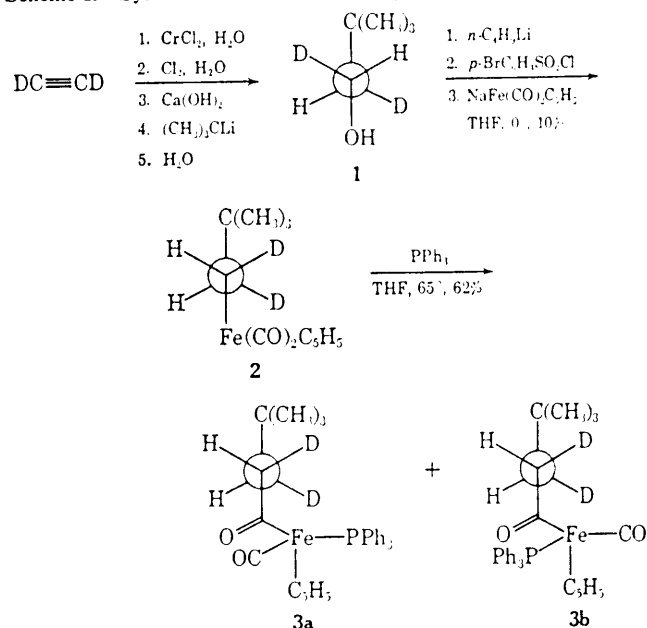


Reaction of *threo*-(CH₃)₃CCHDCHDFe(CO)₂-π-C₃H₅ with Triphenylphosphine¹

Sir:

The present understanding of the mechanism of the hydroformylation and related carbonylation reactions is based in part on studies of stereochemistry around the metal atom during the steps in which the initially formed alkylmetallic intermediates are converted to acylmetallic compounds.² Information concerning the stereochemistry at carbon during typical carbonylation reactions is clearly required for a complete description of the mechanisms of these reactions, but has not been reported.³ We wish to describe the synthesis of π-cyclopentadienyl-dicarbonyliron *threo*-3,3-dimethylbutyl-1,2-d₂ (2) and evidence establishing that its reaction with triphenylphosphine to yield π-cyclopentadienylcarbonyltriphenylphosphineiron *threo*-4,4-dimethylpentanoyl-2,3-d₂ (3) proceeds with retention of configuration at carbon.

Scheme I. Synthesis of Deuterated Organoiron Compounds^a



^a Only one enantiomer is shown for each compound.

The synthesis outlined in Scheme I was used to convert acetylene-d₂ to 3,3-dimethylbutan-1-ol-1,2-d₂ (1).⁴ The deuterium-decoupled 100-MHz nmr spectrum of the CHDCHD protons of 1 is an AX pattern with δ_A

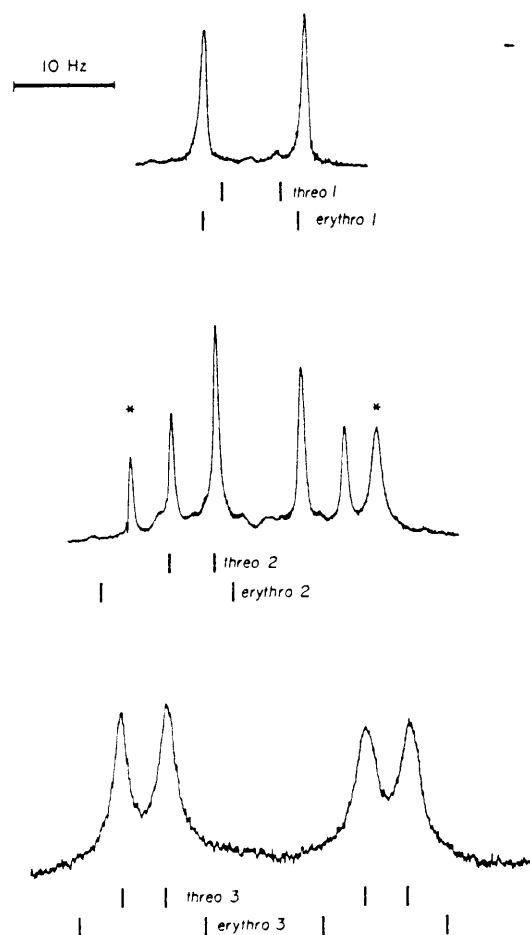


Figure 1. Deuterium-decoupled 100-MHz nmr spectra of the -CHDOH proton of 1, the -CHDCHD- protons of 2, and the -CHDCO- protons of 3. The peaks marked with an asterisk in the spectrum of 2 are due to impurities. For comparison the positions of the lines characterizing the *threo* and *erythro* diastereomers of 1, 2, and 3 are given below the traces; these frequencies were calculated on the basis of coupling constants obtained by analysis of the spectra of the nondeuterated analogs of these compounds.

3.38, δ_X 1.23, and $J = 10.0$ Hz (Figure 1). The nmr spectra of *erythro* and *threo* diastereomers of 1 are easily distinguishable on the basis of their characteristic vicinal coupling constants: $J_{\text{erythro}} = 9.5$ and $J_{\text{threo}} = 5.8$ Hz.⁵ The magnitude of the coupling constant observed in the nmr spectrum of 1 confirms the *erythro* configuration expected from the method of synthesis; the absence of observable peaks in this spectrum attributable to the *threo* diastereomer indicates that the *erythro* diastereomer must constitute >95% of the 3,3-dimethylbutan-1-ol-d₂ produced.

(4) This synthesis is based on the preparation of *trans*-1,2-dideuterioethylene oxide reported by C. C. Price and R. Spector, *J. Amer. Chem. Soc.*, **88**, 4171 (1966).

(5) G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *ibid.*, **89**, 1135 (1967). The coupling constants J_{erythro} and J_{threo} are identical with the vicinal coupling constants J and J' obtained on analysis of the AA'XX' spectrum of 3,3-dimethylbutan-1-ol-d₂. The small difference between the magnitude of the observed coupling constant for 1 and J_{erythro} obtained from the AA'XX' analysis probably reflects a solvent effect on the free-energy difference between the *gauche* and *trans* conformers of this alcohol.

(1) Supported in part by the National Science Foundation, Grant GP-7266.

(2) (a) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967); (b) R. F. Heck, *Advan. Organometal. Chem.*, **4**, 243 (1966); (c) R. F. Heck, *Accounts Chem. Res.*, **2**, 10 (1969); (d) K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, **7**, 345 (1968); (e) P. K. Maples and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **90**, 6645 (1968), and references in each. The recent demonstration that conversion of pentacarbonylmanganese methyl to pentacarbonylmanganese acetyl takes place by migration of the methyl group from manganese to an adjacent carbon monoxide ligand rather than by insertion of carbon monoxide into the carbon-manganese bond is of particular pertinence to discussions of the mechanism of carbonylation.^{2a}

(3) The decarbonylation of optically active PhCH₂CH(CH₃)COMn(CO)₅ occurs with retention of the sign of rotation: F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966).

Compound **1** was converted to *erythro*-3,3-dimethylbutyl-1,2-*d*₂-*p*-bromobenzenesulfonate ($J = 8.6$ Hz), and thence to **2** by reaction with $\text{Na}[\text{Fe}(\text{CO})_2\text{C}_3\text{H}_5]$. The nmr spectrum of the *CHDC**HD* region of **2** consisted of a *single* AB quartet centered at δ 1.38, with $\Delta\nu = 0.122$ ppm and $J = 4.4$ Hz (Figure 1); the infrared spectrum of **2** in the carbonyl stretching region consisted of bands at 2005 and 1955 cm^{-1} . An independent analysis of the nmr spectrum of 2-*d*₆ established that the *threo* and *erythro* diastereomers of **2** are characterized by vicinal coupling constants $J_{\text{erythro}} = 13.1$ and $J_{\text{threo}} = 4.5$ Hz. Thus, transformation of **1** to **2** takes place with *inversion* of configuration.⁶ Within the limits of detection of our experiment, no (<5%) *erythro* diastereomer is produced in this reaction.

It is worthwhile pointing out that this stereochemical result is of considerable interest in its own right. It provides the first direct evidence that nucleophilic displacement on an alkyl carbon atom by a metalate anion proceeds with inversion of configuration at carbon.⁷ Further, the observation that no detectable loss in stereochemistry was observed in **2** on standing for >12 hr at 30° provides an indication of the configurational stability to be expected for this class of carbon-transition metal σ bonds.

Reaction of **2** with triphenylphosphine in THF followed by unexceptional work-up gave **3** as a yellow solid, mp 143° dec. The deuterium-decoupled nmr spectrum of the compound consists of two, equally intense, AX patterns arising from the two pairs of diastereomers represented by **3a** and **3b**.⁸ The -*CHD*-CO- resonances of **3** occurred at δ 2.72 and 2.46; both patterns were characterized by the same vicinal coupling

constant, $J = 4.4$ Hz (Figure 1). The infrared spectrum of **3** in the carbonyl stretching region consisted of bands at 1925 and 1615 cm^{-1} . *Anal.* Calcd for $\text{C}_{31}\text{H}_{33}\text{O}_2\text{-FeP}$: C, 71.00; H, 6.34. Found: C, 70.55; H, 6.43. Comparison of the observed coupling constant with those estimated for the *threo* ($J = 4.2$ Hz) and *erythro* ($J = 12.5$ Hz) diastereomers of **3** from analysis of the ABXY spectrum of 3-*d*₆ establishes that conversion of the alkyl-iron bond of **2** to the corresponding carbon-carbon bond of **3** has taken place with complete (>95%) *retention* of configuration.

Related studies of the stereochemistry of other reactions occurring at carbon-transition metal σ bonds will be reported later.

Acknowledgment. We gratefully acknowledge the experimental assistance of Dr. J. Fleming and Mr. J. Simms.

(6) A similar technique has been used to determine the stereochemistry of solvolysis of 2-phenylethyl tosylate: R. J. Jablonski and E. I. Snyder, *Tetrahedron Letters*, 1103 (1968); see also R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968).

(7) For recent discussions of the nucleophilic reactivity of metal atoms toward saturated carbon, see R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, **88**, 5121 (1966); J. P. Birk, J. Halpern, and A. L. Pickard, *ibid.*, **90**, 4491 (1968); J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

(8) A related proton diastereotopism due to chirality at iron has been observed for $\text{C}_6\text{H}_5\text{CH}_2\text{Fe}(\text{CO})(\text{PPh}_3)(\text{C}_6\text{H}_5)$: J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **91**, 1550 (1969).

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