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A Nuclear Magnetic Resonance Study of σ-Cyclopentadienyl(triethylphosphine)copper(I)[1]

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Abstract: The nmr spectrum of cyclopentadienyl(triethylphosphine)copper(I) has been examined as a function of temperature between 0 and −70°. The high-temperature spectrum of the cyclopentadienyl group consists of a single line; the corresponding low-temperature spectrum is composed of three lines having relative areas 2:2:1. The latter spectrum requires that the organometallic compound exist in solution as a copper σ-cyclopentadienide. Analysis of the spectral line shapes in the exchange-broadened region indicates that the averaging of chemical shifts observed at high temperatures must occur by either a sequence of 1,2 or 1,3 shifts of the metal atom around the cyclopentadienyl ring, and that it cannot take place by a sequence of random shifts. Chemical shift data are tentatively interpreted to support the 1,3-shift mechanism for the averaging.

Compounds containing a σ bond connecting carbon and copper(I) usually show a low order of thermal stability.[2] Details of the factors responsible for the thermal lability of this class of organometallic compounds are not well understood: the stability of the incipient radical formed during homolytic cleavage of the carbon–metal bond,[3] the ionic character of the bond,[4] and the magnitude of the energy separating the highest filled and lowest unfilled σ molecular orbitals[5] have been variously proposed to determine the stability of these and other transition metal alkyls.

As part of an investigation of the structural features influencing the rate of decomposition of several organocopper(I) reagents, we have had opportunity to examine some of the properties of cyclopentadienyl(triethylphosphine)copper(I).[6] Wilkinson and Piper have formulated this compound as a σ-cyclopentadienide rather than a π-cyclopentadienide, on the basis of spectral evidence.[6] However, the thermal stability of this material is unexpectedly greater than that of other simple alkylcopper(I) compounds; moreover, its room-temperature nmr spectrum shows only a single sharp peak for the protons on the cyclopentadienyl ring.[6b] The possibility that cyclopentadienyl(triethylphosphine)copper is a member of the group of metal σ-cyclopentadienides characterized by rapid migration of the metal atom between carbon atoms in the cyclopentadienyl ring[6b–8] has led us to examine the temperature dependence of its nmr spectrum, in hope of learning more about its structure and the reasons for its unexpected thermal stability. In this paper we wish to report evidence which confirms the structure suggested by Piper and Wilkinson, and which sheds some light on the process which averages the chemical shifts of the cyclopentadienyl protons.

Results

The nmr spectrum of the cyclopentadienyl protons of cyclopentadienyl(triethylphosphine)copper in sulfur dioxide solution at 0° consists of a sharp line at 6.30 ppm downfield from internal tetramethylsilane (Figure 1); resonances due to triethylphosphine occur at higher field and are omitted from this figure. As the temperature of the sample is lowered, the cyclopentadienyl proton resonance broadens and splits into three lines

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[1] This research was supported by the National Science Foundation through Grant GP 2018. Calculations were carried out in part at the Massachusetts Institute of Technology Computation Center, Cambridge, Mass.

[2] For examples, see G. M. Whitesides and C. P. Casey, *J. Am. Chem. Soc.*, **88**, 4541 (1966); H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966); C. E. H. Bawn and R. Johnson, *J. Chem. Soc.*, 4162 (1960); G. Costa, G. Pellizer, and F. Rubessa, *J. Inorg. Nucl. Chem.*, **26**, 961 (1964); H. Gilman, R. G. Jones, and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952); H. Hashimoto and T. Nakano, *ibid.*, **31**, 891 (1966).

[3] F. Glockling and D. Kingston, *J. Chem. Soc.*, 3001 (1959).

[4] H. H. Jaffé and G. O. Doak, *J. Chem. Phys.*, **21**, 196 (1953); H. H. Jaffé, *ibid.*, **22**, 1462 (1954).

[5] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

[6] (a) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956); (b) T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

[7] H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.* (Amsterdam), **4**, 313 (1965).

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

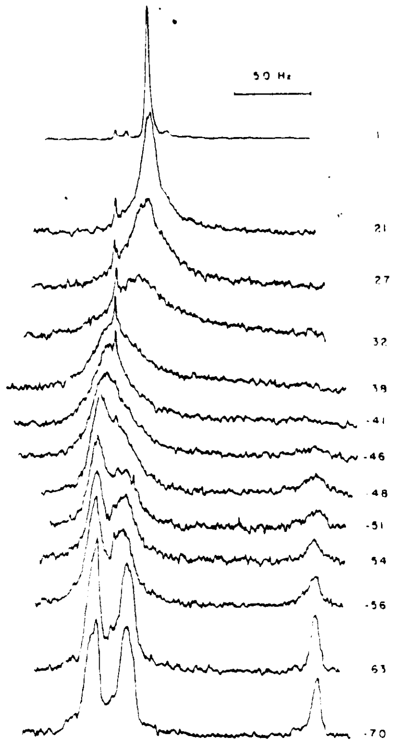
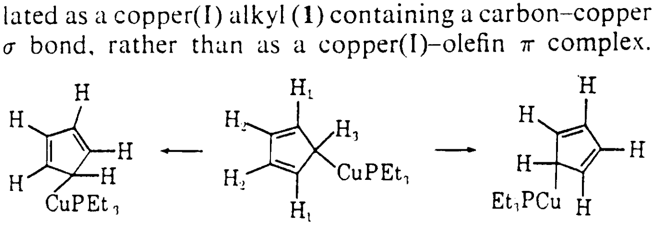


Figure 1. Nmr spectra of the cyclopentadienyl protons of σ-cyclopentadienyl(triethylphosphine)copper(I) in sulfur dioxide solution as a function of temperature. The three peaks in the low-temperature spectrum occur at 6.95, 6.57, and 4.46 ppm from internal tetramethylsilane.

at 6.95, 6.57, and 4.46 ppm, having relative areas approximately 2:2:1. Solutions of cyclopentadienyl(triethylphosphine)copper, in the concentration range used in these studies, crystallize at temperatures below approximately −40° if allowed to stand. In consequence, spectra taken in the exchange-broadened region of the spectrum were obtained on supersaturated solutions. Attempts to lower the temperature of the sample below −70° to examine spin coupling in the true slow-exchange limit were thwarted by crystallization of the organometallic compound from solution.

The observation of three distinct signals for the cyclopentadienyl protons in the low-temperature spectrum of cyclopentadienyl(triethylphosphine)copper immediately establishes that this compound should be formulated as a copper(I) alkyl (**1**) containing a carbon–copper σ bond, rather than as a copper(I)–olefin π complex.



2a **1** **2b**

The highest field peak in the observed spectrum, having relative area 1, can be safely assigned to the C*H*Cu proton; the two lower field peaks are due to the two nonequivalent types of vinylic protons. Unfortunately, it is not presently possible to assign chemical shifts to these protons unambiguously. In the discussions which follow, we make the assumption that the resonance occurring at lowest field can be assigned to the protons in site 1 of **1**. Some justification for this assumption will be offered below.

The single line observed in the high-temperature spectrum of this compound is most easily rationalized on the basis of rapid hopping of the copper atom between carbon atoms in the cyclopentadienyl ring. In principle, this hopping of the metal atom might take place by any one of three distinct paths: each exchange might shift the copper atom only between adjacent carbon atoms (for example, **1** → **2a**); the exchange might shift the copper atom specifically in a 1,3 manner (**1** → **2b**); or exchange might occur indiscriminantly by a random mixture of 1,2 and 1,3 shifts.

The unsymmetrical collapse of the resonance due to the vinyl protons observed in the exchange-broadened region offers a method of distinguishing between these alternatives. By following the method developed by Kubo[9a] and by Sack,[9b] theoretical line shapes can be calculated for each of these possible exchange schemes. In particular, for a sequence of 1,2 hops, the full line-shape function $I(\omega)$, giving the relative intensity of absorption in the spectrum at frequency ω, is given by eq 1. This equation applies to the labeling of the cyclopentadienyl protons indicated in **1**. Here, for example, ω_1 is the chemical shift of the protons at site 1, T_2^1 is the relaxation time for the protons at this site in the absence of exchange, and τ is the mean time the copper atom spends at each carbon atom between exchanges. Re indicates that only the real part of the expression inside the brackets is considered. The appropriate kinetic transfer matrices **K** for a 1,3-hopping scheme and for random exchange are given by eq 2 and 3. The corresponding line-shape functions are obtained by substituting these matrices for the exchange terms in eq 1.

1,2 shifts

$$I(\omega) \propto$$

$$\mathrm{Re}\left[(2,2,1)\begin{pmatrix} -i(\omega_1-\omega)-1/T_2^{1}-1/\tau & 0.5/\tau & 0.5/\tau \\ 0.5/\tau & -i(\omega_2-\omega)-1/T_2^{2}-0.5/\tau & 0 \\ 1/\tau & 0 & -i(\omega_3-\omega)-1/T_2^{3}-1/\tau \end{pmatrix}^{-1}\begin{pmatrix}1\\1\\1\end{pmatrix}\right] \quad (1)$$

1,3 shifts

$$\mathbf{K} = \begin{pmatrix} -0.5/\tau & 0.5/\tau & 0 \\ 0.5/\tau & -1/\tau & 0.5/\tau \\ 0 & 1/\tau & -1/\tau \end{pmatrix} \quad (2)$$

Random shifts

$$\mathbf{K} = \begin{pmatrix} -0.75/\tau & 0.5/\tau & 0.25/\tau \\ 0.5/\tau & -0.75/\tau & 0.25/\tau \\ 0.5/\tau & 0.5/\tau & -1/\tau \end{pmatrix} \quad (3)$$

Line shapes calculated using eq 1–3 for several values of the pre-exchange lifetime τ are given in Figures 2–4. In these calculations, no attempt was made to take into consideration spin–spin coupling in the slow-exchange

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(9) (a) R. Kubo, *Nuovo Cimento Suppl.*, 6, 1063 (1957); (b) R. A. Sack, *Mol. Phys.*, 1, 163 (1958); (c) A. Abragam, "The Principles of Nuclear Magnetism," The Clarendon Press, Oxford, 1961, Chapter 10; (d) C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965); (e) H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, 43, 4107 (1965).

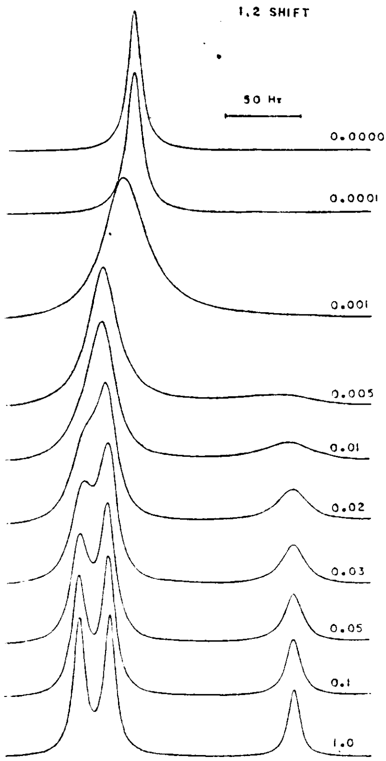

Figure 2. Calculated line shapes for the cyclopentadienyl protons as a function of the mean preexchange lifetime τ (in sec) between successive 1,2 hops. These spectra are based on the assumption that the resonance at lowest field can be assigned to the protons in site 1 of **1**.

spectra. Indeed, T_2 (here set equal to 0.034 sec for all three sites) was adjusted to give line widths at slow exchange which approximated those of the vinylic absorptions in the observed spectra. Since this value of T_2 includes contributions to the line shape from both relaxation and from spin–spin coupling, the calculated line width in the fast exchange limit is appreciably larger than the observed line width. Nonetheless, the qualitative features of these calculated spectra are reliable, and, in particular, the unsymmetrical exchange broadening calculated for the vinyl proton absorptions in the 1,2- and 1,3-hopping schemes is significant.

This asymmetry in the calculated spectra is physically reasonable if it is remembered that in these schemes each exchange changes the precession frequencies of the two kinds of vinyl protons by different amounts. For example, for successive 1,2 shifts, the precession frequency of each of the protons labeled H_1 in **1** changes with equal probability by either ~100 Hz (if exchange transfers the proton considered to the C*H*Cu site) or ~20 Hz (if it is transferred to the second vinylic site). Similarly, the corresponding changes in the precession frequency of each of the protons labeled H_2 are either ~20 or 0 Hz. Since the relative line broadening for the two types of protons is related to the relative "uncertainty" in their precessional frequencies, the resonance of the proton experiencing the larger changes in frequency per unit time would be expected to broaden most rapidly on increasing the rate of exchange.[10]

Comparison of the calculated and observed spectra in the region of exchange broadening indicates that the averaging of the chemical shifts of the cyclopentadienyl protons occurs by a sequence of 1,3 hops of the metal atom around the ring, *provided* that the assignment of relative chemical shifts to the two kinds of vinylic protons is correct.[11] If this assignment is

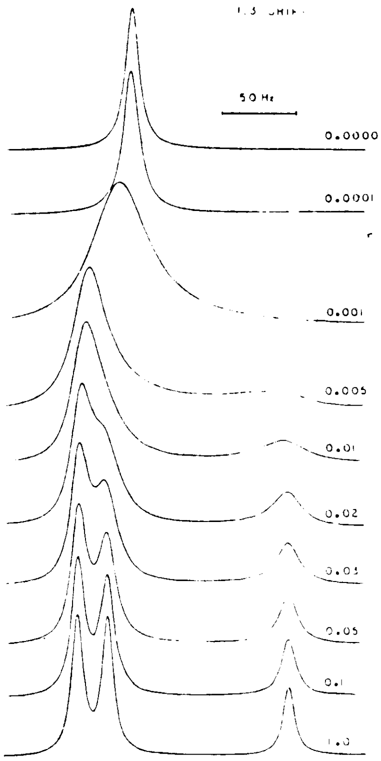

Figure 3. Calculated line shapes for the cyclopentadienyl protons as a function of τ for successive 1,3 hops.

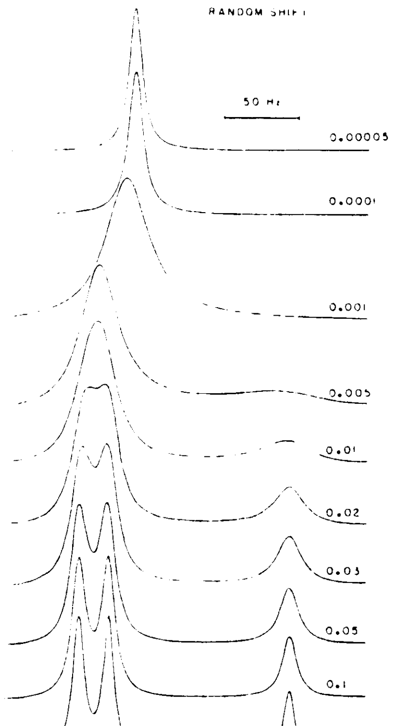

Figure 4. Calculated line shapes for the cyclopentadienyl protons as a function of τ for random hops.

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(10) For a more detailed presentation of this argument, see S. Meiboom, *Z. Elektrochem.*, **64**, 50 (1960); see also ref 8.

(11) Similar calculations have been applied to a number of related problems: see, for examples, C. MacLean and E. L. Mackor, *Discussions*

reversed, the spectra calculated for the random exchange scheme are unaffected, but the spectra calculated for 1,2- and 1,3-hopping schemes must be interchanged. In this circumstance, comparison of calculated and observed spectra would indicate that averaging occurred by a 1,2-hopping process.

The temperature dependences observed for the spectrum of this organometallic compound in propionitrile and petroleum ether solutions were qualitatively similar to that observed in sulfur dioxide, although the chemical shift of the C*H*Cu proton was appreciably solvent dependent. Further, the copper compound could be recovered from sulfur dioxide solution without apparent change. These observations exclude the possibility that the compound whose spectrum was observed in sulfur dioxide was actually an adduct of the organocopper compound with sulfur dioxide.[12] Spectra taken in triethylamine or triethylphosphine solutions showed only a single line for the cyclopentadienyl protons at temperatures as low as −70°. Spectra taken in solutions consisting of mixtures of sulfur dioxide and triethylamine or triethylphosphine showed qualitatively the same changes in line shapes as were observed in pure sulfur dioxide; in particular, the same asymmetry was observed in the vinyl proton signals in the exchange-broadened region. However, lower temperatures were required to produce exchange broadening in the mixed solvents than in sulfur dioxide alone.

No direct evidence is available on the extent of association of cyclopentadienyl(triethylphosphine)copper in solution. However, the observations that this compound sublimes readily, and that its mass spectrum shows a clearly defined parent ion (*m/e* 247 and 249) but no evidence of dimeric or more highly aggregated species, suggest that it is probably unassociated in the vapor phase, and that by inference it is probably also unassociated in a hydrocarbon solvent.[13] It is of some further interest that the only other relatively abundant ions in the spectrum which clearly contain copper correspond to $(C_2H_5)_3PCu^+$ (*m/e* 181 and 183). The absence of a strong peak corresponding to $C_5H_5Cu^+$ lends further support to a formulation of this compound as a σ-cyclopentadienide.[14]

Discussion

Comparison of the observed and calculated temperature dependence for the spectra of σ-cyclopentadienyl(triethylphosphine)copper(I) permits the conclusion that the averaging of chemical shifts observed at high temperatures is not the result of *random* hopping of the metal atom between carbon atoms; however, the question of whether the averaging reflects a sequence of successive 1,2 or 1,3 shifts can be answered unambiguously only by correctly assigning chemical shifts to the two kinds of olefinic protons. This assignment cannot at present be made with great assurance.

The relative magnitudes of the coupling constants between the C*H*Cu proton and the two vinyl protons cannot easily be used in assigning chemical shifts, both because the poor resolution in the spectra at the lowest temperatures utilized makes detailed spectral analysis impractical, and because analogous coupling constants in the few model compounds which have been examined suggest that these two coupling constants have approximately the same magnitude.[16] An assignment based on chemical-shift correlations suffers from the scarcity of data from model compounds. Nonetheless, the spectra of cyclopentadienyltrimethylsilane[7] and -trimethylgermane,[7] π-cyclopentadienyliron dicarbonyl σ-cyclopentadienide,[8] and cyclopentadienyl(triethylphosphine)copper share in common the feature that the resonance of at least one of the two kinds of vinylic protons of the cyclopentadienyl group of each compound occurs near 6.6 ppm. If it is assumed that the chemical shift of the vinylic protons which are four bonds removed from the metal atom will be relatively insensitive to the nature of the metal and its ligands,[19] the 6.57-ppm resonance in the copper organometallic compound can be tentatively assigned to H_2 of **1**, and consequently, the 6.95-ppm resonance can be assigned to H_1. Provided these assignments are correct, the high-temperature averaging of the chemical shifts must take place *via* 1,3 shifts of the copper atom.[20] However, this conclusion must obviously remain tentative until further experimental work on related compounds is available.

Details of the mechanism of the metal atom shift might be examined by determining the influence of appropriate solution variables on the rate of this reaction. Unfortunately, the spin–spin splitting present in the slow exchange limit severely limits the accuracy

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Faraday Soc., **34**, 165 (1962); M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964); A. Allerhand and H. S. Gutowsky, *ibid.*, **87**, 4092 (1965), and references therein; C. S. Johnson, Jr., and J. C. Tully, *J. Chem. Phys.*, **40**, 1744 (1964).

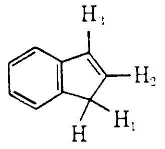
(12) Insertion of sulfur dioxide into carbon–metal bonds is well known in the chemistry of other transition metal alkyls: J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, **88**, 4862 (1966), and references therein.

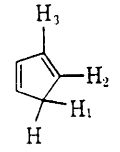
(13) Other copper(I) and silver(I) organometallic compounds are probably associated both in solution in the crystalline state: P. W. R. Corfield and H. M. M. Shearer, *Acta Cryst.*, **16**, A71 (1963); **20**, 502 (1966); A. F. Wells, *Z. Krist.*, **94**, 447 (1936); F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936); D. Blake, G. Calvin, and G. E. Coates, *Proc. Chem. Soc.*, 396 (1959); G. E. Coates and C. Parkin, *J. Inorg. Nucl. Chem.*, **22**, 59 (1961).

(14) π-Cyclopentadienylmetal compounds ordinarily show prominant peaks corresponding to $C_5H_5M^+$.[15] Although the presence of an ion, $C_5H_5Cu^+$ (*m/e* 128 and 130), cannot be excluded in the spectrum, it certainly does not provide a major pathway for fragmentation.

(15) For example, see R. G. Denning and R. A. D. Wentworth, *J. Am. Chem. Soc.*, **88**, 4619 (1966).

(16) Manatt and Elleman have observed J_{12} = +2.02 Hz and J_{13} = −1.98 Hz for indene,[17] and J_{12} = +1.3 Hz and J_{13} = −1.5 Hz for cyclopentadiene.[18] However, both three- and four-bond couplings are strongly dependent on the geometry of the molecular fragment concerned. In consequence, coupling constants in these hydrocarbons may not provide reliable model parameters for the corresponding coupling constants in the organometallic compounds. For reviews of theoretical and experimental evidence pertinent to the geometrical dependence of these couplings, see M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964); A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 195 (1965); E. W. Garbish, Jr., *J. Am. Chem. Soc.*, **86**, 5561 (1964).





(17) D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962).

(18) S. L. Manatt, personal communication.

(19) The chemical shifts observed for the methyl and methylene protons of ethyl-substituted organometallic compounds offers some support for this assumption: A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963); M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965).

(20) This type of equilibration is known in allylic organometallic compounds: G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962); K. C. Ramey and G. L. Statton, *J. Am. Chem. Soc.*, **88**, 4387 (1966), and references therein.

of detailed kinetic analysis.[21] Qualitatively, the significant rate increase observed on adding σ-donor ligands to the sample suggests that, in going to the transition state for the metal atom shift, the compound progresses to an appreciable extent along the path toward dissociated cyclopentadienide anion and metal cation, and that the added ligand serves to increase the rate by stabilizing the increased partial positive charge on the metal atom during the shift. However, the persistence of the unsymmetrical mode of collapse of the vinyl signals in the presence of added donor ligands indicates that even under these circumstances dissociation does not become complete.

It is of some interest that the temperature dependence of the nmr spectrum of π-cyclopentadienyliron dicarbonyl σ-cyclopentadienide has been interpreted as indicating that the metal atom in this compound shifts around the cyclopentadienyl ring by a sequence of 1,2 hops.[8] If both this interpretation and that proposed for the organocopper reagent are correct, the difference between these compounds poses an interesting problem. However, the assignment of the vinylic proton chemical shifts in the iron organometallic compound was based on the assumption that the magnitude of the three-bond coupling between the C*H*Fe proton and the vicinal vinyl proton was greater than that of the corresponding four-bond coupling, and the ambiguity in this type of assignment has already been indicated.[16] In consequence, comparison of the two compounds is most profitably deferred until the stereochemistry of the metal atom shift in each has been more clearly defined.

Experimental Section[22]

σ-Cyclopentadienyl(triethylphosphine)copper was prepared using a modification of Wilkinson and Piper's method.[6a] Commercial cuprous oxide (3.6 g), 10 ml of freshly distilled cyclopentadiene, 7 ml of triethylphosphine, and 20 ml of petroleum ether (bp 30–60°) were refluxed under a nitrogen atmosphere with magnetic stirring for 2 hr and then allowed to stir at ambient temperature for 6 hr. The solvent was removed under reduced pressure, and the resulting brown-black syrup was transferred in a nitrogen-filled glove bag directly to a sublimation apparatus. The product was obtained as hard white or pale yellow-green crystals by slow sublimation at 60° and 0.1 mm. The crystals were moderately stable in the absence of oxygen; *solutions* of the organometallic were much less stable.

Nmr samples were prepared by transferring a suitable quantity of the freshly sublimed material to a flame-dried nmr tube under nitrogen. The tube was capped with a serum stopper and cooled to the temperature of a Dry Ice–acetone bath, at which temperature, sulfur dioxide was condensed into the tube. The sample was warmed briefly to approximately −35°, to allow the organocopper reagent to dissolve, and then inserted into the precooled (−40°) probe of the nmr spectrometer. If the sample was permitted to warm to temperatures above −40° for more than approximately 5 min, decomposition of the sample introduced significant absorption due to impurities in the olefin absorption region.

Acknowledgments. We wish to express our thanks to Dr. Robert Siekman for his help in obtaining mass spectra, and to Drs. S. L. Manatt and D. D. Elleman for permission to use their data prior to publication.

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(21) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

(22) Nmr spectra were taken at 60 MHz using a Varian A-60 spectrometer equipped with a V-6040 variable-temperature probe and controller. Sweep widths were calibrated using a Krohn-Hite Model 450 oscillator and a Hewlett-Packard Model 524 electronic counter. Calibration of the temperature controller was accomplished by measuring peak separations in a methanol sample. Mass spectra were determined with a Hitachi Perkin-Elmer RMU-6D spectrometer. Spectral calculations were carried out using an IBM 7094 computer, and spectra were plotted by a Calcomp plotter.