(4) Hoard, J. L.; Hamor, M. J.; Hamor, T. A.; Caughey, W. S. *J. Am. Chem. Soc.* **1965**, *87*, 2312–2319.
(5) Reed, C. A. "Metal Ions in Biological Systems", Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 7.
(6) Mashiko, T.; Kastner, M. E.; Spartalian, K.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 6354–6362.
(7) Scheidt, W. R.; Cohen, I. A.; Kastner, M. E. *Biochemistry*, in press.
(8) Gans, P.; Buisson, G.; Due, E.; Regnard, J-R.; Marchon, J-C. *J. Chem. Soc., Chem. Commun.* **1979**, 393–395.
(9) Jameson, G. B.; Robinson, W. T.; Collman, J. P.; Sorrell, T. N. *Inorg. Chem.* **1978**, *17*, 858–864.
(10) Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 6769–6770.
(11) Collman, J. P.; Reed, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 2048–2049.
(12) Brault, D.; Rougee, M. *Biochemistry* **1974**, *13*, 4591–4597.
(13) Abbreviations used in this paper: TPP for dianion of *meso*-tetraphenylporphyrin; THF for tetrahydrofuran; Pip for piperidine; 1-MeIm for 1-methylimidazole; THT for tetrahydrothiophene; 2-MeIm for 2-methylimidazole; TMSO for tetramethylene sulfoxide.
(14) Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676–2681.
(15) Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 84–89.
(16) Radonovich, L. J.; Bloom, A.; Hoard, L. J. *J. Am. Chem. Soc.* **1972**, *94*, 2073–2078.
(17) Programs used in this study included local modifications of Jacobson's ALFF, Park's REFINE, Busing and Levy's ORFFE, and Johnson's ORTEP2.
(18) Atomic form factors were from Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321–323, with real and imaginary corrections for anomalous dispersion in the form factor of the iron atom from Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898. Scattering factors for hydrogen were from Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *Ibid.* **1965**, *42*, 3175–3187.
(19) The assignment[20] of an intermediate spin state to $Fe(TPP)(THF)_2$ is in error, probably owing to aerobic decomposition.
(20) Kobayashi, H.; Yanagawa, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 450–456.
(21) Kent, T. A.; Spartalian, K.; Lang, G.; Yonetani, T.; Reed, C. A.; Collman, J. P. *Biochim. Biophys. Acta*, in press.
(22) Johnson, C. E. *Proc. Phys. Soc., London* **1967**, *92*, 748–757.
(23) Steffen, W. L.; Chun, H. K.; Hoard, J. L.; Reed, C. A. "Abstracts of Papers", 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 13–17, 1978; American Chemical Society: Washington, D.C., 1978; INORG 15.
(24) Mashiko, T.; Marchon, J-C.; Musser, D. T.; Reed, C. A.; Kastner, M. E.; Scheidt, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 3653–3655.
(25) Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339–345.
(26) Buckingham, D. A.; Collman, J. P.; Hoard, J. L.; Lang, G.; Radonovich, L. J.; Reed, C. A.; Robinson, W. T., to be published.
(27) Hoard, J. L. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 18–31. Collins, D.M.; Scheidt, W. R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 6689–6696.
(28) Fons, M.; Haller, K.; Reed, C. A.; Scheidt, W. R., work in progress.
(29) Geise, H. J.; Adams, W. J.; Bartell, L. S. *Tetrahedron* **1969**, *25*, 3045–3052. Engerholm, G. G.; Luntz, A. C.; Gwinn, W. D.; Harris, D. O. *J. Chem. Phys.* **1969**, *50*, 2466–2457. Greenhouse, J. A.; Strauss, H. L. *Ibid.* **1969**, *50*, 124–134. Lafferty, W. J.; Robinson, D. W.; St. Louis, R. V.; Russell, J. W.; Strauss, H. L. *Ibid.* **1965**, *42*, 2915–2919.
(30) Brauer, D. J.; Kruger, C. *Inorg. Chem.* **1975**, *14*, 3053–3056. Hodgson, K. O.; Raymond, K. N. *Ibid.* **1972**, *11*, 171–175. Brauer, D. J.; Stucky, G. D. *J. Organomet. Chem.* **1972**, *37*, 217–232. Brauer, D. J.; Kruger, C. *Ibid.* **1972**, *42*, 129–137. Atwood, J. L.; Smith, K. D. *J. Chem. Soc., Dalton Trans.* **1974**, 921–923. Daly, J. J.; Sneeden, R. P. A. *J. Chem. Soc. A* **1967**, 736–740.
(31) Dolphin, D.; Sams, J. R.; Tsin, T. B.; Wong, K. L. *J. Am. Chem. Soc.* **1976**, *98*, 6970–6975.
(32) Spiro, T. G.; Stong, J. D.; Stein, P. *J. Am. Chem. Soc.* **1979**, *101*, 2648–2655.

Isotopic Perturbation of Degeneracy. A New Technique for Distinguishing Monohapto and Pentahapto Cyclopentadienyl Rings in Fluxional Systems with Low Rearrangement Barriers

J. W. Faller,* H. H. Murray, and M. Saunders*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received October 11, 1979*

Abstract: A new technique which enables one to distinguish between unsymmetrically bonded, rapidly exchanging systems and symmetrically bound ones is applied here to an organometallic system. The degenerate equilibrium for rearrangement in the $(\eta^1\text{-}C_5H_5)Sn(CH_3)_3$ complex is perturbed by deuterium incorporation. Chemical-shift differences observed in the ^{13}C spectra between the perprotio species and the monodeuterio species are temperature dependent. The ^{13}C NMR of 1,1′-bisdeuterioferrocene, in contrast, is not found to be temperature independent, as expected for a system with no degenerate equilibrium to be perturbed.

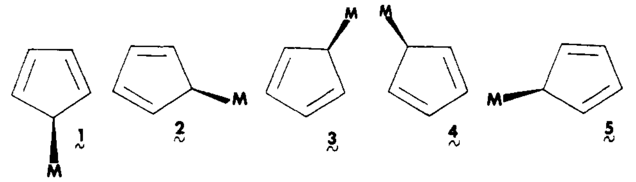
The perturbation of rapid, degenerate equilibria by isotopic substitution can be readily detected by ^{13}C NMR spectroscopy owing to the large chemical-shift splittings in the isotopic molecules of peaks which are averaged to single lines in the unlabeled systems by rapid interconversions.[1] As might be expected, symmetric nonequilibrium systems are perturbed very much less by isotopes.[2] The investigation of isotope effects on ^{13}C spectra arising from deuterium incorporation thus provides a valuable new method for distinguishing symmetrical from unsymmetrical bonding patterns.[3] We will demonstrate here that this is a straightforward technique for distinguishing a fluxional $\eta^1\text{-}C_5H_5$ ring from a $\eta^5\text{-}C_5H_5$ ring.

Rapid migration of the metal around the ring in many η^1-cyclopentadienyl complexes results in averaging in the NMR spectrum of both the ring protons and the ring carbons to a single sharp resonance at room temperature.[4,5] Thus, the observation of a single carbon peak for a cyclopentadienyl group cannot be considered prima facie evidence for a η^5-cyclopentadienyl ring. Lowering the temperature in a monohapto system sometimes produces a spectrum which shows broadening and eventual resolution into the AA′BB′X pattern in the ^1H NMR spectrum or a three-line pattern in the proton-decoupled carbon spectrum characteristic of a η^1 ring. If, however, the barrier is sufficiently low so as to prevent the observation of line broadening at accessible temperatures, this method fails. In some of these cases where NMR spectroscopy has not been able to make a distinction between η^1- and η^5-bonded rings, infrared spectroscopy[6] and crystallography *have* been able to clarify the issue.

In order to illustrate this new technique for making a distinction between η^1- and η^5-cyclopentadienyl rings by ^{13}C NMR spectroscopy, we will consider the effect of an isotopic perturbation of the rearrangement of a monohaptocyclopentadienyl metal complex. In the MC_5H_5 system, the metal could be attached to each of the five positions on the ring with equal probability. Thus the equilibrium constant (K) for attachment

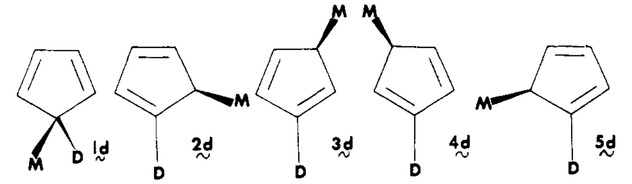
0002-7863/80/1502-2306$01.00/0

to carbon 2 vs. carbon 1 would be one. Thus, we could define K for each of these systems as follows:



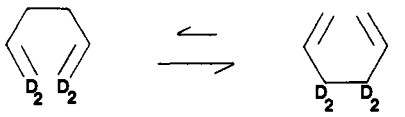
$$K_{(C_5H_5)} = [\mathbf{2}]/[\mathbf{1}] = [\mathbf{3}]/[\mathbf{1}] = [\mathbf{4}]/[\mathbf{1}] = [\mathbf{5}]/[\mathbf{1}] = 1.0 \quad (1)$$

When a deuterium atom is substituted for one of the ring hydrogens, these equilibrium constants are no longer unity. Since the deuterium isotope effect is due to changes in zero-point energy, we will simplify the problem by assuming that the stretching and bending force constants for the olefinic protons are equal but differ significantly from the proton on the carbon to which the metal is attached. With this simplifying assumption, one would expect the equilibrium constant to be the same for each deuterated olefin.



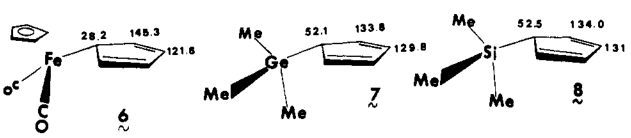
$$K_{(C_5H_4D)} = [\mathbf{2d}]/[\mathbf{1d}] = [\mathbf{3d}]/[\mathbf{1d}] = [\mathbf{4d}]/[\mathbf{1d}] = [\mathbf{5d}]/[\mathbf{1d}] \neq 1.0 \quad (2)$$

A similar structural difference is the origin of an equilibrium isotope effect on the Cope rearrangement in deuterated biallyl.[8] In this case, the equilibrium isotope effect (due to four H-D pairs) is 1.41 for the reaction.



We wish to examine the effect of deuteration on the ^{13}C NMR spectrum. Even in a symmetric, *nonfluxional* system one would expect the introduction of *deuterium* to shift the resonance of the deuterated carbon upfield relative to the protio compound about 0.2-0.4 ppm.[2] For example, each deuterium introduced into the methyl group of toluene produces an upfield shift of 0.21 ppm/D atom.[9] The shift of the directly substituted carbon is termed the *α intrinsic isotope shift.* Smaller shifts are observed on nearby carbons; there is a β intrinsic shift for the carbon adjacent to the D-substituted carbon atom and a γ shift for the next, etc. All of these intrinsic shifts have been found to be smaller than 0.5 ppm and can be predicted fairly accurately from consideration of model compounds.

Much larger effects are produced by the perturbation of equilibria by isotopes. The isotopically induced ^{13}C splittings in carbonium ions which are due to *isotopic perturbation of equilibrium* are as large as 100 ppm.[1] These large effects are due to a combination of large chemical-shift differences between the carbons interchanged by the reaction and a significant isotope effect. The analogous shifts in organometallic systems can be predicted by considering the unperturbed shifts in limiting low-temperature spectra of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$,[10] $(\eta^1\text{-}C_5H_5)Si(CH_3)$,[11] and $(\eta^1\text{-}C_5H_5)Ge(CH_3)_3$.[12] These were assigned for the protio compound as follows.



As the temperature is raised and site exchange becomes rapid, the lines would broaden and finally average to produce a single resonance at the position determined by the population weighted average of all the original lines. Thus the averaged resonance position would be expected as follows, if one assumes that the resonance of the metal-substituted carbon would occur at 30 ppm and the olefinic carbon would appear at 130 ppm.[13]

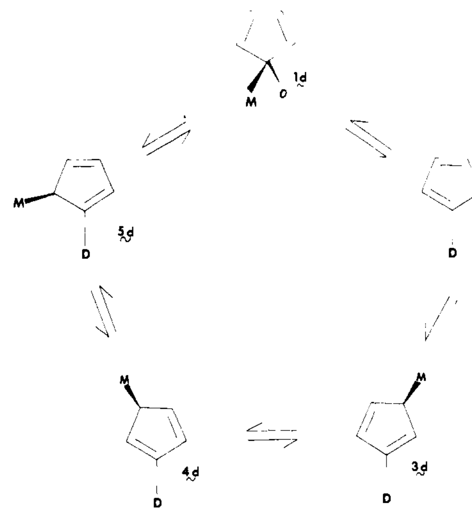
$$((1 \times 30) + (1 \times 130) + (1 \times 130) + (1 \times 130) + (1 \times 130))/5 = 110 = \delta_H \quad (3)$$

In the case of the monodeuterio compound the relative populations in each site would no longer be the same and the average for the deuterated carbon would be as follows:

$$((1 \times 30) + (K \times 130) + (K \times 130) + (K \times 130) + (K \times 130))/(1 + 4K) = \delta_D \quad (4)$$

If the isotope effect were about 1.1, a typical value for a deuterium isotope effect, the shifts would differ by approximately 2 ppm. It is convenient to define the quantity δ_E as the difference between the shift in the perprotio and monodeuterio species arising from the perturbed equilibrium (i.e., the experimentally observed shift, δ, corrected for the intrinsic shifts). Since we are using a ^{13}C spectrometer at 67.88 MHz, these shifts should be expected to be about 100 Hz. Therefore, it should be straightforward to distinguish a rapidly rearranging $\eta^1\text{-}C_5H_5$ ring from a $\eta^5\text{-}C_5H_5$ ring which would show only the normal intrinsic isotope effect of ~10-20 Hz.

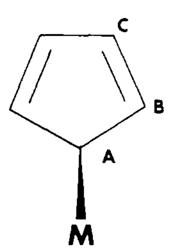
The equilibrium constant can be extracted most conveniently from the chemical-shift difference of the carbon bonded to the metal and the olefinic carbons of the monodeuterated cyclopentadienyl ring in the fast exchange limit [i.e., $\delta_{E'} = \delta_E(\alpha) - \delta_E(\beta)$].



The chemical shift of a particular carbon is the weighted average of the shifts of that carbon in the compounds undergoing rapid interconversion. Specially, for the α carbon

$$\delta_E(\alpha) = \frac{[\mathbf{1d}]A + [\mathbf{2d}]B + [\mathbf{3d}]C + [\mathbf{4d}]C + [\mathbf{5d}]B}{[\mathbf{1d}] + [\mathbf{2d}] + [\mathbf{3d}] + [\mathbf{4d}] + [\mathbf{5d}]} \quad (5)$$

where A, B, and C are the chemical shifts of the perprotio



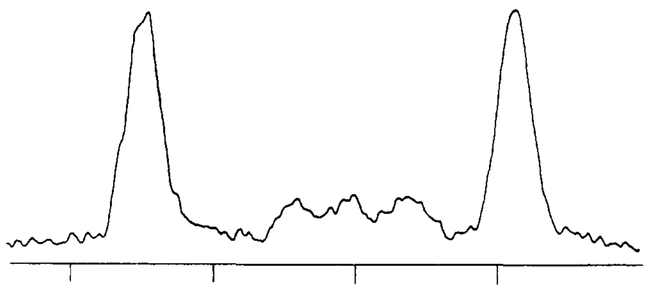


Figure 1. The proton-coupled ^{13}C NMR spectrum of the cyclopentadienyl ring of the 1:1 mixture of $(\eta^5\text{-}C_5H_4D)_2Fe$ to $(\eta^5\text{-}C_5H_5)_2Fe$ at 67.88 MHz at 25 °C in acetone. The broad 1:1:1 triplet upfield of the center of the doublet is assigned to the carbon directly bonded to the deuterium. The doublet is assigned to the carbons bearing the protons in the $\eta^5\text{-}C_5H_4D$ and $\eta^5\text{-}C_5H_5$ ring of ferrocene. In this spectrum the β and γ intrinsic shifts are not resolved from the perprotio resonance.

Figure 2. The proton-coupled ^{13}C NMR spectrum of the cyclopentadienyl ring of a 1:4:2 mixture of perprotio-:monodeuterio-:dideuteriocyclopentadienyltrimethyltin at 67.88 MHz at 25 °C in acetone. The broad 1:1:1 triplet downfield of the center of the doublet is assigned to the carbon directly bonded to the deuterium. The doublet is assigned to the carbons bearing the protons in the cyclopentadienyl ring. In this spectrum the shoulder observed on the doublet is due to the dideuterio compound. In this spectrum $\delta_E(\gamma)$ is not resolved from the perprotio resonances.

complex in the slow exchange limit for the metal, the carbon next to it, etc. Substitution of [**1d**]$K_{(C_5H_4D)}$ for [**2d**], [**3d**], [**4d**], and [**5d**] reduces this expression for the chemical shift of the α carbon (the carbon bearing the deuterium) to[13]

$$\delta_E(\alpha) = \frac{A + 2K(B + C)}{1 + 4K} \tag{6}$$

For the β carbon,[13] the carbon next to the deuterium-substituted carbon of $M(C_5H_4D)$, substitution gives the following:

$$\delta_E(\beta) = \frac{B + 2KC + K(A + B)}{1 + 4K} \tag{7}$$

and likewise for the γ carbon:[13]

$$\delta_E(\gamma) = \frac{C + 2KB + K(A + C)}{1 + 4K} \tag{8}$$

The difference between eq 6 and 7 gives

$$\delta'_E(\alpha - \beta) = \delta_E(\alpha) - \delta_E(\beta) = \frac{A - B - K(A - B)}{1 + 4K} \tag{9}$$

Defining the separation between the metal-substituted and olefinic carbons (A-B) of the perprotio complex in the slow exchange as Δ,[13] the above equation is further simplified to

$$K \approx \frac{\Delta - \delta'_E(\alpha - \beta)}{\Delta + 4\delta'_E(\alpha - \beta)} \tag{10}$$

Also one should note that the deuterated carbon should show the largest perturbed shift, δ_E, but the others should show a compensating shift in the opposite direction of $-\delta_E/4$. Regardless, the overall effect is that a large isotopic splitting corresponds to a fluxional system and can be readily used to identify fluxional molecules with low barriers.

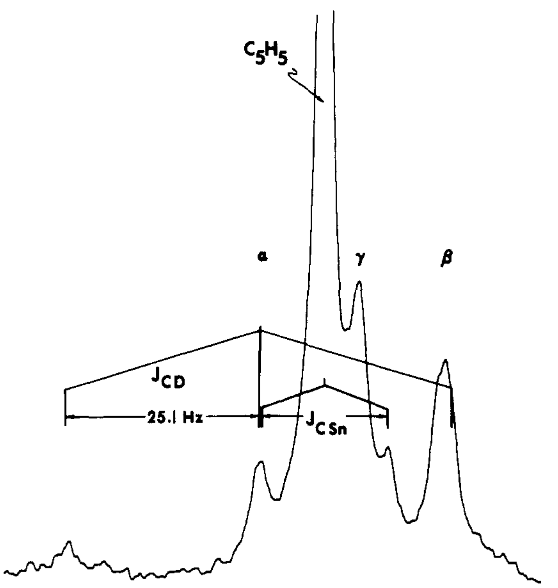


Figure 3. The proton-decoupled ^{13}C NMR spectrum of the cyclopentadienyl region of a 2:1 mixture of perprotio- and monodeuteriocyclopentadienyltrimethyltin at 67.88 MHz at 25 °C in acetone.

In order to illustrate and test the method we have investigated two key systems for which the structures are known. The proton-coupled ^{13}C spectrum of 1,1′-bisdeuterioferrocene is shown in Figure 1, wherein the α intrinsic isotope effect of 12 Hz in the deuterated carbon (center triplet) can be noted by its slight upfield shift relative to center of the doublet due to the other carbons, split by the large C-H coupling (177 Hz).[14] In the $(\eta^1\text{-}C_5H_4D)Sn(CH_3)_3$ spectrum show in Figure 2, a clear *downfield* shift of 22 Hz of the deuterated carbon is seen relative to the centroid of the protonated carbons. Corrected for the intrinsic shifts this corresponds to an apparent δ'_E of 35 Hz.[15,16]

Since the shift is *downfield*, the isotope effect, K_H/K_D, of approximately 0.96 at 25 °C based on eq 10 demonstrates a deuterium preference for the olefinic carbon relative to the metal-substituted carbon.[17]

Reference to the proton-decoupled spectrum in Figure 3 indicates that the β and γ carbons are actually resolved.[16] Although this could arise from a difference in equilibrium constant, it most probably arises from a difference in the chemical shifts of the B and C carbons in the static spectrum of approximately 20 ppm.[18] Thus the Δ in eq 10 should refer specifically to the $A - B$ difference; however, K is not a sensitive function of Δ.

The more accurate shifts provided in the decoupled spectra give $\delta(\alpha - \beta) = 24.9$ Hz, which on corrections for the intrinsic shifts[16] gives $\delta'_E(\alpha - \beta) = 40$ Hz and $K = 1.03_4$ assuming $\Delta \simeq -90$ ppm.

To confirm that the unusual downfield shift in the ^{13}C NMR of the $(C_5H_4D)Sn(CH_3)_3$ complex is, in fact, due to the perturbation of an otherwise degenerate equilibria, the temperature dependence of the ^{13}C NMR of both $(\eta^5\text{-}C_5H_4D)_2Fe$ and $(\eta^1\text{-}C_5H_4D)Sn(CH_3)_3$ was examined. As expected, only for the tin complex, being an equilibrium mixture of three different isomers (**1d**, **2d** or **5d**, and **3d** or **4d**), was the spectrum seen to change with temperature. Over a 79 °C temperature range we observed a significant increase (from 11 to 17 Hz) in $\delta(\gamma - \beta)$ for the $(\eta^1\text{-}C_5H_4D)Sn(CH_3)_3$ complex on lowering the temperature. In the 1,1′-bisdeuterioferrocene over a similar temperature range, no change in $\delta(\alpha - \beta)$ was observed. This is consistent with a symmetrically bound, nonexchanging η^5-C_5H_4D ring of the ferrocene complex.

The temperature independence of the spectrum of the η^5-C_5H_4D ring in ferrocene as compared with the temperature dependence of the η^1-C_5H_4D ring in the tin complex is quite indicative. The temperature-dependence data for the tin complex are complicated by decomposition at high temperature, but approximate values of $\Delta H = -0.32$ cal/mol and $\Delta S = -0.11$ cal/mol·deg were obtained.

Experimental Section

Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6 spectrometer. Deuterium incorporation was measured to ±3%. The ^{13}C NMR spectra were obtained on a Bruker HX-270 at 67.88 MHz. Temperature calibration for the ^{13}C NMR was performed with a 2-chlorobutane standard sample.

All solvents were distilled before use. All complexes were handled under a nitrogen atmosphere except for $Tl(C_5H_4D)$ and ferrocene. Trimethyltin chloride was purchased from Ventron Corp. and was used without further purification. All thallium cyclopentadienide was sublimed before use.

Preparation of Compounds. 1,1′-Bisdeuterioferrocene. The 1,1′-bisdeuterioferrocene was synthesized from perprotioferrocene by proton abstraction using *n*-butyllithium in dry hexanes containing TMEDA as described in the literature.[20] The resulting dianion was then quenched with excess D_2O giving 1,1′-bisdeuterioferrocene in 90% yield after chromatography.

Thallium Cyclopentadienide. Thallium cyclopentadienide was synthesized by combining 15 mL (0.18 mol) of freshly distilled cyclopentadiene to an aqueous mixture of 8.8 g (0.21 mol) of NaOH and 55.2 g (0.11 mol) of Tl_2SO_4. The mixture was allowed to stir at room temperature for 24 h. Sublimation of the resulting precipitate at 90 °C gave an 81% yield at $Tl(C_5H_5)$.

$(C_5H_4D)Tl$. The following reaction sequence was found to be the most efficient method for monodeuterating $Tl(C_5H_5)$.

$$1.\quad Tl(C_5H_5) + \text{excess } HCl/DCl \xrightarrow{THF} TlCl + C_5H_5D$$

$$2.\quad C_5H_5D + n\text{-butyllithium} \xrightarrow{THF} Li(C_5H_4D) + C_4H_{10}$$

$$3.\quad Li(C_5H_4D) + {}^1\!/_2Tl_2SO_4 \xrightarrow{THF} Tl(C_5H_4D) + {}^1\!/_2Li_2SO_4$$

In the first reaction a 1:1 mixture of DCl-HCl was generated from PCl_5 and a 1:1 D_2O-H_2O mixture. When 100% D_2O was used, a substantial percentage of the dideuterio complex was found. The excess DCl-HCl remaining after the first reaction was eliminated by the addition of an excess of finely powdered dry K_2CO_3. The solids were removed by centrifugation before the addition of *n*-butyllithium to the THF-cyclopentadiene solution. The third reaction was stirred at room temperature for 24 h. The addition of distilled water to the THF solution followed by the sublimation of the precipitate at 90 °C gave a 40% yield (based on $Tl(C_5H_5)$) which was found by mass spectroscopy to the 61% perprotio, 36% monodeuterio, and 3% dideuterio.

$(C_5H_4D)Sn(CH_3)_3$. Cyclopentadienyltrimethyltin was synthesized by refluxing 1.1 g (5.5 mmol) of $Sn(CH_3)_3Cl$ and 1.5 g (5.5 mmol) of $Tl(C_5H_4D)$ in freshly distilled THF for 3 h. The TlCl was separated by centrifugation and the solvent removed by vacuum. The resulting tin complex was sufficiently pure for ^{13}C NMR spectroscopy.

Acknowledgments. M.S. and J.W.F. wish to acknowledge support for this research by grants from the National Science Foundation. The NMR spectra were obtained using the Southern New England High Field NMR facility supported by the Biotechnology Resources Program of the National Institutes of Health (RR-798).

References and Notes

(1) M. Saunders, L. Telkowski, and M. R. Kates, *J. Am. Chem. Soc.*, **99**, 8070 (1977).

(2) M. Saunders and M. R. Kates, *J. Am. Chem. Soc.*, **99**, 8071 (1977).

(3) M. Saunders, M. R. Kates, K. B. Wiberg, and W. Pratt, *J. Am. Chem. Soc.*, **99**, 8072 (1977).

(4) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

(5) Lloyd M. Jackman and F. A. Cotton, "Dynamic Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, 1975.

(6) F. A. Cotton and T. J. Marks, *J. Am. Chem. Soc.*, **91**, 7281 (1969).

(7) G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, **89**, 2855 (1967).

(8) K. Humski, R. Malojcic, S. Borcic, and D. E. Sunko, *J. Am. Chem. Soc.*, **92**, 6543 (1970).

(9) D. Lauer, E. L. Motell, D. D. Traficante, and G. E. Maciel, *J. Am. Chem. Soc.*, **94**, 5335 (1972).

(10) D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organomet. Chem.*, **42**, 159 (1972).

(11) Yu. K. Grishin, N. M. Sergeyev, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, **22**, 361 (1970).

(12) Yu. K. Grishin, N. M. Sergeyev, and Y. A. Ustynyuk, *Org. Magn. Reson.*, **4**, 377 (1972).

(13) Approximate formulas are used in this example. Appropriate modification would be necessary to consider unequal chemical shifts and equilibrium constants for the different olefin positions.

(14) All resonances are broad owing to smaller three- and five-bond couplings, as well as coupling to deuterium. A proton and deuterium decoupled spectrum yielded values for the α, β, and γ intrinsic shifts of 12.0, 6.6, and 2.6 Hz, respectively.

(15) Intrinsic shifts for the model compound, $Me_3Ge(C_5H_4D)$, imply that the α intrinsic shift for the metal-bonded carbon is 20.6 Hz and for the olefinic carbons 16.9 and 16.8 Hz. The correction for the α carbon would be the weighted averages for the positions, i.e., 17.6 Hz. Several β and γ intrinsic shifts are observed in the isomers owing to the symmetry of the **2**-*d* and **3**-*d* isomers. Significantly different shifts are expected for a β effect through a σ or π bond based on methyl substituent effects on olefin resonances.[17] Thus, for the low-field carbon resonance, δ 129.3 (assigned to the β carbon[12]) the β_π and β_σ shifts were 10.7 and 5.2 Hz and the γ shifts were ~2.4 Hz. For the higher field resonance at δ 124.6 (C), β_π and β_σ were 11.8 and 4.7 Hz and the γ shifts ~2.7 Hz. For the high-field resonance at δ 51.4, the β shift was 6.9 Hz and the γ shift was not resolved.

(16) From the proton decoupled spectrum one observes a $\delta(\beta) = -16.1$ and $\delta(\gamma) = -4.7$ Hz which corrected for intrinsic shifts corresponds to $\delta_E(\beta) = -8.2$ and $\delta_E(\gamma) = -2.2$ Hz. The separation of the β and γ carbons should not be observed if one assumes that shifts for the olefinic protons are equal in the static spectrum.[13] A $^{117,119}Sn-^{13}C$ coupling of 17.3 Hz can be observed on the C_5H_5 resonance, but is not resolved in the C_5H_4D resonances. From the outer line of the α carbon ($J_{CD} = 25.1$ Hz) at -33.7 Hz, the calculated $\delta(\alpha) = +8.6$ Hz yields a corrected $\delta_E(\alpha) = 26.4$ Hz. Twice the sum of $\delta_E(\gamma)$ and $\delta_E(\beta)$ is -21.6 Hz and should equal $-\delta_E(\alpha)$. This discrepancy presumably arises from assuming that the intrinsic shifts of the germanium complex can be transferred to the tin complex.

(17) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 75.

(18) This preference is the reverse of that shown by biallyl. The cause of this reversal is not obvious to us.

(19) Although we cannot accurately evaluate the shifts in the static spectra as well as *K*, the shifts for A suggested by the model compounds indicate that a separation between B and C of ~15 ppm would be expected.

(20) J. J. Bishop, A Davison, M. L. Katcher, D. W. Litchenbera, R. E. Merril, and J. C. Smith. *J. Organomet. Chem.*, **27**, 241 (1971).