishes its isotopic composition to be 1.0% d_0, 3.9% d_1, 93.4% d_2, 1.7% d_3, and 0.0% d_4. Certain of the extraneous lines in the spectra of Figure 1 are due to these isotopic impurities.

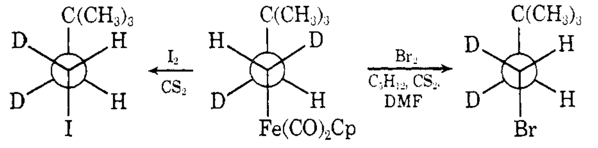
[34] G. S. Koermer, M. L. Hall, and T. G. Traylor, *J. Amer. Chem. Soc.*, **94**, 7205 (1972).

[35] H. G. Kuivila, J. L. Considine, and J. D. Kennedy, *J. Amer. Chem. Soc.*, **94**, 7206 (1972).

retention at carbon is observed in certain instances when the nucleophilic reagent is $(CH_3)_3SnLi$. We find that attack of $CpFe(CO)_2^-M^+$ on brosylates derived from **1** takes place with >95% inversion of configuration at carbon for $M^+ = Na^+$, Li^+, and $MgBr^+$[36-38] and that reaction of $CpFe(CO)_2Li$ with 3,3-dimethylbutyl-*1,2-d*$_2$ bromide also proceeds with inversion. Thus, there is no suggestion in this system of the mechanistic duality that apparently exists in analogous reactions using trimethyltin lithium. Typical spectra for the *erythro*- and *threo*-**2** are shown in Figure 1. The spectrum of the erythro diasteriomer provides an example of the line broadening that has occasionally proved troublesome in these studies; this broadening presumably reflects paramagnetic impurities present in the solution that are not removed by the purifications employed for **2**.

The observation that nucleophilic displacement by $CpFe(CO)_2^-$ on the brosylate derived from *threo*-**1** yields *erythro*-**2** establishes two useful facts: first, that this displacement has the stereochemical characteristics expected of an unexceptional S$_N$2 displacement, and second, that the carbon–iron σ bond of **2** is configurationally stable over periods of time sufficiently long for it to be a useful substrate for mechanistic studies.[39,40]

Reactions of *erythro*-2 with Halogens. Reaction of *erythro*-**2** with molecular bromine in pentane and carbon disulfide occurs rapidly at 0°, yielding *threo*-$(CH_3)_3$-CCHDCHDBr (**3**) with greater than 95% inversion of configuration at carbon (Figure 2); reaction in dimethylformamide (DMF) yields a 9:1 mixture of *threo*- and *erythro*-**3**; reaction in methanol yields no **3** but carbonyl containing products (*vide infra*). Reaction of *threo*-**2** with bromine in chloroform-*d*$_1$ had previously been shown to yield *erythro*-**3** with greater than 95% inversion of stereochemistry.[21] The partial loss of stereochemistry observed in DMF may be an artifact of the work-up procedure; bromide ion catalyzed epimerization of **3** might be sufficiently rapid in DMF under the conditions used in these experiments to influence the apparent stereochemistry of the reaction. Cleavage of the carbon–iron bond of **2** with bromine thus proceeds with inversion of configuration, in a reaction whose stereochemistry shows no significant dependence on solvent polarity.[41,42]



threo-4 *threo*-3

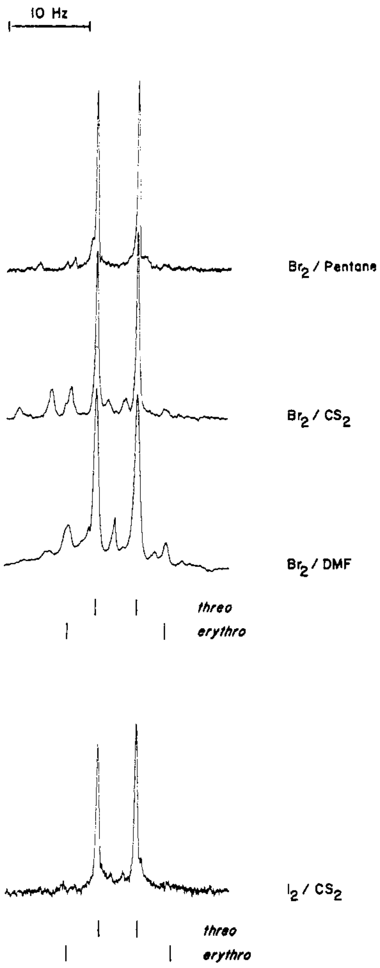


Figure 2. Deuterium-decoupled 100-MHz nmr spectra of the C*H*DBr resonances of (CH_3)CCHDBr obtained by bromination of *erythro*-**2** in pentane and CS_2, the $(CH_3)_3$CC*H*D resonances from its bromination in DMF, and the C*H*DI proton from its iodination in CS_2.

Reaction of *erythro*-**2** with molecular iodine in carbon disulfide yielded *threo*-$(CH_3)_3$CCHDCHDI (**4**) and therefore also proceeds with inversion of stereochemistry (Figure 2). We were able to detect only small quantities (~5%) of 3,3-dimethylbutyl chloride on reaction of **2** with chlorine in chloroform at −20°; the corresponding acid chloride was the major product (*vide infra*).

"Carbonyl Insertion" Reactions of 2. The mechanisms by which carbon monoxide "inserts" into carbon–metal bonds have been studied in greater detail than most transition metal organometallic reactions and are generally believed to involve a concerted migration of the alkyl group to an adjacent, coordinated, carbonyl ligand.[43,44] We have shown that reaction of *threo*-**2** with triphenylphosphine yields *threo*-$(CH_3)_3$-

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(36) The sodium salt is produced by reduction of $[CpFe(CO)_2]_2$ with sodium amalgam,[8] the lithium salt by reduction with lithium (1% sodium) wire, and the magnesium bromide salt by reaction with magnesium and 1,2-dibromoethane.[37]

(37) J. M. Burlitch and S. W. Ulmer, *J. Organometal. Chem.*, **19**, P21 (1969).

(38) The alkylation of $CpFe(CO)_2^-$ by D-(+)-*sec*-butyl bromide has been inferred to proceed with 75% inversion of configuration at carbon *cf.* ref 14d.

(39) Alkylcobaloxime compounds undergo a reaction with cobaloxime anion analogous to the Finkelstein reaction: *cf.* ref 11d and D. Dodd and M. D. Johnson, *Chem. Commun.*, 1371 (1971); S. N. Anderson, D. H. Ballard, J. Z. Chrzastowski, D. Dodd, and M. D. Johnson, *ibid.*, 685 (1972).

(40) We have seen no evidence of epimerization of **2** on standing as a solid for longer than 3 weeks at −20° or in solution in CCl_4 or $CDCl_3$ at room temperature for 12 hr.

(41) The stereochemistry of halogenation of other organometallic reagents is strongly dependent on solvent: *cf.* F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, pp 87 and 90.

(42) F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, **93**, 4047, 4048 (1971).

(43) Review: A. Wojcicki, *Advan. Organometal. Chem.*, **11**, 88 (1973). For a dissenting view, *cf.* H. M. Walborsky and L. E. Allen, *J. Amer. Chem. Soc.*, **93**, 5465 (1971).

(44) It has been suggested that these reactions should be called ligand transfer processes (*cf.* ref 8b and F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, p 578.

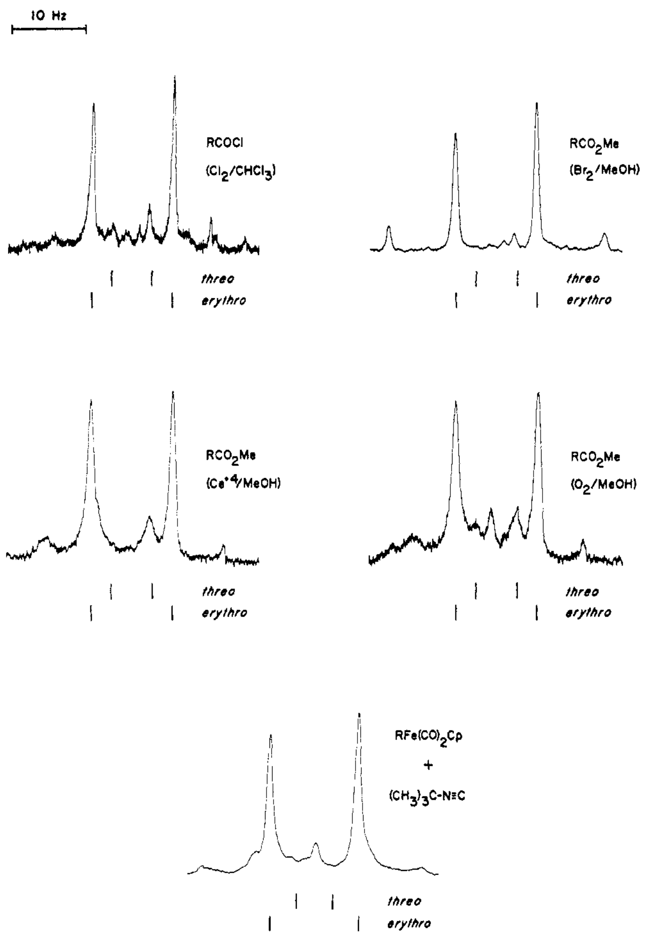
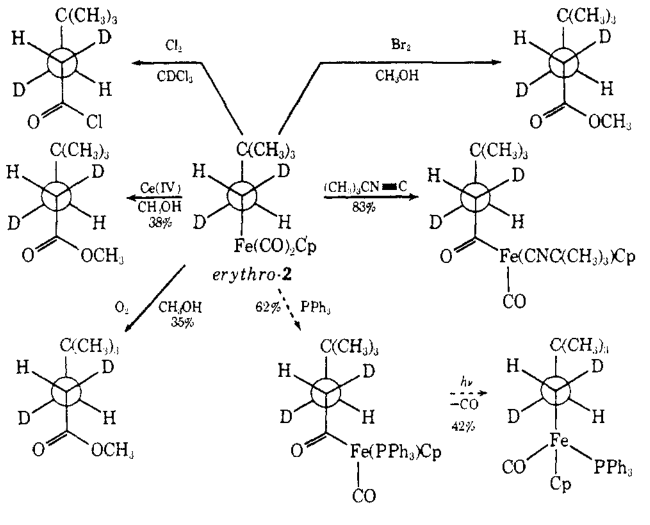


Figure 3. Deuterium-decoupled 100-MHz nmr spectra of products resulting from carbonyl insertion reactions of *erythro*-**2**.

$CCHDCHDCOFe(CO)(PPh_3)Cp$[21] with greater than 95% retention of stereochemistry at carbon. Similar stereochemical results are obtained in a variety of other reactions that lead to carbonyl insertion (Scheme II).

Scheme II. Reactions of **2** Resulting in Carbonylation of the 3,3-Dimethylbutyl Moiety



For convenience, the reaction of **2** with triphenylphosphine and the decarbonylation of the resulting acyliron compound are both included in this scheme, although these reactions were carried out in the opposite diastereomeric series. Reaction of *erythro*-**2** with *tert*-butyl isocyanide led to the carbonyl insertion product[45] with the expected retention of stereochemistry. Less expectedly, reaction of *erythro*-**2** with a number of oxidizing agents (bromine, ceric ammonium nitrate (CAN), oxygen, all in methanol, and chlorine in chloroform) also lead to carbonyl inserted products, all characterized by >95% retention of configuration at carbon (Figure 3).[46]

Sulfur Dioxide Insertion. The mechanism of insertion of sulfur dioxide into carbon-iron σ bonds remains a puzzle, despite extensive investigation.[47] The reaction is characterized by large, negative, entropies of activation and by rate acceleration from electron-releasing substituents on the alkyl group attached to the metal; *O*-sulfinato complexes have been implicated as intermediates,[48] and the reaction occurs with high stereoselectivity (and presumably with retention of configuration) at iron.[49] These data are compatible with a mechanism for sulfur dioxide insertion resembling that for carbon monoxide insertion. However, the stereochemistry at carbon for these two reactions is opposite. We have examined carefully the *S*-sulfinato complex obtained by reaction of *erythro*-**2** with sulfur dioxide in a variety of solvents and find in each instance that the reaction proceeds with greater than 95% inversion of configuration at carbon (Figure 4); by contrast, carbon monoxide insertion proceeds stereospecifically with retention of configuration at carbon (*vide supra*).

Addition of *erythro*-2 to Dimethyl Acetylenedicarboxylate. Elimination of *tert*-Butylethylene on Thermal Decomposition of *erythro*-2. The addition of transition metal alkyls to carbon-carbon multiple bonds,[50] and the generation of carbon-carbon unsaturation by metal hydride elimination from transition metal alkyls,[12] are both reaction types of central importance in catalysis. Organoiron compound **2** does not add to simple olefins or to most of the reactive carbon-carbon unsaturations commonly used in organometallic chemistry (tetracyanoethylene,[51] tetrafluoroethylene,[52,53] hexafluorobut-2-yne,[53] or diphenylacetylene). However, when *erythro*-**2** was heated with dimethyl acetylenedicarboxylate in THF for 24 hr at 50-60° a new compound was produced which could be isolated in 60% yield as a black oil. This compound was assigned the structure **5** based on spectroscopic data summarized in the Experimental Section.

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(45) Y. Yamamoto and H. Yamazaki, *Inorg. Chem.*, **11**, 211 (1972).

(46) S. N. Anderson, C. W. Fong, and M. D. Johnson, *Chem. Commun.*, 163 (1973), have reported that oxidation of $p\text{-F-C}_6H_4CH_2Mo(CO)_3Cp$ with CAN in methanol yields the corresponding methyl ester. Nicholas and Rosenblum have recently established that oxidation of cyclopentadienyldicarbonyliron derivatives of cyclohexane yield carbonylated products with retention of stereochemistry on oxidation with copper(II),[10] and J. P. Collman, S. R. Winter, and R. G. Komoto, *J. Amer. Chem. Soc.*, **95**, 249 (1973), have observed ligand migration on oxidation of compounds having the composition $RFe(CO)_4^-$.

(47) A. Wojcicki, *Accounts Chem. Res.*, **4**, 344 (1971); W. Kitching and C. W. Fong, *Organometal. Chem. Rev., Sect. A*, **5**, 281 (1970).

(48) S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Inorg. Chem.*, **12**, 717 (1973).

(49) T. C. Flood and D. L. Miles, *J. Amer. Chem. Soc.*, **95**, 6460 (1973).

(50) R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968); G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968); G. Henrci-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **10**, 776 (1971).

(51) S. R. Su, J. A. Hanna, and A. Wojcicki, *J. Organometal. Chem.*, **21**, P21 (1970).

(52) J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc., London*, 218 (1963).

(53) H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, **9**, 2670 (1970).

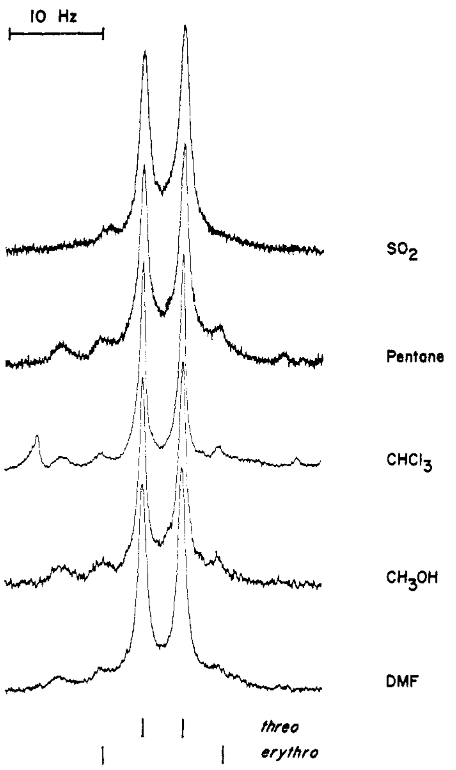


Figure 4. Deuterium-decoupled 100-MHz nmr spectra of the C*H*DSO$_2$ protons of (CH$_3$)$_3$CCHDCHDSO$_2$Fe(CO)$_2$Cp produced by reaction of *erythro*-**2** with sulfur dioxide in a variety of solvents. The approximate concentrations of SO$_2$ in each solvent (v/v) are: SO$_2$ (100); pentane (10); CHCl$_3$ (10); CH$_3$OH (10); DMF (10).

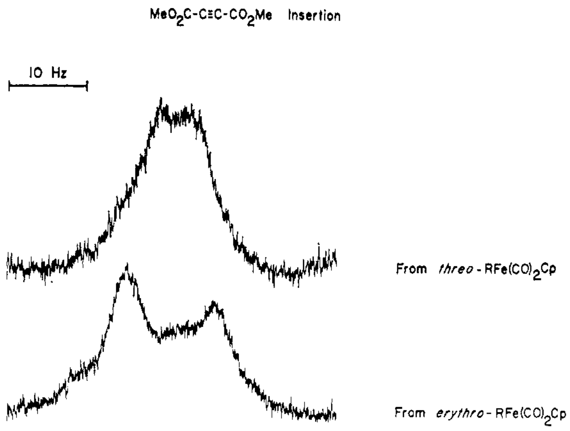
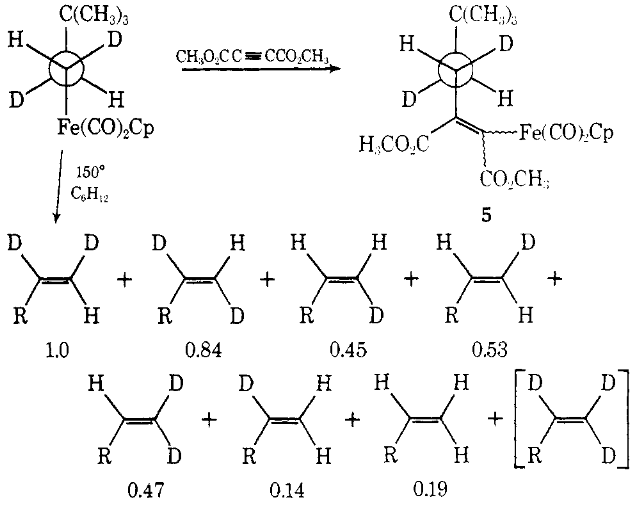


Figure 5. Deuterium-decoupled 100-MHz nmr spectra of the product of insertion of dimethyl acetylenedicarboxylate into the carbon–iron bond of *threo*-**2** (upper) and *erythro*-**2** (lower).

Scheme III. Insertion of Dimethyl Acetylenedicarboxylate into **2** (Thermal Decomposition) of **2**



Although the stereochemistry around the carbon–carbon double bond cannot be assigned with any assurance, examination of the nmr spectrum of the 3,3-dimethylbutyl-d_2 moiety of this compound indicates that the transfer of this alkyl group to the acetylenic bond has occurred with $\geq 80\%$ retention of configuration (Figure 5). The low precision of this estimate reflects the poor quality of the spectrum; we were unable to eliminate the broadening of the lines, even after extensive purification. To increase our confidence in this conclusion, the same experiment was carried through starting with *threo*-**2**. The spectrum of the resulting adduct was also broad (Figure 5) but again gave no indication of inversion of configuration in the product.

An effort to determine the stereochemistry of the process leading to generation of 3,3-dimethylbut-1-ene on thermal decomposition of **1** was not successful; the yield of olefins was low (*ca.* 15%), and, although the signals of the various possible isotopic substitution patterns could be clearly resolved (Figure 6), the mixture of products obtained strongly suggested that the rates of both intra- and intermolecular scrambling processes were rapid under the conditions used.[54]

Discussion

The retention of configuration at carbon observed for reactions resulting in carbonylation of the 3,3-dimethylbutyl moiety of **2** is the result anticipated on the basis of previous studies of related reactions.[10,21,43] This reaction promises to be very useful in future studies of the stereochemistry of reactions involving transition metal organometallic compounds; a wide variety of organometallic substances can be carbonylated, and with only one possible exception,[55] all carbonylations and decarbonylations whose stereochemistry has been deter-

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[54] Evidence from other systems suggests that metal hydride addition to olefins commonly occurs cis: C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 6785 (1970); W. E. Fichteman and M. Orchin, *J. Org. Chem.*, **34**, 2790 (1969); L. M. Jackman, J. A. Hamilton, and J. M. Lawlor, *J. Amer. Chem. Soc.*, **90**, 1914 (1968).

[55] F. Calderazzo and K. Noack[14] have reported that the conversion of optically active i to ii preserves the sign of rotation, while conversion of optically active iii to iv results in change in sign.[56] Without knowing the relative configuration of i and ii, and of iii and iv, it is impossible to

$$\underset{\text{i}}{(+)_{\text{D}}\text{-PhCH}_2\text{CH(CH}_3\text{)COMn(CO)}_5} \rightleftharpoons \underset{\text{ii}}{(+)_{\text{D}}\text{-PhCH}_2\text{CH(CH}_3\text{)Mn(CO)}_5} + \text{CO}$$

$$\underset{\text{iii}}{(-)_{546}\text{-PhCH(CH}_3\text{)COFe(CO)}_2\text{Cp}} + \text{Rh(PPh}_3)_3\text{Cl} \longrightarrow \underset{\text{iv}}{(+)_{546}\text{-PhCH(CH}_3\text{)Fe(CO)}_2\text{Cp}} + \text{Rh(CO)(PPh}_3)_2\text{Cl}$$

interpret these signs of rotation in any convincing way. Further, conversion of i to ii was low, and the rotation result is open to some suspicion. Nonetheless, the fact that two, at least superficially similar, transformations take place with opposite effects on the signs of rotation suggests that one might take place with inversion of configuration at carbon.

[56] J. J. Alexander and A. Wojcicki, *J. Organometal. Chem.*, **15**, P23 (1968).

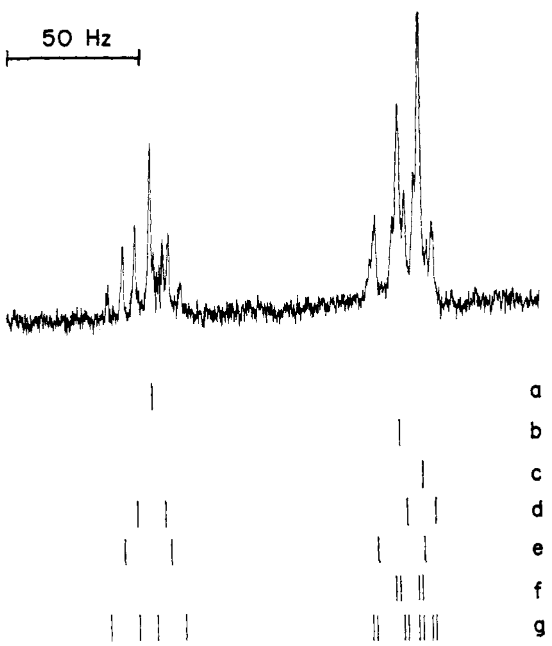
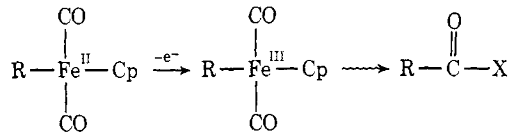


Figure 6. Deuterium-decoupled 100-MHz nmr spectra of the mixture of olefins obtained by thermal decomposition of *erythro*-**2**. The stick spectra under the experimental spectrum represent the positions of the various deuterated olefins, based on coupling constants of 1.6 Hz (geminal), 10.6 Hz (cis), and 17.4 Hz (trans); where indicated, *Z* and *E* designate the configuration of the substance around the olefinic bond: a, *1,1*-d_2, 3,3-dimethylbut-1-ene-*1,1*-d_2; b, -*E-1,2*-d_2; c, -*Z-1,2*-d_2; d, -*Z-1*-d_1; e, *E-1*-d_1; f, -*2*-d_1; g, -d_0. The chemical shifts used for these spectra varied slightly between compounds as a result of isotope effects, but (approximately) $\nu_1 \sim 5.81\ \delta$, $\nu_2 = 4.80\ \delta$, and $\nu_3 = 4.88\ \delta$.

mined have been found to take place with retention of stereochemistry at carbon. Thus, carbonylation and decarbonylation may prove to be the stereochemical equivalent of the SN2 reaction in aliphatic organic chemistry, in the sense of providing reactions of dependable stereochemical course that can be relied on in chemical correlations of configuration in the organometallic series. The mechanism(s) of the oxidative carbonylations is not presently known. Conversion of tetracarbonylalkyliron anions, $RFe(CO)_4^-$, to acyl compounds is Lewis acid catalyzed;[57] certain of the reactions reported in Scheme II might also be. However, those of these reactions run in the presence of oxidizing agents more probably involve electron transfer as an important step. It is not immediately evident why oxidation should encourage acyl formation, but the phenomenon occurs both in the several examples summarized in Scheme II and elsewhere.[10,46]



$$R-\overset{\overset{CO}{|}}{\underset{\underset{CO}{|}}{Fe^{II}}}-Cp \xrightarrow{-e^-} R-\overset{\overset{CO}{|}}{\underset{\underset{CO}{|}}{Fe^{III}}}-Cp \longrightarrow R-\overset{\overset{O}{\|}}{C}-X$$

The halogenation reactions studied here that result in carbon-halogen bond formation all occur cleanly with inversion of configuration at carbon. Inversion of configuration has also been inferred to be the major stereochemical result of halogenation of several organolithium,[19,58] -boron,[59] -cobalt,[15,60] silicon,[42] germanium,[42] tin,[42] and lead[42] compounds. Retention has been observed for palladium(II),[17] manganese,[14d] and mercury[41] alkyls. It is not yet possible to construct convincing rationalizations for all of these stereochemical results. The retention of configuration observed for palladium(II) probably reflects an oxidative addition of halogen followed by reductive elimination of alkyl halide and would be expected to characterize halogenations of similar, coordinatively unsaturated, d^8 alkyls. The mechanism describing the bromination of **2** is less obvious, but the stereochemistry-determining transition state probably resembles either that pro-

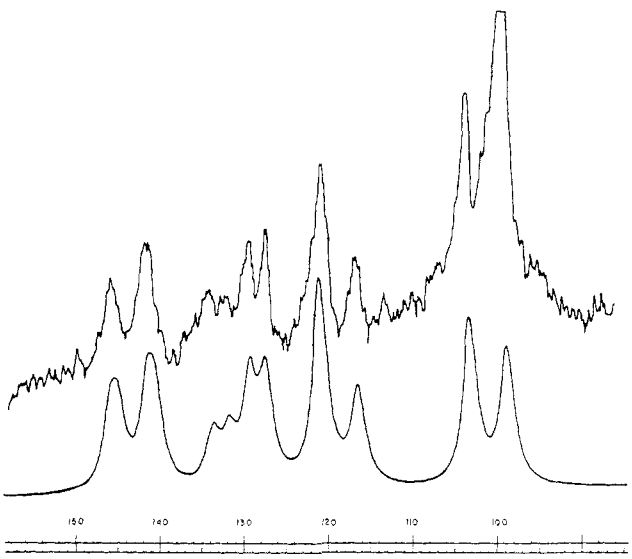
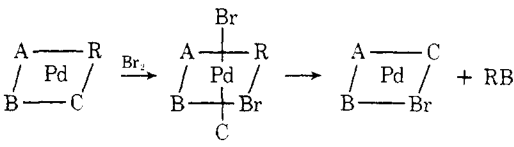
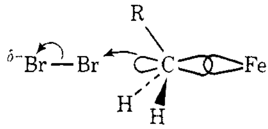


Figure 7. Deuterium-decoupled 100-MHz nmr spectrum of the C*H*DC*H*D protons of *threo*-$(CH_3)_3CCHDCHDFe(CO)(PPh_3)Cp$. For comparison, the computer simulated spectrum is given below the observed trace. The large peak at *ca.* 0.98 ppm is due to an impurity.



posed by Jensen for tetraallytin reagents (**6**), and probably important for bromination of boronate ions,[59] or the substance formally obtained by oxidative addition of bromonium ion to iron (**7**). Since the compound resulting from oxidative addition of a full equivalent of molecular bromine to **2** would both contain a formal



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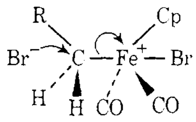

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iron(IV) species and violate the 18-electron rule,[61] a halogenation mechanism analogous to that discussed for palladium seems unlikely for **2**. The partial oxidative addition represented by **7** would serve to convert the $CpFe(CO)_2$ moiety into a $[CpFe(CO)_2Br]^+$ group;

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(57) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Amer. Chem. Soc.*, **94**, 5905 (1972).

(58) D. E. Applequist and G. N. Chmurny, *J. Amer. Chem. Soc.*, **89**, 875 (1967).

(59) H. C. Brown and C. F. Lane, *Chem. Commun.*, 521 (1971).

(60) F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, **93**, 5283 (1971).

(61) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).

the latter would be expected to be an excellent leaving group. The several plausible radical chain pathways for the bromination of **2** that involve one-electron oxidation seem unlikely, because the carbonylation products that apparently characterize the oxidation of **2** do not occur during its bromination, at least in apolar solvents. Sufficiently little is known about bromination of the lithium, cobalt, and manganese organometallic compounds that no distinctions between SE2 and electron transfer mechanisms are possible at present.

$$RFe(CO)_2Cp + Br_2 \longrightarrow [RFe(CO)_2Cp]\cdot^+ + Br\cdot + Br^-$$

$$Br\cdot + RFe(CO)_2Cp \longrightarrow [RFe(CO)_2Cp]\cdot^+ + Br^-$$

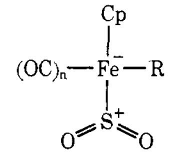
$$Br^- + [RFe(CO)_2Cp]\cdot^+ \longrightarrow BrR + Fe(CO)_2Cp$$

$$Fe(CO)_2Cp + Br_2 \longrightarrow BrFe(CO)_2Cp + Br\cdot$$

$$Fe(CO)_2Cp + Br\cdot \longrightarrow BrFe(CO)_2Cp$$

Regardless of the details of the mechanisms of these halogenation reactions, it is evident that the stereochemical course of halogenation of organometallic compounds may be either inversion, retention, or epimerization,[41,42] depending on structure and reaction conditions, and that halogenation cannot presently be used to relate the configurations of organometallic compounds to products of their reactions.

The mechanistic significance of the inversion of configuration observed on reaction of **2** with sulfur dioxide has been discussed by Wojcicki,[47,48,62] and needs no lengthy elaboration here. To take place by a process analogous to that occurring during carbonylation sulfur dioxide insertion would have to involve initial coordination to the iron atom of **2** and formation of an intermediate **8**, followed by migration of an alkyl group from iron to sulfur. With hindsight, it seems less likely that an incoming sulfur dioxide molecule would coordinate to iron in the sense indicated by **8** than it would induce carbonylation. Direct electrophilic attack on the iron–carbon bond, either frontside or backside (**9**), seems the more plausible reaction course. The stereochemical results reported here clearly support backside attack. Wojcicki has proposed that an ion pair, **10**, is an intermediate in the reaction; this proposal is consistent with the available kinetic and stereochemical data.[63]



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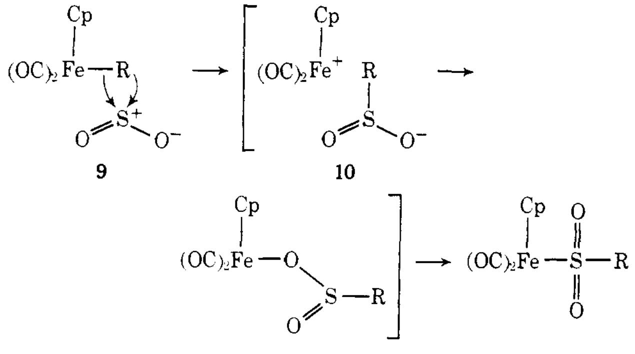
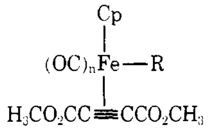


The retention of stereochemistry observed on insertion of dimethyl acetylenedicarboxylate into the carbon–iron bond of **2** is not an altogether expected result, in light of the stereochemical course observed for sulfur dioxide insertion. An intermediate (**11**) resulting from coordination of the acetylene to iron appears no more attractive than does **8**, but if this reaction actually involves electrophilic attack on the carbon–iron bond without prior coordination, it is not evident that it should not also follow whatever dictates that lead to backside attack in reaction with sulfur dioxide. However, it is pertinent that cleavage of the carbon–iron bond of **2** with mercuric chloride, normally an electrophilic reagent, occurs cleanly with retention of configuration at carbon.[21]



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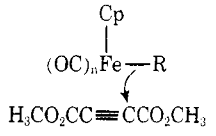

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In summary, reactions at the carbon–iron bond of **2** appear to involve at least three types of processes: alkyl shift, with retention of configuration at carbon, to coordinated carbon monoxide induced by an attacking nucleophile and/or by oxidation of the iron; attack on a noncoordinated electrophile with inversion of configuration; and transfer to an electrophile with retention of configuration. Too few data are presently available to resolve these processes into detailed mechanisms capable of predicting the stereochemical course of new reactions, but the high stereoselectivity characterizing reactions of **2**, and the configurational stability of its carbon–metal bond, establish that stereochemical studies should prove as useful in the elaboration of the mechanisms of reactions of organometallic derivatives of transition metals as they have of organic compounds.

Experimental Section

General Methods. All reactions involving organometallic compounds were carried out under nitrogen. Prepurified nitrogen was passed through a 12-in. tube containing Drierite. All solvents were reagent grade; THF was distilled from a dark purple solution of benzophenone dianion before use; ether was distilled from lithium aluminum hydride; other solvents were dried over molecular sieves and degassed by bubbling a vigorous stream of nitrogen through them. Methyl- and *n*-butyllithium were supplied by Foote Mineral Corp. or Ventron Corp. Cyclopentadienyldicarbonyliron dimer was obtained from Strem Chemicals Inc. and was recrystallized before use by dissolving in the minimum amount of acetone at room temperature, adding $^1/_3$ that volume of water, and cooling in a refrigerator maintained at $-20°$. Technical grade deuterium gas was obtained from the Matheson Co., Inc. Platinum black catalyst was supplied by Engelhard Ind. Stainless steel cannulas were obtained on special order from Popper and Sons Co., New York, N. Y. 10010. Melting points and boiling points are uncorrected. Infrared spectra were taken in sodium chloride cells on a Perkin-Elmer Model 237 grating spectrophotometer. Routine nmr spectra were recorded on a Varian T-60 spectrometer; chemi-

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[62] A. Wojcicki, *Advan. Organometal. Chem.*, in press.

[63] Flood and Miles have provided evidence that sulfur dioxide insertion into a carbon–iron bond proceeds with high stereoselectivity at iron.[49] If an ion pair is an intermediate in this reaction, the observation that stereochemistry at iron is (presumed to be) retained suggests that stereochemical studies at metallic centers will be less useful for identifying ionic intermediates than are analogous studies at carbon centers.

cal shifts are reported in parts per million downfield from tetramethylsilane. Microanalyses were performed by Midwest Microlabs, Ltd., Indianapolis, Ind. Liquid samples for elemental and spectral analysis were purified by use of a Hewlett-Packard Model 700 thermal conductivity glpc. Analytical glpc analyses were performed on an F and M 810 instrument, using internal standard techniques with response factors obtained using authentic samples. Deuterogenation and sulfur dioxide insertion reactions were carried out in aerosol reaction vessels obtained from VWR Scientific. Deuterium decoupled nmr spectra were obtained using a Varian HA-100 spectrometer, with the deuterium decoupled signal derived from Schomandl Model MS100M frequency synthesizer. This signal was noise-modulated by mixing with the signal from a Digilab FTS/NMR Model 50-80 decoupler or with a 1-V square-wave signal swept from 0 to 300 Hz at 10 Hz/sec. The noise modulated signal was amplified using a Perkin-Elmer R-209 PA power amplifier. An ENI Model 350 L radiofrequency power amplifier was used for final amplification of the decoupling signal.

3,3-Dimethylbutyric acid was prepared using a modification of a literature procedure.[30] A 1-l. round-bottomed flask equipped with a magnetic stirring bar and a No-Air stopper was charged with 500 ml of concentrated sulfuric acid, tared, and cooled by immersion in an ice bath. Boron trifluoride gas[64] was introduced with a syringe needle through the No-Air stopper and was allowed to bubble through the rapidly stirred solution. The flask and contents were weighed occasionally, and, after a total of 180 g of boron trifluoride had dissolved, the contents of the flask was transferred by forced siphon through a stainless steel cannula into a 5-l. three-necked flask, equipped with a mechanical stirrer, Dry Ice condenser, and No-Air stopper, containing an additional 500 ml of concentrated sulfuric acid. The No-Air stopper was replaced with a dropping funnel,[65] the flask was immersed in an ice bath, and rapid stirring was initiated. A solution of 458 g (6.18 mol) of *tert*-butyl alcohol in 884 g (9.11 mol) of 1,1-dichloroethylene was added slowly from the dropping funnel to the stirred sulfuric acid over 6.5 hr. Evolution of hydrochloric acid began immediately; the evolved gas was vented through a short hypodermic syringe needle inserted through a No-Air stopper at the top of the Dry Ice condenser. After the addition was complete, the reaction mixture was allowed to stir for an additional hour at 0° and then was allowed to warm to room temperature. The mixture was poured onto *ca.* 1 kg of ice. Crude 3,3-dimethylbutyric acid separated as an oil which was separated from the aqueous lower layer with a separatory funnel. The acid was taken up in 500 ml of ether and treated with 20% aqueous sodium hydroxide until the lower aqueous layer had pH 9. The aqueous layer was separated and washed with three 200-ml portions of ether; its acidity was adjusted to pH 3 using 6 *N* HCl. The crude acid layer which separated was taken up in 500 ml of ether, washed with three 500-ml portions of water and once with 200 ml of brine, and dried ($MgSO_4$). The ether was removed by distillation through a 15-cm Vigreux column, leaving 610 g (5.26 mol, 86% based on *tert*-butyl alcohol) of crude acid. This material could be used without further purification in the synthesis of 3,3-dimethylbutanal that follows. If further purification was required, the pressure was reduced, and 587 g (5.06 mol, 82%) of 3,3-dimethylbutyric acid was isolated by distillation: bp 91–92° (25 mm) (lit.[30] bp 80–82° (12 mm)); ir (neat) 3450–2400 (OH), 2960, 1705 (C=O), 1475, 1370, 1265 cm^{-1}; nmr (CCl_4) δ 12.1 (s, 1), 2.14 (s, 2), 1.0 (s, 9).

3,3-Dimethylbutanal was prepared following the procedure of Bedenbaugh.[31] A 5-l. three-necked flask was fitted with a mechanical stirrer, a Dry Ice condenser, and a No-Air stopper. The apparatus was flushed with nitrogen and immersed in a Dry Ice–2-propanol bath, and 3 l. of monomethylamine was condensed into it. Crude 3,3-dimethylbutyric acid (230 g, 1.98 mol) was degassed by bubbling a vigorous stream of nitrogen through it for 5 min; it was then transferred into the reaction vessel through the No-Air stopper by forced siphon through a stainless steel cannula. The No-Air stopper was replaced with a glass stopper and stirring was initiated, and the contents of the flask was allowed to warm to reflux temperature. Lithium wire (13.7 g, 1.98 g-atom) was added cautiously[66] in 1-g quantities over a period of 30 min. The resulting deep blue solution was allowed to stir at reflux for 1 hr, and an additional 27.4 g (3.96 g-atom) of lithium wire was cautiously added over a period of 1 hr. The solution was allowed to continue stirring at reflux for 14 hr during which time the blue color persisted. The glass stopper was replaced with a distillation head capped with a Dry Ice condenser and leading to a 3-l. flask immersed in a Dry Ice–2-propanol bath. The reaction flask was heated on a steam bath, and the majority of the monomethylamine was removed by distillation. The recovered amine may be stored at −20° and saved for another reduction or discarded. The distillation apparatus was replaced with a dropping funnel, and a water condenser was substituted for the Dry Ice condenser. Saturated aqueous ammonium chloride solution (1 l.) was added to the reaction mixture from the dropping funnel over 15 min. The white precipitate which formed was separated by filtration, and the filtrate was extracted with five 200-ml portions of ether. The ethereal extracts were washed repeatedly with 10% aqueous hydrochloric acid until the washings remained acidic and once with saturated aqueous sodium bicarbonate solution and dried ($MgSO_4$). Distillation through a 50-cm Vigreux column yielded 115 g (1.15 mol, 57%) of 3,3-dimethylbutanal: bp 102–104° (lit.[67] 102–103°); ir (neat) 2955, 2860, 2720, 1720 (C=O), 1470, 1365 cm^{-1}; nmr (CCl_4) δ 9.7 (t, 1), 2.06 (d, 2), 1.0 (s, 9).

***cis*- and *trans*-1-Acetoxy-3,3-dimethylbut-1-ene.** Following a procedure described by House,[32] a solution of 210 g (2.10 mol) of isopropenyl acetate and 1.30 g of *p*-toluenesulfonic acid was mixed with 104 g (1.03 mol) of 3,3-dimethylbutanal in a 500-ml three-necked flask equipped with a magnetic stirring bar, a glass stopper, and a No-Air stopper. The flask and contents were flushed with a stream of nitrogen, and the flask was attached to a 60-cm platinum spinning band distillation column that had previously been flushed with nitrogen. The reaction mixture was heated to 120° by immersion in an oil bath, and the mixture was stirred at total reflux under a nitrogen atmosphere. The acetone which is produced in this reaction caused the column head temperature to slowly decline, and when the temperature was 60°, material was allowed to distill over until the temperature climbed above 60°. This operation was repeated throughout the course of the reaction. The reaction was followed by glpc analysis of aliquots taken from the flask by a syringe needle inserted through the No-Air stopper. After 64 hr no unreacted aldehyde remained. The reaction mixture was cooled to room temperature and was taken up in 200 ml of pentane. The pentane solution was washed with three 100-ml portions of saturated aqueous sodium bicarbonate solution and once with 100 ml of water and dried ($MgSO_4$). A rapid distillation[68] of the crude product through a 60-cm Teflon annular spinning band distillation column yielded 111 g (0.81 mol, 78%) of a 2:3 mixture of *cis*- and *trans*-1-acetoxy-3,3-dimethylbut-1-ene, bp 125–160°. Careful distillation of this mixture using the Teflon spinning band column yielded 8.8 g of pure (>99% by glpc) *cis*-1-acetoxy-3,3-dimethylbut-1-ene, bp 145–146°; 36.7 g of pure (>99% by glpc) *trans*-1-acetoxy-3,3-dimethylbut-1-ene, bp 154.5°; and 26.8 g of a mixture of the isomers. *cis*-1-Acetoxy-3,3-dimethylbut-1-ene had: ir (neat) 2955, 2900, 2860, 1760 (C=O), 1660 (C=C), 1475, 1380, 1215 (C—O), 1055, 940, 880, and 730 cm^{-1}; nmr (CCl_4) δ 9.85 (d, 1, J = 7 Hz), 4.66 (d, 1, J = 7 Hz), 2.06 (s, 3), 1.06 (s, 9).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.77; H, 9.89.

trans-1-Acetoxy-3,3-dimethylbut-1-ene had: ir (neat) 3100, 2980, 2900, 2860, 1750 (C=O), 1668 (C=C), 1480, 1370, 1220 (C—O), 1085, 1030, 940, 890 cm^{-1}; nmr (CCl_4) δ 7.05 (d, 1, J = 13 Hz), 5.40 (d, 1, J = 13 Hz), 2.24 (s, 3), 1.06 (s, 9).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.33; H, 9.90.

***trans*-1-Acetoxy-3,3-dimethylbut-1-ene.** A 2-l. three-necked flask was equipped with a mechanical stirrer, a pressure-equalizing dropping funnel capped with a No-Air stopper, and a No-Air stopper. The flask was flushed with nitrogen, and a solution of 170 g (1.00 mol) of diphenylamine in 1 l. of dry, degassed ether was added to the flask by forced siphon through a stainless steel cannula. The flask and contents were cooled by immersion in a Dry Ice–acetone bath. A solution of 606 ml (1.00 mol) of 1.65 *N* methyllithium in

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[64] Boron trifluoride is a highly caustic material. All operations involving this material should be carried out in a well-ventilated hood while wearing appropriate protective clothing for the hands and arms.

[65] A pressure equalizing dropping funnel should not be used in this preparation, since the HCl gas produced in the reaction can diffuse along the side arm of the funnel and polymerize its contents.

[66] Large quantities of hydrogen gas are produced in an exothermic reaction during the addition. Too rapid addition of the lithium will result in uncontrollable effervescence.

[67] L. Schmerling, *J. Amer. Chem. Soc.*, **68**, 1650 (1946).

[68] The impure material has a tendency to polymerize during the slow spinning band distillation. A quick distillation prior to the slow one vastly improves the yield of enol acetate obtained.

ether, transferred by cannula into the dropping funnel, was added over a 45-min period to the rapidly stirred diphenylamine solution. Evolution of methane began immediately and continued for several minutes after the addition was complete. The resulting solution was a clear dark green. The dropping funnel was rinsed with 10 ml of dry, degassed ether and charged with 92.2 g (0.92 mol) of 3,3-dimethylbutanal. The aldehyde was slowly added with continued stirring to the cold solution of lithium diphenylamide; addition was complete in 30 min.[69] The mechanical stirrer and dropping funnel were replaced with No-Air stoppers, and the solution was set aside in a Dry Ice bath.

A 5-l. three-necked flask was equipped with a mechanical stirrer and two No-Air stoppers. Acetic anhydride (1 kg) was added to the flask, and the reaction vessel and contents were flushed with a stream of nitrogen introduced through one of the No-Air stoppers by use of a syringe needle. Stirring was begun, and the flask was cooled with an ice bath. The green enolate solution was added over 1.5 hr by forced siphon through a cannula inserted through the other No-Air stopper. The resulting solution turned cloudy white and thickened considerably. One of the No-Air stoppers was replaced with a dropping funnel, the other with a reflux condenser. The dropping funnel was charged with a solution of 350 g of sodium hydroxide in 500 ml of water, and this solution was added cautiously to the cooled reaction mixture; this hydrolysis is very exothermic. After the resulting solution had been allowed to stir for 0.5 hr, it was allowed to warm to room temperature and was extracted with four 200-ml portions of ether. The ether extracts were concentrated to a volume of 500 ml and washed with 10% aqueous sodium hydroxide solution until the washings remained basic. The extracts were then washed once with 100 ml of 5% aqueous hydrochloric acid solution, once with 100 ml of saturated aqueous sodium bicarbonate solution, once with 100 ml of brine and dried (MgSO$_4$). Distillation at reduced pressure through a 60-cm Vigreux column yielded 93.5 g (0.66 mol, 71% based on 3,3-dimethylbutanal) of a fraction with bp 60–62° (20 mm). Glpc and spectroscopic analysis showed the material to be >99% pure *trans*-1-acetoxy-3,3-dimethylbut-1-ene.

threo-**1-Acetoxy-3,3-dimethylbutane-*1,2*-d_2** (*threo*-**1**). A magnetic stirring bar was placed in a 200-ml glass aerosol reaction vessel (VWR or Fisher-Porter), fitted with appropriate pressure gauge and inlet valve system, and 40 ml of dry (molecular sieves) ethyl acetate and 200 mg[70] of Platinum Black catalyst were introduced. The vessel was stoppered with a No-Air stopper and cooled in an ice bath, and the contents was degassed by bubbling a vigorous stream of nitrogen through them for 5 min. The No-Air stopper was removed, and the reaction vessel was quickly attached to the rest of the pressure reaction apparatus which had itself been previously flushed with nitrogen. Rapid stirring was initiated, and the apparatus was pressurized to 50 psi with deuterium. After 30 min the apparatus was vented. Two further equilibrations of the catalyst with deuterium were carried out at 50 and 100 psi, respectively. Vinyl acetate (0.75 ml) was introduced through the No-Air stopper by use of a syringe, and the apparatus was pressurized to 100 psi. After 1.5 hr deuterium uptake stopped at $\Delta P = 18$ psi. The reaction vessel was cooled in an ice bath and vented, and 4 ml (3.62 g, 2.55 mmol) of *trans*-1-acetoxy-3,3-dimethylbut-1-ene was injected with a syringe. The apparatus was pressurized to 200 psi, and the pressure was maintained between 175 and 200 psi during the course of the reaction. After 2.75 hr deuterium uptake ceased at a total $\Delta P = 53$ psi (theoretical 54 psi.). The apparatus was vented, the glass reaction vessel was detached and flushed with nitrogen, and the contents was filtered. All of the filtrate having bp <100° was separated by distillation through a 20-cm stainless steel spinning band column, leaving crude *threo*-1-acetoxy-3,3-dimethylbutane-*1,2*-d_2. A 100-mg sample of this material, purified by glpc for spectroscopic analysis, had a glpc retention time indistinguishable from that of an authentic sample of 1-acetoxy-3,3-dimethylbutane prepared from 3,3-dimethylbutan-1-ol and acetyl chloride and had: ir (CHCl$_3$) 2950, 2180, 1740, 1465, 1365, 1240, 1045 cm^{-1}; deuterium-decoupled nmr (CHCl$_3$) δ 4.02 (d, 1, $J = 6.1$ Hz), 1.95 (s, 3), 1.50 (d, 1, $J = 6.1$ Hz), 0.93 (s, 9).

The crude acetate was hydrolyzed without further purification.

threo-**3,3-Dimethylbutan-1-ol-*1,2*-d_2.** To 3.75 g of crude *threo*-**1** was added 15 ml of 20% (w/w) sodium hydroxide in water solution, and the reaction mixture was allowed to stir at reflux overnight. Glpc analysis indicated that all the acetate had been hydrolyzed. The reaction mixture was extracted with five 5-ml portions of ether, and the ether extracts were washed twice with 5-ml portions of water and dried (MgSO$_4$). The ether was removed by distillation through a 10-cm Vigreux column, and the higher boiling material was distilled through a Minilab microdistillation apparatus, yielding 1.86 g (1.84 mmol, 68% based on *trans*-1-acetoxy-3,3-dimethylbut-1-ene) of *threo*-3,3-dimethylbutan-1-ol-*1,2*-d_2: bp 140–144° (lit.[22] bp 140–145°); ir (CHCl$_3$) 3600, 3440, 2950, 2150 (C–D), 1420, 1340, 1040, 1040, 940 cm^{-1}; deuterium-decoupled nmr (CHCl$_3$): δ 3.59 (d, 1, $J = 5.8$ Hz), 3.40 (s, 1), 1.46 (d, 1, $J = 5.8$ Hz), 0.92 (s, 9).

erythro-**1-Acetoxy-3,3-dimethylbutane-1,2-d_2.** *erythro*-**1** was prepared from *cis*-1-acetoxy-3,3-dimethylbut-1-ene following the method described above for *threo*-**1**. The product had the same retention time as an authentic sample of 1-acetoxy-3,3-dimethylbutane and had: deuterium-decoupled nmr (CHCl$_3$) δ 3.99 (d, 1, $J = 8.8$ Hz), 1.92 (s, 3), 1.49 (d, 1, $J = 8.8$ Hz), 0.93 (s, 9).

erythro-**3,3-Dimethylbutan-1-ol-1,2-d_2** was prepared by the hydrolysis of *erythro*-**1**, using the method described for the synthesis of *threo*-**2**. The product had the same glpc retention time as an authentic sample of 3,3-dimethylbutanol and had: deuterium-decoupled nmr (CHCl$_3$) δ 3.61 (d, 1, $J = 9.2$ Hz), 3.41 (s, 1), 1.44 (d, 1, $J = 9.2$ Hz), 0.93 (s, 9).

π-Cyclopentadienyldicarbonyliron *erythro*-**3,3-Dimethylbutyl-*1,2*-d_2 (3).** A. Using a literature procedure,[37] magnesium powder (40 mesh, 0.68 g, 28 mg-atoms), 2.84 g (8.0 mmol) of π-cyclopentadienyldicarbonyliron dimer, 0.69 ml (1.50 g, 8.0 mmol) of 1,2-dibromoethane, and 100 ml of dried, degassed THF were placed in a flame-dried 200-ml flask equipped with a magnetic stirring bar and a nitrogen inlet. This reaction mixture was allowed to stir at room temperature for 19 hr. A 40-ml centrifuge tube was equipped with a magnetic stirring bar and a No-Air stopper and was flame dried. Anhydrous ether (10 ml) and 1.58 g (15.2 mmol) of *erythro*-**1** were introduced throgh the stopper using a syringe, and the mixture was cooled and stirred in an ice bath. To this solution was added 7.0 ml (16.0 mmol) of a 2.28 *M* solution of *n*-butyllithium in hexane. A white precipitate formed during the slow addition of the lithium reagent. After the addition was complete, the reaction mixture was allowed to stir for 15 min, and 3.88 g (15.2 mmol) of *p*-bromobenzenesulfonyl chloride was cautiously added. The solution was allowed to warm to room temperature and to continue stirring for 1 hr. The solution was centrifuged and the supernatant liquid was removed and stored under nitrogen. The remaining white precipitate was washed three times with 10-ml portions of degassed ether, and the solutions of brosylate and washings were added by forced siphon through a stainless steel cannula to the previously prepared solution of iron anion. The resulting solution was allowed to stir under nitrogen at room temperature for 3 hr. The solvent was removed at room temperature at 0.1 mm of pressure, and the solid residue was extracted with five 25-ml portions of degassed pentane. The extracts were concentrated to a 10-ml volume and chromatographed under nitrogen on a 2 × 20-cm column of Merck acid-washed alumina, using degassed pentane as the eluent. One yellow band eluted; removal of the pentane at room temperature and 0.1 mm of pressure left 2.64 g (10.0 mmol, 66% based on *erythro*-**1**) of a yellow solid: mp 33–34°; ir (CHCl$_3$) 2950, 2005, 1955 cm^{-1}; deuterium-decoupled nmr (CHCl$_3$) δ 0.86 (s, 9), 1.40 (d, 1, $J = 13.1$ Hz), 1.26 (d, 1, $J = 13.1$ Hz), 4.68 (s, 5).

B. π-Cyclopentadienyldicarbonyliron dimer (1.42 g, 4.0 mmol) and 50 ml of dry, degassed THF were placed in a flame-dried 100-ml flask equipped with a magnetic stirring bar and a nitrogen inlet. Finely chopped lithium wire (0.18 g, 26 mg-atom) was added, and the reaction mixture was allowed to stir for 9 hr. A solution of 5.0 mmol of *threo*-3,3-dimethylbutan-1-ol-*1,2*-d_2 brosylate was added to the reaction mixture by forced siphon through a stainless steel cannula. The resulting mixture was allowed to stir for 3 hr. Work-up as before produced 0.91 g (3.4 mmol, 68%) of a yellow solid whose ir and nmr spectra were identical with those reported above.

erythro-**1-Bromo-3,3-dimethylbutene-*1,2*-d_2.** A 50-ml round-bottomed flask equipped with a magnetic stirring bar, a thermometer, and a No-Air stopper was flame dried, and 20 ml of dry (molecular

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[69] A variety of other bases including lithium and potassium triphenylmethides, lithium diisopropylamide, lithium dicyclohexylamide, and cyclopentadienyllithium were tried. All of these proved to be inferior to lithium diphenylamide, either because their use led to lower yields of trans enol acetate or because they led to a product mixture containing some cis enol acetate.

[70] The amount of catalyst required depends on its activity. Good results were obtained by using an amount of catalyst which effected complete hydrogenation in 2–3 hr.

sieves), degassed dimethylformamide, 5.61 g (21.4 mmol) of triphenylphosphine, and 2.08 g (20.0 mmol) of *threo*-**1** were introduced. The solution was cooled to −10°, and bromine (1.05 ml, 3.10 g, 20.0 mmol) was added in drops to this rapidly stirred solution. The bromine was added at a rate that kept the solution temperature between −10 and 5°. After the addition was complete, the mixture was allowed to warm to room temperature. The volatile contents was distilled at 30° and 0.02 Torr into a collector held at −78°. The distillate was transferred to a separatory funnel, ice–water (20 ml) was added, and the lower layer was separated and dried (MgSO$_4$). The yield of alkyl bromide was 1.46 g (40%): deuterium-decoupled nmr (CDCl$_3$) δ 0.92 (s, 9), 1.80 (1, 2 overlapping doublets, J = 12.5 Hz and J' = 5.3 Hz in a ratio of 90:10).

π-Cyclopentadienyldicarbonyliron *threo*-3,3-Dimethylbutyl-*1,2*-d_2. π-Cyclopentadienyldicarbonyliron dimer (0.71 g, 2.0 mmol), 25 ml of dry, degassed THF, and 5 ml of dry, degassed HMPA were placed in a flame-dried 50-ml flask equipped with a magnetic stirring bar and a nitrogen inlet. Lithium dispersion (50% in hexane, 0.070 g, 5.0 mg-atom) was added, and the reaction mixture was allowed to stir overnight. An approximately 90:10 mixture of *erythro*- and *threo*-1-bromo-3,3-dimethylbutane-*1,2*-d_2 (330 mg, 2.0 mmol) was added by syringe, and the resulting mixture was allowed to stir for 3 hr. Work-up as before produced 225 mg (0.86 mmol, 43%) of a yellow solid whose ir spectrum was indistinguishable from that reported above: deuterium-decoupled nmr (CHCl$_3$) δ 0.86 (s, 9), 1.44 (d, 1, J = 4.5 Hz), 1.31 (d, 1, J = 4.5 Hz). The lines were broad and small amounts (10%) of the erythro diastereomer probably would not have been detected.

1-Bromo-3,3-dimethylbutane-1,2-d_2 for Mass Spectral Analysis. A 25-ml round-bottomed flask equipped with a magnetic stirring bar and a No-Air stopper was flame dried, and 10-ml of dry (molecular sieves), degassed dimethylformamide, 1.28 g (4.9 mmol) of triphenylphosphine, and 0.50 g (4.9 mmol) of *erythro*-**1** were introduced. Bromine (0.27 ml, 0.88 g, 4.9 mmol) was added in drops to this rapidly stirred solution over 5 min. After the addition was complete, the mixture was allowed to stir for 30 min, and the contents was distilled bulb-to-bulb at 0.05 Torr into a collector held at −78°. Collection of product by glpc afforded a sample of 1-bromo-3,3-dimethylbutane-*1,2*-d_2 which showed isotopic composition (70 eV): 1.0% d_0, 3.9% d_1, 93.4% d_2, 1.7% d_3, and 0.0% d_4.

Reaction of 2 with Bromine. Bromine vapor (0.15 ml, 2.7 mmol) was swept with a stream of nitrogen through a rapidly stirred solution of 450 mg (1.7 mmol) of the alkyliron compound **2** in 0.5 ml of solvent (pentane, carbon disulfide, or dimethylformamide) under a nitrogen atmosphere at 0°. After 15 min all of the bromine had been bubbled through the reaction mixture, and the components of this mixture were distilled at room temperature (60° for the reaction mixture employing DMF) and 0.005 Torr into a trap cooled with a liquid nitrogen bath. Glpc analysis of the product mixtures indicated the presence of 1-bromo-3,3-dimethylbutane-*1,2*-d_2: deuterium-decoupled nmr (pentane) δ 3.26 (d, 1, J = 5.1 Hz) (other peaks were obscured by solvent peaks); in carbon disulfide δ 3.24 (d, 1, J = 5.1 Hz), 1.78 (d, 1, J = 5.1 Hz), 0.92 (s, 9); in dimethylformamide δ 1.78 (d, 1, J = 5.1 Hz), 0.91 (s, 9); the doublet at 3.24 was obscured by dimethylformamide absorptions.

Methyl *erythro*-4,4-Dimethylpentanoate-*2,3*-d_2. The bromination of **2** was carried out as described above, using anhydrous methanol as the solvent. Glpc analysis of the crude product mixture showed only a minor amount (∼5% of the major product) of the alkyl bromide **4**, the majority of the product being identified as methyl *erythro*-4,4-dimethylpentanoate-*2,3*-d_2: ir (CHCl$_3$) 2950, 1730, 1460, 1360, 1285, 1125 cm^{-1}; deuterium-decoupled nmr (CHCl$_3$) δ 3.53 (s, 2.26 (d, q, J = 11.0 Hz), 1.50 (d, 1, J = 11.0 Hz), 0.82 (s, 9).

Oxidation of 2 in Methanol Solution. A. Using O$_2$. A 5-ml flask was equipped with a magnetic stirring bar, a syringe needle functioning as an oxygen inlet, 290 mg (1.1 mmol) of **2**, and 1.5 ml of anhydrous methanol. A slow stream of oxygen was bubbled through the stirred solution for an hour, during which time a yellow-brown precipitate was produced. All volatile material was distilled at 0.05 Torr and 35° into a trap cooled by liquid nitrogen: deuterium-decoupled nmr δ 3.63 (s, 3), 2.26 (d, 1, J = 11.1 Hz), 1.49 (d, 1, J = 11.1 Hz), 0.89 (s, 9).

B. Using Ceric Ammonium Nitrate. A solution/slurry of 1.10 g (2.0 mmol) of ceric ammonium nitrate in 0.75 ml of degassed anhydrous methanol was stirred at room temperature, and 540 mg (2.0 mmol) of **2** was added as a solid. The solution turned brownish black. After 30 min of continued stirring all volatile material was distilled at 0.05 mm of pressure and room temperature into a trap cooled with liquid nitrogen. The deuterium-decoupled nmr was indistinguishable from the reported in part A above.

Reaction of 2 with Iodine. A solution of 134 mg (0.5 mmol) of iodine in 0.5 ml of carbon disulfide was stirred under a nitrogen atmosphere at room temperature. A solution of 134 mg (0.5 mmol) of **2** in 0.25 ml of degassed carbon disulfide was added in drops to the stirred iodine solution over a period of 5 min. The reaction vessel was immersed in a water bath held at 20–25° during the addition. The black product mixture was allowed to stir for 15 min, and all volatile material was separated by distillation at 25° (0.002 Torr) into a trap cooled in a liquid nitrogen bath. Glpc *analysis of the crude product mixture indicated a major product* with the same retention time as an authentic sample of neohexyl iodide: deuterium-decoupled nmr (CS$_2$) δ 3.06 (d, 1, J = 4.7 Hz), 1.84 (d, 1, J = 4.7 Hz), 0.90 Hz), 0.90 (s, 9).

Reaction of 2 with Chlorine. A 25-ml round-bottomed flask was flushed with chlorine gas, and the chlorine (25 ml, 1.1 mmol) was then condensed into a liquid nitrogen cooled trap on a vacuum line. The chlorine was allowed to bulb-to-bulb distill into a 5-ml flask held at −195° and containing 0.5 ml of dry (Molecular Sieves), degassed CHCl$_3$ and a magnetic stirring bar. The flask was stoppered with a No-Air stopper and transferred to a bath held at −20°. To this rapidly stirred chlorine solution was added in drops over a 2 min period a solution of 100 mg (0.38 mmol) of **2** in 0.20 ml of dry, degassed CHCl$_3$. The reaction mixture immediately turned brown. The reaction mixture was allowed to warm to room temperature, and all volatile material was distilled at 25° (0.005 mm). Glpc analysis of the crude product mixture indicated one major product, *erythro*-4,4-dimethylpentanoyl-2,3-d_2-chloride, identified on the basis of its ir and nmr spectra:[22] ir (CHCl$_3$) 2930, 1790, 1510, 1360, 1280, 955 cm^{-1}; deuterium-decoupled nmr δ 0.94 (s, 9), 1.62 (d, 1, J = 11.0 Hz), 2.78 (d, 1, J = 11.0 Hz).

π-Cyclopentadienyl(triphenylphosphine)carbonyliron *threo*-4,4-Dimethylpentanoyl-*2,3*-d_2. *threo*-**2**, 0.25 g (9.3 mmol), was dissolved in 2 ml of THF and added to 0.52 g (20 mmol) of triphenylphosphine in a 25-ml flask equipped with a water-cooled reflux condenser and a magnetic stirring bar. The mixture was heated to 65° for 19 hr. An ir spectrum of an aliquot of the reaction mixture indicated carbonyl stretching at 1920 and 1615 cm^{-1}. The solvent was removed under reduced pressure and the red-orange residue was dissolved in 2 ml of chloroform and chromatographed on a 2 × 20 cm column of Activity III neutral alumina (Woelm). Two yellow bands separated. The first was collected with 50 ml of cyclopentane eluent and had an ir spectrum with carbonyl stretching at 2005 and 1955 cm^{-1}. The second yellow fraction collected with 1:1 ether; cyclopentane had carbonyl stretching at 1920 and 1615 cm^{-1}. Evaporation of the solvent from the second fraction gave 0.32 g (62%) of iron acyl having mp 143° dec. Spectral data: ir (HCCl$_3$) 3050, 2950, 1920, 1615, 1475, 1450, 1360, 1090 cm^{-1}; deuterium-decoupled nmr (DCCl$_3$) δ 0.72 (9 H, s), 0.85 (0.5 H, d, J = 4.4 Hz), 1.18 (0.5 H, d, J = 4.4 Hz), 2.46 (0.5 H, d, J = 4.4 Hz), 2.72 (0.5 H, d, J = 4.4 Hz), 4.40 (5 H, d, J = 1.0 Hz), 7.33 (15 H, m).

The nmr spectrum of the nondeuterated analog prepared in the same manner consisted of an ABXY pattern for the CHDCHD protons characterized by the following chemical shifts and coupling constants: ν_A = 0.85 ppm, ν_B = 1.18 ppm, ν_X = 2.57 ppm, ν_Y = 2.80 ppm, J_{AB} = ± 13.6 Hz, J_{XY} = ±15.7 Hz, J_{AX} = J_{BY} = ∓4.2 Hz. J_{AY} = J_{BX} = ∓12.5 Hz.

Anal. Calcd for C$_{31}$H$_{33}$O$_2$FeP: C, 71.00; H, 6.34. Found: C, 70.55; H, 6.43.

π-Cyclopentadienyl(triphenylphosphine)carbonyliron *threo*-3,3-Dimethylbutyl-*1,2*-d_2. A solution of 100 mg of the mixture of π-cyclopentadienyl(triphenylphosphine)carbonyliron *threo*-4,4-dimethylpentanoyl-*2,3*-d_2 diasteriomers in 15 ml of benzene was prepared under nitrogen and transferred by cannula into a quartz tube equipped with a water-cooled cold finger, a magnetic stirring bar, and a serum stopper. The reaction mixture was irradiated for 2 hr in a Rayonet Photochemical Reactor using 4 No. RPR 3000-Å and 12 No. RPR 3500-Å lamps. The benzene was removed under vacuum and the residue chromatographed under nitrogen on a 2.0 × 25-cm column of neutral alumina packed in pentane. Elution with benzene gave one orange band with ν(CHCl$_3$) = 1900 cm^{-1}. Removal of solvent afforded *ca.* 40 mg (42%) of orange, semisolid product, having ir (CHCl$_3$) 3040, 2910, 1910, 1480, 1440, 1360, 1090, 995, and 815 cm^{-1}; deuterium-decoupled nmr (benzene) for the CHDCHD moiety, two equally intense ABX spectra with ν_A = 1.01, ν_B = 1.43, J_{AB} = 4.4 Hz, J_{BX} = 0.7 Hz, J_{AX} = 0 Hz; $\nu_{A'}$ = 1.19, $\nu_{B'}$ = 1.30, $J_{A'B'}$ = 4.4 Hz, $J_{B'X'}$ = 2.0 Hz, $J_{A'X'}$ = 0 Hz.

The experimental spectrum, and the theoretical spectrum generated using these parameters, are reproduced in Figure 6.

π-Cyclopentadienyl(*tert*-butyl isocyanide)carbonyliron *threo*-4,4-Dimethylpentanoyl-*1,2*-d_2. A solution of 0.23 g (0.87 mmol) of the alkyliron compound **2** and 0.28 g (3.5 mmol) of *tert*-butyl isocyanide[71] in 10 ml of dry, degassed tetrahydrofuran was stirred at reflux under nitrogen for 16 hr. Most of the solvent was removed at room temperature and 0.05 Torr. The concentrated crude reaction mixture was chromatographed on a 2 × 20-cm column of Merck acid-washed alumina using ether as eluent. Only one mobile yellow band appeared on the column under these conditions. The yellow band was collected under nitrogen, the solvent was removed, and 250 mg (0.72 mmol, 83%) of yellow crystals were collected: mp 63–66°; ir (CCl_4) 2950, 2150, 1940, and 1630 cm^{-1}; deuterium-decoupled nmr ($CHCl_3$) δ 0.73 (s, 9), 1.24 (d, 1, J = 11.9 Hz), 1.34 (s, 9), 2.64 (d, 1, J = 11.9 Hz), 4.48 (s, 5).

A sample of **9**-d_0 prepared in a manner analogous to the above preparation yielded yellow crystals giving elemental analysis below.

Anal. Calcd for $C_{18}H_{27}O_2FeN$: C, 62.63; H, 7.89; N, 4.06. Found: C, 63.12; H, 7.78; N, 4.13.

Reactions of 2 with Sulfur Dioxide. In Neat SO_2. A solution of 180 mg (0.68 mmol) of the alkyliron compound **3** in 50 ml of liquid sulfur dioxide was stirred under nitrogen at reflux for 16 hr. The SO_2 was allowed to evaporate, and the resulting orange residue was chromatographed twice under nitrogen on a 2 × 20 cm column of Merck acid-washed alumina, using degassed ether as eluent.

In Other Solvents. Reactions were carried out in an 85-ml glass aerosol vessel. This vessel was equipped with a magnetic stirring bar and was flushed with nitrogen. The solvent (5 ml), dried and degassed, was introduced along with a weighted quantity of **2** (200 mg, 0.76 mmol) and the reaction vessel capped. Rapid stirring was initiated, and the apparatus was pressurized twice with 42 psi of SO_2, vented twice, and pressurized to 42 psi. After 8 hr the apparatus was vented. The reaction mixture was transferred to a 10-ml round-bottomed flask, the solvent was removed at room temperature and 0.05 mm of pressure, and the orange residue was chromatographed twice under nitrogen, using ether as eluent.

All reactions with sulfur dioxide led to yellow crystalline solids which were stable indefinitely at −20° and which were identified as π-cyclopentadienyldicarbonyliron *threo*-3,3-dimethyl-*1,2*-d_2-sulfinates on the basis of ir and nmr spectra: mp 174° dec (lit.[21] 175°); ir ($CHCL_3$) 2955, 2005, 1190, 1180, 1045 cm^{-1}; deuterium-decoupled nmr ($CHCl_3$) δ 0.86 (s, 9), 1.66 (d, 1, J = 4.3 Hz), 2.95 (d, 1, J = 4.3 Hz). Yields in the various solvents were 45% (SO_2), 54% (pentane), 83% ($CHCl_3$), 62% (CH_3OH), and 94% (DMF).

Reaction of 2 with Dimethyl Acetylenedicarboxylate. Dry, degassed tetrahydrofuran (5 ml) and 0.70 g (4.9 mmol) of dimethyl acetylenedicarboxylate were placed in a flame-dried 10-ml flask equipped with a magnetic stirring bar, a No-Air, stopper, and a nitrogen inlet. The flask and contents were degassed by bubbling a stream of nitrogen through the flask and contents. Alkyliron compound *threo*-**2** (264 mg, 1.0 mmol) was introduced, and degassing was continued for 10 min. The nitrogen inlet was removed, the flask was stoppered, and the flask was heated at 50–60° with stirring for 24 hr. All volatile material was distilled at 60° and 0.05 Torr into a trap cooled with a liquid nitrogen bath. The residue was extracted with 5 ml of degassed reagent grade chloroform, and the extracts were chromatographed under nitrogen on a 2 × 20-cm column of Merck acid-washed alumina using degassed pentane to elute unreacted **3** followed by degassed acetone to elute the greenish band of product. The acetone was evaporated from the crude product, leaving 244 mg (0.60 mmol, 60%) of a dark brown viscous oil. This material was rechromatographed using acetone as eluent, and the product was assigned structure **5** on the basis of its ir and nmr spectrum: ir ($CHCl_3$) 2960, 2870, 1995, 1970, 1700, 1630, 1525, 1430, 1360, 1180; deuterium-decoupled nmr ($CDCl_3$) δ 4.64 (s, 5), 3.87 (s, 3), 3.71 (s, 3), 2.83 (d, 1, J = 10.5 + 0.5 Hz), 1.32 (d, 1, J = 10.5 + 0.5 Hz), 0.83 (s, 9). An analogous procedure was used to convert *erythro*-**2** to product having J = 4.9 Hz.

A sample of **5**-d_0 prepared in an analogous manner yielded a dark brown oil whose AA′XX′ spectrum yields vicinal coupling constants J = 12.0 Hz, J' = 4.9 Hz.

Anal. Calcd for $C_{19}H_{24}O_6Fe$: C, 56.45; H, 5.98. Found: C, 56.21; H, 6.21.

Thermal Decomposition of 2. A 12/5 spherical joint was sealed at the jointless end and 530 mg (2.0 mmol) of **2**-d_0 was introduced. The tube and contents were attached to a vacuum line and degassed by twice evacuating and refilling with nitrogen. Cyclohexane, 0.5 ml, dried over molecular sieves and degassed in a stream of nitrogen, was added to the tube, and the tube and contents were degassed by four freeze–thaw cycles. The reaction tube was sealed and heated at 150° for 24 hr during which time the contents turned dark brown and became quite viscous. The contents of the tube were distilled at 0.02 mm of pressure and 100° into a trap cooled by a liquid nitrogen bath. 1-Hexene was added as an internal standard, and the crude reaction mixture was analyzed by glpc. Four major products, two having low boiling points and two having high boiling points, were produced in the approximate ratio of 1 : 1 : 2 : 1. The two low boiling substances were identified by coinjection of authenic samples as 3,3-dimethylbutene and 3,3-dimethylbutane, and they were produced in 11 and 15% yields, respectively.

The experiment was repeated using labeled *erythro*-**2**. The 3,3-dimethylbutene was collected by glpc and analyzed by deuterium-decoupled nmr. The resulting spectrum is shown in Figure 6.

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(71) *tert*-Butyl isocyanide was prepared following a literature method: I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).