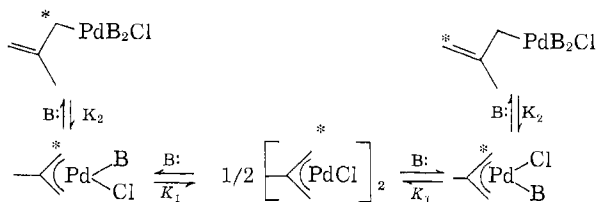equilibration of structures "intermediate between π- and σ-methallyl with carbon atoms only weakly bonded to the palladium."[6]

More complex equilibria or the specific details of particular pathways might be envisaged, but an effective switching of base and halogen, as in the k_1 equilibria, would produce the observed $ABCDX_3 \rightarrow A_2B_2X_3$ coalescence. Equilibria involving a σ-methallyl (K_2) suggests a rationale for the $A_2B_2X_3 \rightarrow A_4X_3$ coalescence.[12]

Similar arguments can be proposed for crotyl complexes; however, these present a more involved problem due to possible isomeric attachment of both the π-crotyl and the σ-butenyl. Either or both σ-butenyl forms provide a pathway for equilibration of the *syn* and *anti* protons in the observed $ABCDX_3 \rightarrow ABC_2X_3$ coalescences (Table IV). The absence of additional resonances at a temperature of $-50°$ suggests that the 1:1 triphenylphosphine adduct with π-crotylpalladium chloride is extensively in the form of one isomer. The phosphorus coupling to the methyl protons, as well as the broadness of the H_d resonance, suggests that the predominant isomer has the methyl group *trans* to the triphenylphosphine.[13,14] Again at high temperatures the well-resolved spectra show no evidence for averaged phosphorus coupling implying that exchange is occurring. Since the chemical shift of proton d does not change appreciably during coalescence of any of the crotyl spectra, in Table II, it does not seem likely that the major species in solution is a σ complex (this contention is supported by the infrared spectra) and that an end-for-end exchange accounts for the observed spectra. However, if the π-bonded complex is the major species, a sufficiently rapid equilibrium with a very small percentage of σ-butenyl would provide a pathway for an equilibration of environments compatible with the observed spectra.[15]

Since dynamic allyl spectra have not been found in the absence of basic ligands with palladium, it seems likely that the equilibria above are responsible for, as well as consistent with, all of the presently available

(12) The behavior of the *syn* and *anti* proton resonances of allylpalladium chloride with a Pd : P(C₆H₅)₃ ratio of 1 : 1 is similar to that in the published spectra of the methallyl complex;[5] however, the intermediate collapse to two resonances is not so evident. Nevertheless, the greater resolution obtained in the spectra of this complex allows a more detailed interpretation of the spectra. The basis of the assignments of the resonances to individual protons has been outlined previously,[4] and confidence in this assignment is further strengthened by the observation that J_{ad} in the π-allyl complex is a representative *trans* coupling constant (Table III). In particular, the absence of averaged phosphorus coupling in the higher temperature spectra and during the initial stages of coalescence in both the methallyl and allyl complexes implies that dissociation or transfer of the triphenylphosphine has occurred.

(13) Presumably *syn* and *anti* forms of the crotyl are possible, but *syn* forms are generally more stable,[14] and in view of the magnitude of the coupling constants, the *syn* isomer is most probable.

(14) J. A. Bertrand, H. B. Jonassen, and D. W. Moore, *Inorg. Chem.*, **2**, 601 (1963).

data on palladium allyl, methallyl, and crotyl complexes. Consequently, it is proposed that the temperature-dependent nmr spectra of the complexes in Table II (save perhaps $Zn(allyl)_2$[16–21]) are manifestations of equilibrium exchange processes.[22]

(15) In order to demonstrate further the nature of the intermediates in these averaging processes, we attempted to obtain low-temperature nmr spectra in dimethyl sulfide solutions since lower temperatures could be reached than with DMSO; however, no evidence for a σ-bonded complex was observed. Studies of the σ complexes formed with excess triphenylphosphine were thwarted by rapid decomposition in concentrated solutions to yield $Pd((C_6H_5)_3P)_2Cl_2$. The coalescence temperatures were lowered with additional triphenylphosphine, and more complex spectra were noted at low temperatures; however, interpretation of these spectra in view of the uncertainties regarding the species remaining in solution and the possibility of isomers in the crotyl case requires more information and courage than is presently available.

(16) In $Zr(allyl)_4$ Becconsall and O'Brien,[4] as well as Wilke,[2] propose that the temperature dependence of the nmr spectrum is due to rotation of the CH_2 about the C–C bond. One might also propose a mechanism involving a flip through a planar intermediate.[17] Even rotation about an axis perpendicular to the C–C–C plane could be invoked to explain some of the palladium allyl spectra.[17a] It has been proposed in particular that rotation is responsible for the temperature-dependent nmr in the palladium allyl system.[4] The evidence presented here does not imply that these mechanisms do not occur, but only that, in Pd complexes, equilibria are primarily responsible for the temperature dependence, whereas in the Zr case such mechanisms may play a major role. In addition, the available crystal structures[18–21] of π-allyl complexes have shown the lengths of the C–C bonds of the π-allyl portion to be equal within three standard deviations of the reported error, apparent differences being readily attributable to adventitious packing distortions. Therefore, there appears at present to be no need for the recent resurrections[5,6,18] of localized double bonds in π-allylic complexes. Indeed, to describe[6] the rather small distortion of the C_3H_5Pd geometry from the symmetrical form it has in $[C_3H_5PdCl]_2$ to that[18] which it has in $C_3H_5PdClP(C_6H_5)_3$ as a complete change to the extreme

$$\underset{Pd}{\overset{C=C——C}{\diagdown\;\diagup}}$$
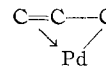
form seems very unwise. Such a bond structure is actually geometrically impossible, because if the Pd lies in a suitable position to form a decent μ bond, it is far away from the right location to form a σ bond to an sp³ orbital of the other carbon atom and *vice versa*. The definite but relatively small dissymmetry which results from the presence of two different ligands, Cl and $P(C_6H_5)_3$, opposite to the π-allyl group can be properly described in terms of small perturbations of a molecular orbital description of the unperturbed, symmetrical C_3H_5Pd moiety.

(17) *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, Nov 15–17, 1965," especially p 184 ff.

(17a) NOTE ADDED IN PROOF.—Very recently, a case in which just such a rotation must evidently be invoked has been reported: J. K. Becconsall and S. O'Brien, *Chem. Commun.*, 720 (1966).

(18) R. Mason and D. R. Russell, *ibid.*, 26 (1966).

(19) A. E. Smith, *Acta Cryst.*, **18**, 331 (1965).

(20) W. E. Oberhansli and L. F. Dahl, *J. Organometal. Chem.* (Amsterdam), **3**, 43 (1965).

(21) M. R. Churchill and R. Mason, *Nature*, **204**, 777 (1964).

(22) Research supported by the National Science Foundation.

(23) NSF Predoctoral Fellow, 1963–1966.

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RECEIVED AUGUST 12, 1966

Stereochemically Nonrigid Organometallic Compounds. V. Configurational Equilibria in Bis(acetylacetonato)tin Complexes

Sir:

Recently Kawasaki and Tanaka have cited nmr evidence, in particular two distinct methyl resonances, for an equilibria between localized double bonds in

acetylacetonates,[1] implying an isolated existence of structures Ia and Ib. Since this represents the unexpected effective isolation of the canonical resonance forms of the commonly described structure (II), closer examination of the experimental evidence seems in order.

Ia　　⇌　　Ib　　　　　II
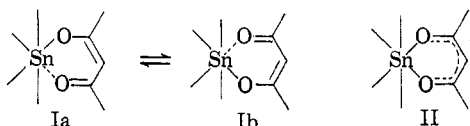
If $SnCl_2(acac)_2$ were *trans* and symmetrical bonding (as in II) were obtained, the compound would have D_{2h} symmetry and all of the methyl groups would be equivalent.[2,3] However, the coincident bands in the infrared and Raman spectra (Table I), particularly

TABLE I

THE INFRARED AND RAMAN SPECTRA OF $SnCl_2(acac)_2$ FROM 250 TO 1400 CM^{-1} [a]

Infrared		Raman	
Solution (CHCl₃)	Solid (Nujol)	Solid	Solution (CH₂Cl₂)
340 m, b	335 m	337 m	344 m, pol
415 m[b]	{413 m / 420 m}	~414 vw	
457 m	460 m	460 s	459 s, pol
~555 w	553 w	~553 vw	~557 w
~588 m	590 m		
647 w	647 w		
c	682 m	683 w	c
c	807 m		
938 s	936 s	940 w	941 m
1024 s	1020 s	~1022 vw	~1029 w
~1155 vw	~1150 w	1152 w	1159 w
c	~1200 w	1197 vw	1196 w
1284 s	1284 s	1288 s	1288 s, depol
1347 sh	1340 s		
1363 s, b	1370 s	1367 s	1371 s, depol

[a] Spectra were obtained using a Perkin-Elmer 521 infrared spectrometer and a Cary 81 Raman spectrometer. Data are given in cm^{-1} followed by an indication of intensity. The following abbreviations are used: s, strong; m, medium; w, weak; vw, very weak; b, broad; sh, shoulder; pol, polarized; depol, depolarized. [b] Under higher resolution, two shoulders are resolved giving absorptions at 410, 414, and 418 cm^{-1}. [c] Presumably these bands are obscured by solvent absorption.

those in the low-frequency region attributable to tin–oxygen[4] and tin–chlorine[5] vibrations, imply the absence of a center of inversion and consequently the C_2 symmetry of *cis*-$SnCl_2(acac)_2$. This *cis* structure (III) has two sets of nonequivalent methyl groups (A and B) which has lead to a previous proposal of the *cis* isomer on the basis of nmr evidence alone.[6]

With the evidence overwhelmingly in favor of the *cis* structure, the collapse of the two methyl resonances to the single signal observed at higher temperatures (Table II) is then explicable by conversion of one
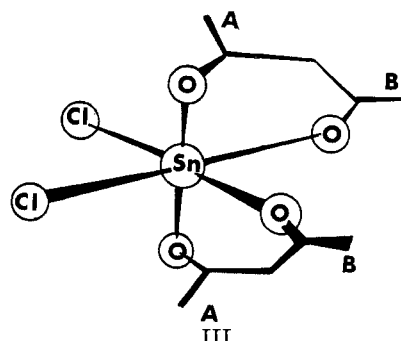
(1) Y. Kawasaki and T. Tanaka, *J. Chem. Phys.*, **43**, 3396 (1965).
(2) Although occasional reports have suggested the contrary in similar complexes,[3] current nmr, Raman, and infrared evidence indicates that, particularly in the absence of basic ligands, the principal species in solution contain chelated acetylacetonyl moieties.
(3) W. P. Neumann and F. G. Kleiner, *Tetrahedron Letters*, 3779 (1964).
(4) M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).
(5) P. Taimsalu and J. L. Wood, *Spectrochim. Acta*, **20**, 1043 (1964).
(6) J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965).

III

TABLE II

CHEMICAL SHIFTS AND COUPLING CONSTANTS (CPS) IN $SnCl_2(acac)_2$ IN $CDCl_3$[a]

Temp, °C	τ(CH₃)	τ(CH)	J(Sn–CH₃)	J(Sn–CH)
40	7.82, 7.90	4.27	6.6, 5.8	5.8
140	7.86	4.27	6.1	5.8

[a] High-temperature spectra were obtained using sealed tubes on a Varian A-60 nmr spectrometer equipped with a variable-temperature probe. The 40° spectrum is essentially the same as that previously reported.[1,6] The two principal methyl absorptions coalesce at ~90°.

enantiomer of III to the other at a rate which is fast on the nmr time scale. This effective path of racemization, rather than a "rapid exchange of somewhat localized double bonds,"[1] would account for the difficulties experienced in attempts to resolve similar β-diketone complexes of tin.[7]

Some insight into the mechanism causing the collapse can be gained by following the tin–proton coupling. Coupling to the γ-proton is observed before, during, and after the coalescence of the methyl protons. Averaged coupling to the methyl protons is observed at high temperatures (Table II). These observations require that a given acetylacetonate must be attached to the same Sn atom before and after whatever configurational change occurs, which causes the averaging. Hence, a nondissociative mechanism is preferred. For instance, a "twist" mechanism *via* a C_{2v} intermediate, if occurring rapidly enough, would cause apparent equivalence of the acetylacetonate methyl groups. Also conversion to a five-coordinate intermediate, having a monodentate acetylacetonate group, may account for the temperature dependence.[8,9] Presumably a *trans* form in equilibrium with the *cis* could provide a pathway for averaging of the methyl groups; however, the conversion of this type would require more extensive reorientation of the ligands about the central atoms. Reference to the infrared spectra at 30 and 60° suggests that it is unlikely that the *trans* structure is the predominant form in solution and re-

(7) W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 89 (1965).
(8) In principle, these can be distinguished, since this twist mechanism permutes nuclei only between two rather than four environments in complexes of the type $SnYZ(acac)_2$; however, the presently available spectra are not sufficiently well resolved at high temperatures to make the choice between the twist and five-coordinate alternatives.
(9) The addition of acetone to the solution does not appreciably affect the coalescence temperature, indicating that in weakly basic solvents, at least, a six-coordinate intermediate with a free acetyl is not found. Also, attempts to isolate a *trans* complex from the hot solutions were unsuccessful.

Inorganic Chemistry

peated attempts to isolate a *trans* form by rapid cooling were unsuccessful. Consequently, the coalescence observed is not likely to be the result of a *cis–trans* configurational equilibrium with a ΔH such that the configuration is predominantly *trans* above and predominantly *cis* below a narrow range of 15°.

Considering that the averaging in $SnCl_2(acac)_2$ is probably due to interconversion of *cis* forms, additional evidence would be necessary to provide convincing arguments and proof of localized bonding in acetylacetonates. In addition, the alleged barrier to C_6H_5–Sn internal rotation of 3 kcal suggested in C_6H_5–Sn-$(acac)_2$ probably represents the activation energy of *cis* interconversion. For instance, in $C_6H_5ClSn(acac)_2$ the four distinct methyl resonances that are observed can be attributed to nonequivalence of all of the methyls in the C_1 structure having type-II bonding without resort to bond localization of, hindered rotation of, or anisotropic magnetic effects of the phenyl group.

Although configurational equilibria between *cis* and *trans* forms have been invoked to explain the tempera-

ture dependence of $alkylSn(acac)_2$ halides,[10] a *cis* interconversion presents an explanation more consistent with the data. The γ-proton resonance attributed to the *trans* complex in the presence of the *cis* isomer is probably the result of overlap of tin–proton splittings. This point is borne out by the absence of a corresponding resonance attributable to the methyl peaks of the *trans* compound.

Consequently, in view of the alternative explanations in terms of *cis* interconversions, data from one type of physical measurement should be interpreted with extreme caution and with the aid of other physical techniques, particularly variable-temperature infrared and ultraviolet spectra.[11]

(10) Y. Kawasaki, T. Tanaka, and R. Okawara, *Inorg. Nucl. Chem. Letters*, **2**, 9 (1966).
(11) This work was supported by the National Science Foundation.
(12) National Science Foundation Predoctoral Fellow, 1963–1966.

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