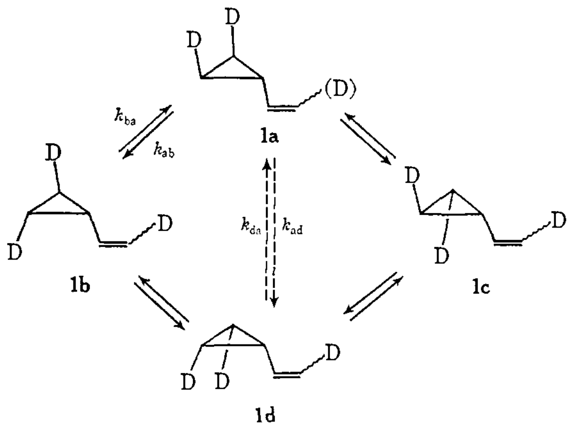
4.[6] This adventitious synthesis provided a route to sizeable quantities of the stereospecifically labeled substrate **1a**.

Gas phase pyrolyses of aliquots of compound **1a** were conducted at 325° (pressures of 100 to 150 torr) in carefully prepared vacuum sealed glass ampoules of 15 to 20 ml volume. The reaction times ranged from 3 to 50 min, corresponding to 0.6 to 10 half-lives for the mixing of the deuterium label. The rate of this reaction was identical with that for the conversion of *trans*-2-deuterio-1-vinylcyclopropane to *cis*-2-deuterio-1-vinylcyclopropane.[5] Moreover, the ratio of the three new vinylcyclopropanes (**1b**, **1c**, and **1d**) at every extent of conversion, as monitored by the appearance of the nmr signal at δ 0.7, was found to be identical but for total intensity. Deuterium-decoupled nmr spectra simplified the δ 0.7 peak to a well-resolved six-line pattern, four lines of which are due to the *trans* compounds **1b** and **1c**, and two due to the *cis* compound **1d**. The spectrum simplification thus permitted us to measure the experimental values for ratio (**1b** + **1c**):**1d** as 2:1.[7]



We find it convenient to formalize the three limiting cases for the motion of the -CHD groups by writing the four ring isomers in the array as shown here, and then considering the rate constants interconnecting them. Those rates connecting **1a**, **1b**, **1c**, and **1d** (k_{ab}, k_{bc}, etc.) are equal by symmetry.[8] The rates connecting compounds **1a** and **1d** (k_{ad}, k_{da}) are also equal, but need not have the same value as k_{ab}. Three different time-dependent behaviors of the system starting from pure **1a** can be generated when we consider relative magnitudes of k_{ab} and k_{ad}. The rate k_{ad} may be much faster than all others (case I), or nonexistent (case II), or equal to k_{ab} (case III). The first mechanism, ruled out by our data, demands formation of compounds **1a** and **1d** with exclusion of compounds **1b** and **1c**. Mechanisms II and III are similar, but solution of the rate expressions by use of random-walk techniques, or by analog computation, reveals that when the nmr peaks which appear at δ 0.7 (from **1b** + **1c** + **1d**) have increased to 50% of their final value the concerted path (case II) has a 6:1 ratio while the random path (case III) has a 2:1 ratio for (**1b** + **1c**):**1d**. Thus, our experimental result is consistent only with a mechanism in which stereochemistry is lost simultaneously at two centers (case III).

It is possible to identify this sharply defined result as evidence for the intervention of a diradical.[9] Extrapolation of the diradical hypothesis to other cyclopropane reactions is obvious, but three recent examples deserve special mention. The Berson–Balquist account of the simultaneous racemization and geometrical isomerization of tetramethylcyclopropane-d_6 leaves no question that the diradical which is generated re-forms the cyclopropyl σ bond faster than the geminal dimethyl groups rotate.[10] Carter and Bergman's[11] observations of simultaneous racemization and geometrical isomerization of (−)-*cis*-1-methyl-2-ethylcyclopropane are explained in terms of a diradical formed by $CHCH_3$–CHC_2H_5 bond scission which then collapses to *cis* and *trans* isomers at slightly different rates. Crawford and Lynch have found that the loss of optical activity from (−)-*trans*-1,2-diphenylcyclopropane is 1.5 times the rate of formation of the *cis* compounds,[12] results exactly predicted by a free rotating diradical intermediate, even if bulky phenyl groups are involved.

Acknowledgment. The authors gratefully acknowledge support of the Robert A. Welch Foundation (Grant E-183) for this research.

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[6] The vinyl substituent contained both *trans*-2-deuteriovinyl and *cis*-2-deuteriovinyl groups, but this partial stereochemistry is not crucial to the present discussion, so we shall omit further mention of it. The fact that all possible starting materials produce the same mixture of trideuteriovinylcyclopropanes raises some interesting mechanistic points which are now under investigation.

[7] The accuracy of the nmr method is such that a ratio of (2.0 ± 0.2):1.0 is not likely to be experimentally significant; however, a ratio of 3:1 is easy to determine and well outside our experimental error. The details of the nmr spectra of all the compounds reported in this paper will be published separately.

[8] This argument ignores equilibrium isotope effects, an assumption which seems valid.

[9] The diradical hypothesis requires that our observations are adequate to describe the behavior at a single molecule during the course of the reaction. If this criterion is not met, then we can only discuss an average symmetry for the entire set of molecules. For this particular case the average symmetry is equivalent to claiming a planar intermediate for the reaction.

[10] J. A. Berson and J. M. Balquist, *J. Am. Chem. Soc.*, 90, 7343 (1968).

[11] W. L. Carter and R. G. Bergman, *ibid.*, 90, 7344 (1968).

[12] R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968).

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Allylic Palladium Acetate Systems. Acetate Bridge Inversion

Sir:

Recent reports have indicated that π-allylic palladium acetate systems are catalytic intermediates in a variety of diene-oligomerization reactions.[1a] As part of a general study of the nature and reactivity of π-allylic ligands, we have carried out variable-temperature nmr studies of several π-allylic palladium acetates.[1b]

In the solid state allylpalladium acetate, $[Pd_2(OAc)_2(C_3H_5)_2]$, has been shown to have structure Ib.[2] Three

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[1] (a) R. Van Helden, C. F. Kohl, D. Medema, G. Verberg, and T. Joukhoff, *Rec. Trav. Chim. Pays-Bas*, 87, 961 (1968), and references therein. (b) Allylic palladium acetate complexes were prepared by the method reported by S. D. Robinson and B. L. Shaw, *J. Organometal. Chem.*, 3, 367 (1965).

[2] M. R. Churchill and R. Mason, *Nature*, **204**, 777 (1964). Ib is a diagrammatic representation of one side of the structure. The arrows represent a side view of the π-allylic ligands, the arrow heads showing the position of the central carbon atoms. The planes defined by the three carbons of the π-allyl ligands are set at angles greater than 90° with respect to the planes defined by the oxygen–palladium–oxygen units (*ca.* 110 and 125°).

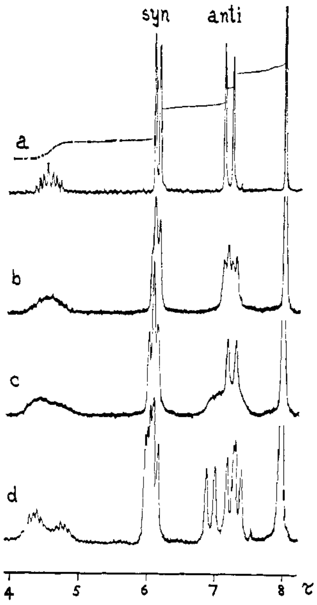
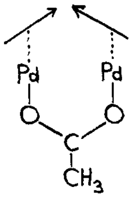
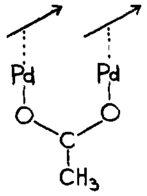


Figure 1. Nmr spectra of allylpalladium acetate at 100 Mc/sec in chloroform-d_1: (a) 30°; (b) $-20°$; (c) $-40°$; (d) $-60°$.

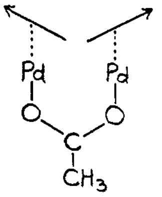
possible conformational isomers can be envisaged for the complex, Ia, Ib, and Ic, giving a total of four different electronic environments for the π-allyl ligands.[3]



Ia



Ib



Ic

The temperature-dependent nmr spectra of allylpalladium acetate are shown in Figure 1. Between 100 and 30° nmr equivalence of the π-allyl ligands are observed (Figure 1a, only one AA'BB'X pattern). At $-20°$ two overlapping AA'BB'X patterns of almost equal intensity are observed (Figure 1b: separation of resonances due to two types of *anti* protons, $\Delta\tau = 0.12$). 2-Methylallyl- and 1,1-dimethylallylpalladium acetate at $-20°$ likewise give two types of π-allylic resonance patterns of relative intensities *ca.* 9:1 and 3.5:1, respectively. These observations are consistent with the presence of at least two different molecular configurations in solution.

At $-60°$ one of the π-allylic resonance patterns (the low-intensity ones in the 2-methylallyl and 1,1-dimethylallyl systems) has split into two further allylic resonance patterns of *equal intensity* (Figure 1d, π-allyl system; $\Delta\tau$ *anti* protons of equal intensity resonances = 0.38). For allylpalladium acetate the relative intensities of the three overlapping AA'BB'X patterns are *ca.* 1:1:1. Thus there is a change in the relative concentrations of the different molecular conformational isomers with temperature.[4] The fact that at $-60°$ two of the π-allylic resonance patterns are of equal intensity suggests that they may be assigned to two nonequivalent allylic ligands in the same molecule, *i.e.*, Ib. A consideration of steric factors, particularly in the case of the 2-methylallyl system, indicates the head-to-head configuration, Ia, is unfavorable. Thus it is most probable that the major solution species are Ib and Ic.

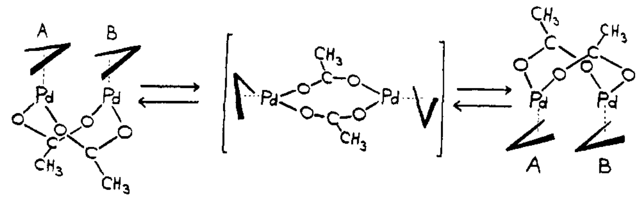


Figure 2. Mechanism of allyl ligand interchange in Ib *via* bridging acetate inversion.

In the allyl–palladium acetate system the concentrations of Ib and Ic are of a similar magnitude; $\Delta\tau$ (*anti* protons) for Ib and Ic at $-20°$ is less than $\Delta\tau$ (*anti* protons) for the nonidentical allyls in Ib at $-60°$; and nmr equivalence of the nonidentical allyls in Ib occurs at a lower temperature than nmr equivalence of Ib and Ic. Consequently the activation energy for the Ib–Ic exchange process is greater than that by which nmr equivalence of the nonidentical allyl groups in Ib is attained. These observations cannot be interpreted in terms of $\pi \rightarrow \sigma \rightarrow \pi$ exchange processes, nor in terms of "terminal CH_2 rotations."[5] An explanation in terms of allyl rotations (and/or flips)[6] would require that the activation energy for synchronized rotations (or flips) of the two nonidentical allyls in Ib (resulting in their nmr equivalence) be lower than that for single allyl rotation (or flip) (resulting in nmr equivalence of Ib and Ic).

A more plausible explanation involves an inversion of the acetate bridges as shown in Figure 2. Such a process results in the interchange of A and B, but does *not* cause interchange of Ib with Ic. The Ib–Ic exchange process could possibly be due to a π-allyl rotation but more probably involves a bimolecular interaction of $[Pd_2(OAc)_2(C_3H_5)_2]$ molecules, similar to that observed for bridged halide exchange in allylpalladium halides[7] and/or dissociation of a palladium acetate bond. Below $-25°$ the resonances due to allylpalladium acetate are unaffected by the addition of allylpalladium chloride. However at 30° such a system gives rise to a single AA'BB'X spectrum consistent with bridging ligand exchange reactions. Addition of weak bridge splitting ligands such as acetic acid or dimethyl sulfoxide to solutions of allylpalladium acetate result in an increase in the rates of the exchange processes.

In view of the catalytic activity of allylic palladium acetate systems, the nondynamic nature of the π-allyl–palladium bond is surprising. Further studies of

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[3] Ia and Ic have a plane of symmetry bisecting the Pd–Pd axis; Ib does not.

[4] Similar temperature dependence of isomer ratios has been observed during nmr studies of bisallylnickel(II): J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc., A*, 423 (1967); H. Bonnemann, B. Bogdanovic, and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **6**, 804 (1967).

[5] See K. C. Ramey, D. C. Lini, and W. B. Wise, *J. Am. Chem. Soc.*, **90**, 4275 (1968), and references therein.

[6] J. W. Faller, M. J. Incorvia, and M. E. Thomsen, *ibid.*, **91**, 518 (1969), and references therein.

[7] D. L. Tibbetts and T. L. Brown, *ibid.*, **91**, 1108 (1969).

allylic palladium acetate–ligand(s) systems are being pursued with a view to elucidating the nature and reactivity of such systems in catalytic processes.

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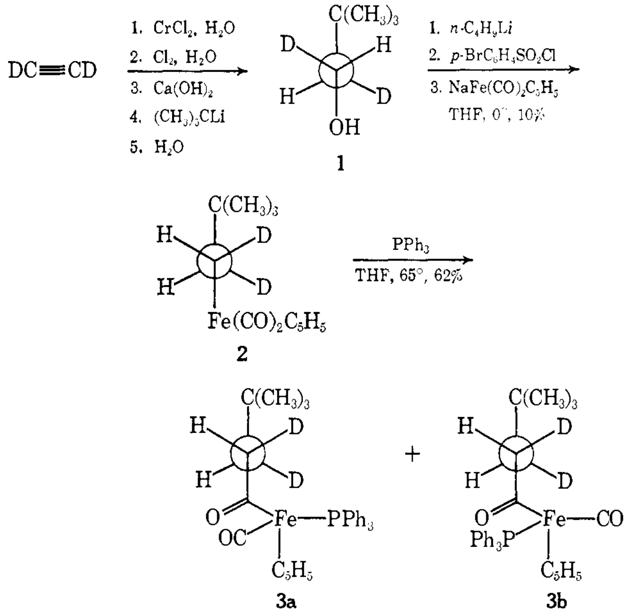
Reaction of *threo*-$(CH_3)_3CCHDCHDFe(CO)_2$-π-C_5H_5 with Triphenylphosphine[1]

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-cyclopentadienyldicarbonyliron *threo*-3,3-dimethylbutyl-1,2-d_2 (**2**) and evidence establishing that its reaction with triphenylphosphine to yield π-cyclopentadienylcarbonyltriphenylphosphineiron *threo*-4,4-dimethylpentanoyl-2,3-d_2 (**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.

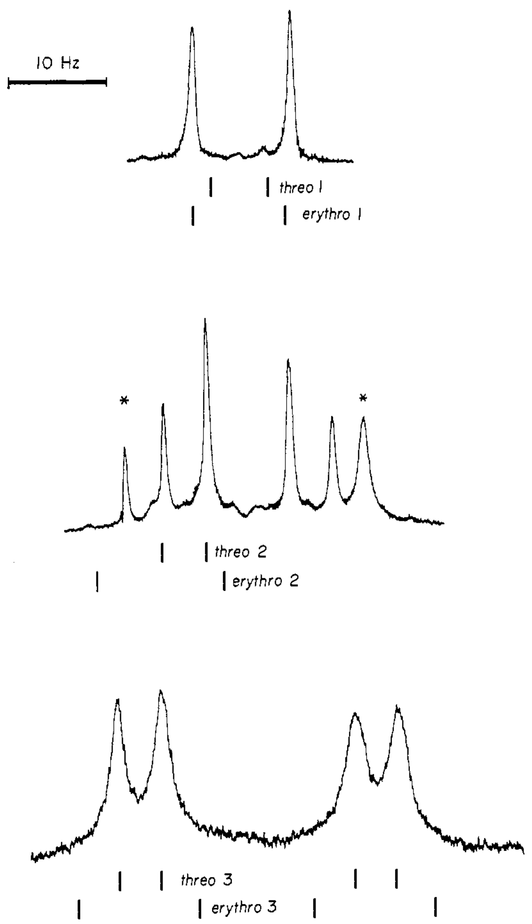


Figure 1. Deuterium-decoupled 100-MHz nmr spectra of the -C*H*DOH proton of **1**, the -C*H*DC*H*D- protons of **2**, and the -C*H*DCO- protons of **3**. The peaks marked with an asterisk in the spectrum of **2** are due to impurities. For comparison the positions of the lines characterizing the *threo* 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.

The synthesis outlined in Scheme I was used to convert acetylene-d_2 to 3,3-dimethylbutan-1-ol-1,2-d_2 (**1**).[4] The deuterium-decoupled 100-MHz nmr spectrum of the C*H*DC*H*D protons of **1** is an AX pattern with δ_A 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: $J_{erythro} = 9.5$ and $J_{threo} = 5.8$ Hz.[5] The magnitude of the coupling constant observed in the nmr spectrum of **1** confirms the *erytho* 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-d_2 produced.

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(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 $PhCH_2CH(CH_3)COMn(CO)_5$ occurs with retention of the *sign* of rotation: F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966).

(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-d_0. 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.