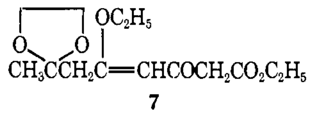
lactone **5**. Treatment of the lactone with potassium methoxide afforded ester **3b**,[5] although ester **1b** was undoubtedly an intermediate. Bram has prepared derivative **7** in which the 7- and 5-carbonyl groups were protected as the ketal and enol ether, respectively.[6] Acid treatment of **7** afforded orcinol, presumably through a process of cyclization, hydrolysis, and decarboxylation.[6] Schmidt and Schwochau[7] have synthesized hemithioketal **8** as well as the corresponding lactone.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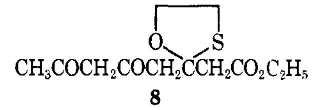
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Acknowledgment. This research was supported by Research Grant GM-12848 from the National Institutes of Health, U. S. Public Health Service.

[6] G. Bram, *Tetrahedron Letters*, 4069 (1967).

[7] U. Schmidt and M. Schwochau, *Monatsh.*, **98**, 1492 (1967).

[8] Alfred P. Sloan Fellow and Career Development Awardee, K3-GM-27013, of the National Institutes of Health, U. S. Public Health Service.

T. Trefor Howarth, George P. Murphy, Thomas M. Harris[8]
Department of Chemistry, Vanderbilt University
Nashville, Tennessee 37203
Received October 24, 1968

Organometallic Conformational Equilibria. III. The Epimerization Mechanism of π-Allyl(amine)palladium(II) Chloride Complexes[1]

Sir:

Several mechanisms have been advanced to explain the dynamic behavior responsible for the variation of the pmr spectra of a large group of π-allylmetal complexes with changes of temperature or solution composition. The averaging of the AA'BB'X spectrum of π-allylpalladium chloride dimer to an A_4X spectrum in the presence of organic phosphines and arsines has generally been attributed to rearrangement *via* a σ-bonded intermediate.[2-4] This intermediate provides a pathway for interchange of *syn* and *anti* protons;[5] however, rearrangements may occur without *syn–anti* interchange, as observed in the interconversion of isomers of π-cyclopentadienyldicarbonylmolybdenum π-allyl. A process that effectively results in the rotation of the π-allyl moiety about an allyl–molybdenum axis probably accounts for the temperature dependence of the pmr of this complex.[6-8] Racemization or epimerization of π-allyl(amine)palladium chlorides could involve either of these mechanisms, a combination of them, or possibly others; we present here our investigations of this process.

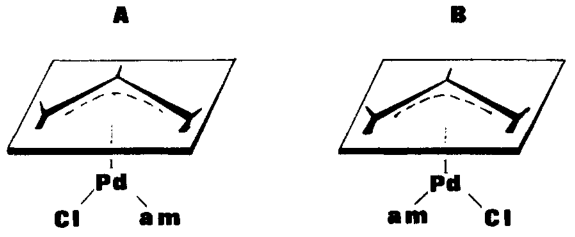

Figure 1. The enantiomers of a π-allyl(amine)palladium chloride complex.

The observation of an AA'BB'X spectrum rather than an ABCDX or A_4X spectrum for the allyl moiety in π-allyl(benzylamine)palladium chloride indicates an averaging process is occurring that interconverts the enantiomers A and B (see Figure 1), but does not involve a σ-bonded intermediate. Furthermore, preparation of the π-allyl(amine)palladium chloride from the optically active (*R*)-α-phenethylamine produces the anticipated mixture of two diastereoisomers. In the limiting low-temperature nmr two superimposed sets of ABCDX allyl resonances in a 1:1 ratio, corresponding to the two diastereoisomers, may be discerned. As the temperature is raised, the accompanying increase in proton site exchange causes broadening and coalescence of the resonances and finally produces an averaged spectrum of two superimposed AA'BB'X allyl resonances (Figure 2). Rotation of the planar allyl moiety, exchange of the amine and chloride ligands, or a planar flip of the allyl group that does not interchange *syn* and *anti* protons[12,14] (see Figure 3) could give rise to these observations. Since the chirality of the amine does not change throughout the process, the mechanisms shown in Figure 3 are all equally plausible in view of the evidence presented thus far. However, only an intermolecular exchange, which effectively averages the chirality of the amine, can account for the single AA'BB'X pattern in the averaged spectrum of the complex prepared from the racemic α-phenethylamine. Furthermore, in the low-temperature spectra of the complexes, weak resonances of the π-allylpalladium chloride dimer can be identified. The onset of broadening of the allyl resonances of the amine complex is accompanied by broadening of the dimer resonances, indicating that dissociation into dimer and

[1] Part II: J. W. Faller, *Inorg. Chem.*, in press.

[2] F. A. Cotton, J. W. Faller, and A. Musco, *ibid.*, **6**, 179 (1967).

[3] K. Vrieze, A. P. Pratt, and P. Cossee, *J. Organometal. Chem.*, **12**, 533 (1968), and references therein.

[4] J. Powell and B. L. Shaw, *J. Chem. Soc., A*, 1839 (1967).

[5] *syn* and *anti* refer respectively to the protons that are *cis* and *trans* to the proton on the central carbon atom of the allyl group.

[6] J. W. Faller and M. J. Incorvia, *Inorg. Chem.*, 7, 840 (1968).

[7] A. Davison and W. C. Rode, *ibid.*, **6**, 2124 (1967).

[8] Planar rotation of π-allyl groups has also been suggested in nickel,[9] rhodium,[10] and tris(pyrazolyl)borate molybdenum[11] complexes.

[9] H. Boennemann, B. Bogdanovic, and G. Wilke, *Angew. Chem. Intern. Ed., Engl.*, **5**, 151 (1966).

[10] J. K. Becconsall and S. O'Brien, *Chem. Commun.*, 720 (1966).

[11] S. Trofimenko, *J. Am. Chem. Soc.*, **90**, 4754 (1968).

[12] The planar flip mechanism could occur either with interchange of *syn* and *anti* sites (*via* a process similar to ring inversion in cyclohexane) or without interchange of *syn* and *anti* sites (perhaps *via* an ion pair, such that the resonance energy of the planar allyl group would not be lost). Generally these possible modes of rearrangement have not been carefully considered in transition metal rearrangements, but have been suggested as possibilities.[2,13]

[13] *Cf.* the remarks by F. A. Cotton in the discussion following the article by G. Wilke in "Proceedings of the 9th Robert A. Welch Conference on Chemical Research, November 17–19, 1965," especially p 184 ff.

[14] Since *syn* and *anti* protons are not interchanged, the rotation of the methylene groups about the carbon–carbon allyl axis, which has been suggested in some cases,[15-18] does not occur in these complexes.

[15] J. K. Becconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc., A*, 423 (1967).

[16] J. K. Becconsall and S. O'Brien, *Chem. Commun.*, 302 (1966).

[17] G. Wilke, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966).

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

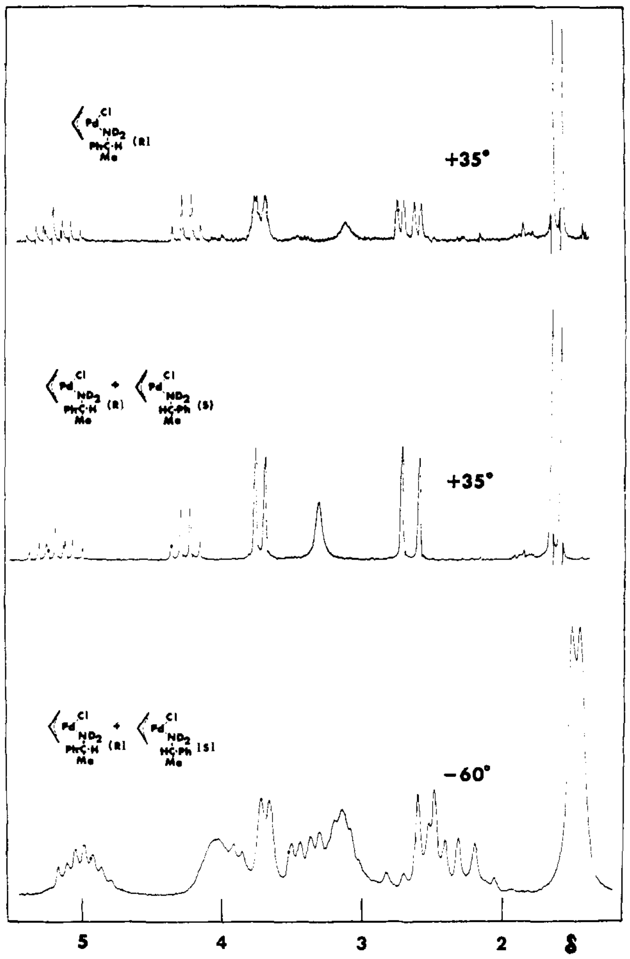

Figure 2. The 100-MHz pmr spectra of the α-phenethylamine derivatives in chloroform-d_1. The solutions have been treated with D_2O to reduce the intensity of the amino protons and simplify the spectra. At −60° the spectrum of the complexes prepared from the (*R*)-α-phenethylamine is identical with that of the complexes prepared from the racemic amine.

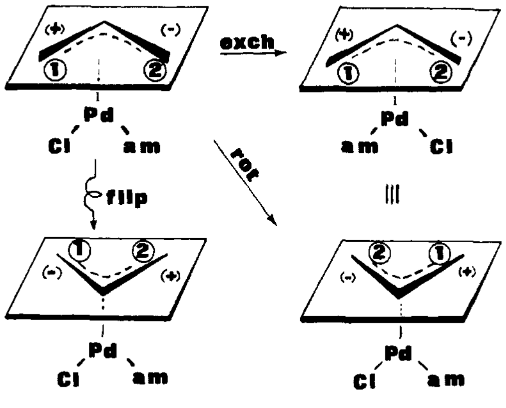

Figure 3. The mechanisms consistent with the averaging process giving rise to the 35° pmr spectrum with the (*R*)-α-phenethylamine complex. The arbitrary symbols (+) and (−) refer to the absolute configurations at the terminal allyl carbon atoms.

free amine occurs and that intermolecular amine exchange dominates proton environment interconversion throughout the accessible temperature range (up to the decomposition point ∼50°).

Having unambiguously demonstrated the existence of intermolecular ligand exchange, the possibility of additional epimerization occurring *via* a flip mechanism remains to be considered. Since the flip mechanism averages different pairs of resonances from the exchange mechanism, the simultaneous occurrence of both mechanisms would coalesce the two $AA'BB'X$ spectra in the (*R*)-α-phenethylamine complex, which is not consistent with the observed spectra.

The study of the pmr of these amine complexes up to 35° allows observation of the effects of a rapid epimerization mechanism ($k > 100$ sec^{-1} at 35°); conceivably other mechanisms with slower rates ($k < 0.5$ sec^{-1} at 35°) could contribute to epimerization, but would not alter the pmr spectrum. Our results lead us to conclude that racemization and epimerization in π-allyl(amine)palladium chloride complexes are primarily a consequence of dissociation of the compound into free amine and dimer, rather than conversion to a σ-bonded intermediate. This is rather surprising in view of the part played by the σ-bonded intermediate in phosphine and arsine derivatives. Consequently, the absence of an effect from a σ-bonded intermediate or a flip mechanism requires that the face of the π-allyl moiety bonded to the palladium atom is invariant during epimerization or racemization caused by amine exchange.[19]

Studies are being pursued to determine the implications of these results in rearrangements of substituted π-allylpalladium derivatives, as well as molybdenum π-allyls.[21,23]

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(19) The configurations at the terminal carbon atoms of the π-allyl group [*i.e.*, the chirality of the Pd—(H_2C^*⩵C) centers] are preserved during the epimerization of the unsubstituted complexes by amine exchange. Inversion of configuration at the terminal carbon atoms *via* a σ-bonded intermediate has been proposed as the most likely mechanism of epimerization in substituted π-allyl derivatives.[20] For the unsubstituted compounds reversible broadening of the *syn* and *anti* resonances (as well as decomposition) is observed in benzene solution above 50°, and this does indeed support an additional epimerization pathway *via* a σ-bonded intermediate. Nevertheless, this mechanism, which allows a different face of the allyl group to become bonded, does not contradict the previous conclusions, since it proceeds at a much slower rate ($k < 0.5$ sec^{-1} at 35°).

(20) P. Corradini, G. Maglio, A. Musco, and G. Paiaro, *Chem. Commun.*, 618 (1966).

(21) The absence of a flip mechanism gives further support to a planar rotation mechanism in molybdenum π-allyl rearrangements. Presumably the ability to undergo facile 3:4 ⇌ 3:3:1 ⇌ 3:4 stereochemically nonrigid rearrangements[22] in this "seven-coordinate" complex might allow the effective planar rotation of the π-allyl, which has not yet been observed in the palladium complexes due to the prior occurrence of exchange.

(22) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

(23) We wish to acknowledge the financial support of the Connecticut Research Commission and The Petroleum Research Fund administered by the American Chemical Society. We wish to thank the National Science Foundation for Grant GP-6938 which allowed the purchase of the Varian HA-100 spectrometer.

J. W. Faller, M. J. Incorvia, M. E. Thomsen
Department of Chemistry, Yale University
New Haven, Connecticut 06511

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Stereochemical Course of the Reaction of an Optically Active Hydrosilane with Carbon Tetrachloride by a Free-Radical Mechanism. Retention of Configuration[1]

Sir:

When free radicals are generated from compounds containing an asymmetric carbon atom, which bears the

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(1) Silyl Radicals. II.