purify adduct samples consisted of pumping for 1–2 hr, it is probable that varying amounts of excess AsF_5 were absorbed on the solid surfaces.

Infrared Spectrum.—Infrared spectra were obtained by pressing powder samples between AgCl optical plates. The samples were examined from 2 to 20 μ with a Perkin-Elmer Model 521 grating spectrometer. The infrared spectrum shows a very strong, broad absorption centered at 695 cm^{-1}, which suggests the presence of hexafluoroarsenate ion.[2] In addition, there are three strong peaks at 922, 1100, and 1295 cm^{-1} which are comparable to absorptions reported by Ruff[1] for the adduct of tetrafluorohydrazine with antimony pentafluoride. There is also a sharp peak of medium intensity at 1500 cm^{-1}.

X-Ray Diffraction Pattern.—Powder diffraction patterns of adduct samples sealed under nitrogen in Pyrex capillaries were photographed using Cu Kα radiation from an Ni filter. The diffraction lines were indexed on a cubic unit cell, $a_0 = 10.8$ A. The principal diffraction lines at 5.37, 4.45, and 3.39 A distinguish the adduct from N_2FAsF_6,[3] another possible reaction product of N_2F_4 with arsenic pentafluoride. Similarly, the pattern clearly shows no indication of the presence of oxygen-containing impurities such as NO_2AsF_6[3] and $NOAsF_6$.[4]

F^{19} Nmr Spectrum.—The F^{19} nmr spectrum of the adduct was obtained on a Varian HR-60 spectrometer at ambient temperature using 25–30% solutions in anhydrous HF. Kel-F tubes were used as sample holders. The chemical shifts of the NF fluorines were observed relative to the HF fluorine and then referred to $CFCl_3$ by a substitution technique. The spectrum shows three very broad (approximately 1000 c) absorptions at ϕ −122, −146, and −180, respectively. The areas under the peaks are virtually identical (1.09:1.09:1.04). As in the case of N_2FAsF_6, no fluorine on arsenic signal was observed because of solvent exchange with the As–F species.[3]

Discussion

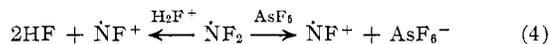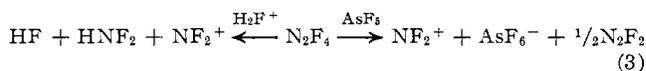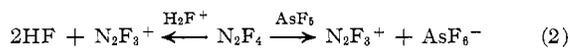**Probable Constitution of NF Species in the Adduct.**—The presence of a strong absorption at 695 cm^{-1} in the infrared spectrum of the adduct suggests that the adduct may be ionic, since this absorption has the shape and frequency characteristic of the ν_3 fundamental of the octahedral AsF_6^- ion. There are three possible NF cations obtainable from N_2F_2 or NF_2 by a single fluoride ion transfer to AsF_5 or $H_2F^+AsF_6^-$ (in the case of preparation of the adduct in HF), namely, $N_2F_3^+$, NF^+, and NF_2^+ (eq 2, 3, and 4). Of these, only

(2) R. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1959).
(3) D. Moy and A. R. Young, II, *J. Am. Chem. Soc.*, **87**, 1889 (1965).
(4) A. R. Young, II, T. Hirata, and S. I. Morrow, *ibid.*, **86**, 20 (1964).

an $N_2F_3^+$ cation is consistent with the observed F^1 nmr and infrared spectra, both of which suggest the presence of a nitrogen-to-nitrogen linkage.

$$2HF + N_2F_3^+ \xleftarrow{H_2F^+} N_2F_4 \xrightarrow{AsF_5} N_2F_3^+ + AsF_6^- \quad (2)$$

$$HF + HNF_2 + NF_2^+ \xleftarrow{H_2F^+} N_2F_4 \xrightarrow{AsF_5} NF_2^+ + AsF_6^- + \tfrac{1}{2}N_2F_2 \quad (3)$$

$$2HF + \dot{N}F^+ \xleftarrow{H_2F^+} \dot{N}F_2 \xrightarrow{AsF_5} \dot{N}F^+ + AsF_6^- \quad (4)$$

The F^{19} nmr spectrum shows three nonequivalent N–F fluorines, as one would predict for an $N_2F_3^+$ species, in which one of the "NF_2" fluorines is *cis* and the other is *trans* with respect to the "NF" fluorine (structure I). The observed broadness of the peaks may be

I
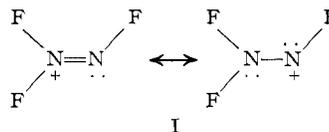
due to *cis*-, *trans*-, and *gem*-fluorine–fluorine couplings, on which the effect of fluorine–nitrogen coupling is superimposed, thus giving three sets of lines which are unresolvable at 60 Mc.

The infrared spectrum of the solid is readily interpreted in terms of structure I. The three strong, sharp absorptions at 922, 1100, and 1295 cm^{-1}, respectively, may reasonably be assigned to NF stretching vibrations of an $N_2F_3^+$ cation. (The recently reported ONF_2^+ ion[5] has NF stretching vibrations at 895 and 1150 cm^{-1}.) Furthermore, the presence of a medium-intensity peak at 1500 cm^{-1} is not inconsistent with the postulated structure (I), since this is just below ($\sim$20 cm^{-1}) the range of observed N=N stretching frequencies.[6,7]

(5) N. Bartlett and J. Passmore, *Chem. Commun.*, 213 (1966).
(6) R. H. Sanborn, *J. Chem. Phys.*, **33**, 1855 (1960).
(7) J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, 919 (1954).

Correspondence

Stereochemically Nonrigid Organometallic Compounds. IV. Some Observations on π-Allylic Complexes

Sir:

Allyl Grignard reagents give rise to an A$_4$X nmr spectrum at room temperature owing to an interconversion which is rapid on the nmr time scale.[1] A$_4$X spectra in π-allyl transition metal complexes[2,3]

and comparable spectra of some crotyl complexes consistent with rapid interconversion have been considered diagnostic for a so-called dynamic allyl. Upon sufficient cooling, a spectrum of a static, rigidly bound π-allyl is often observed. Much speculation and discussion have arisen concerning the interconversions which are responsible for the coalescence of the static π-allyl resonances to the more simple spectrum of a dynamic

(1) G. M. Whitesides, J. E. Norlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962).

(2) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroener, W. Oberkirch, K. Tanaka, and D. Walter, *Angew. Chem. Intern. Ed. Engl.*, **5**, 151 (1966).
(3) J. C. N. Chien and H. C. Dehm, *Chem. Ind.* (London), 745 (1961).

allyl on raising the temperature. Internal rotation[2,4] and σ–π-bond fixation[5,6] have been suggested for palladium complexes and similar stereochemical nonrigidity also proposed[2] for zirconium and thorium allyls. The conflicting interpretations of the nmr data concerning π-allyl and π-crotyl complexes of palladium prompt us to present additional data concerning equilibria in these systems.

Equilibria 1 and 2 have been suggested by cryoscopic and dipole moment measurements[7] and are supported by nmr and infrared data; however, conversion to a σ-bonded complex and the suggested nature of the intermediates have been questioned by Becconsall and O'Brien.[4] Nevertheless, the disappearance of coordinated allyl and the appearance of uncoordinated olefin absorption in the infrared spectra (Table I) of

TABLE I

OLEFIN ABSORPTION IN π-ALLYL INFRARED SPECTRA[a]

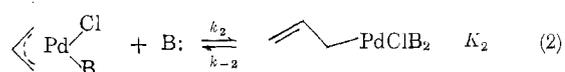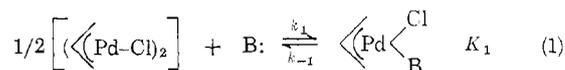|	B:	Molar ratio, B:Pd	C=C	π-Allyl
$\left[\text{ < PdCl}\right]_2$	...	0	...	1458 m
$\left[\text{ < PdCl}\right]_2$	$(C_6H_5)_3P$	1:1	...	1458 m
$\left[\text{ < PdCl}\right]_2$	$(C_6H_5)_3P$	2:1	~1630 w	1458 vw
$\left[\text{ < PdCl}\right]_2$	$(CH_3)_2S$	3:1	(~1611 vw)[c]	1458 m
$\left[\text{ > PdCl}\right]_2$	...	0	...	~1500 m
$\left[\text{ > PdCl}\right]_2$	$(C_6H_5)_3P$[b]	1:1	...	1527 m[d]
$\left[\text{ > PdCl}\right]_2$	$(C_6H_5)_3P$	2:1	e	1527 vw
$\left[\text{ > PdCl}\right]_2$	DMSO	>20:1	(~1650 vw)[c]	1508 m
$\left[\text{ > PdCl}\right]_2$	$(CH_3)_2S$	>20:1	(~1615 vw)[c]	1512 m
$< \text{Mn(CO)}_4$	(ref 9)		...	1505
$/\!\!-\text{Mn(CO)}_5$	(ref 9)		1620	...

[a] Spectra were obtained in chloroform solutions and frequencies are reported in cm^{-1} followed by an indication of relative intensity. CH vibrations indicative of free vinyl are not easily distinguishable owing to overlap of other absorptions. Abbreviations are: DMSO, dimethyl sulfoxide; m, medium; w, weak; vw, very weak. [b] The 1:1 adduct was isolated as the crystalline material before solutions were prepared. [c] These very weak absorptions are tentatively assigned to olefin stretching; however, possible ligand absorption perturbed by coordination may be the origin. Regardless, the spectra indicate that the π-allylic rather than σ-allylic form is predominant. [d] No change in the 1450–1700-cm^{-1} range was observed on warming to ~65°. [e] A weak absorption at ~1625 cm^{-1} is observed, but a higher frequency band may be obscured by ligand absorption.

several allylpalladium complexes in the presence of increasing concentrations of triphenylphosphine clearly demonstrate that a σ-allyl is being formed. The data in Table I indicate that equilibrium 2 lies far to the right with $(C_6H_5)_3P$. With dimethyl sulfoxide and di-

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

(5) G. L. Statton and K. C. Ramey, *J. Am. Chem. Soc.*, **88**, 1327 (1966).

(6) J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Commun.*, 78 (1965).

(7) I. I. Mosieev, E. A. Fedorovskaya, and Ya. K. Syrkin, *Zh. Neorgan. Khim.*, **4**, 2641 (1959). Quoted in ref 3.

TABLE II

NMR TEMPERATURE DEPENDENCE OF π-ALLYL COMPLEXES

	Solvent[a]	Coalescence to dynamic spectrum[b]	Ref
$\left[\text{ < PdCl}\right]_2$	$CHCl_2CHCl_2$	~150°[d]	c
$\left[\text{ < PdCl}\right]_2$	$CDCl_3$ + DMSO	+15°–+60°[e]	c
$\left[\text{ < PdCl}\right]_2$	DMSO	<25°	4
$< \text{PdCl}(P(C_6H_5)_3)$	$CDCl_3$[f]	~70°	c
$\left[\text{ < Pd(dipy)}\right]Cl$	H_2O + DMSO (excess)	~90°	c
$-< \text{PdCl}(P(C_6H_5)_3)$	$C_6H_4Cl_2$	~100°	5
$\left[\text{ > PdCl}\right]_2$	$CDCl_3$ + DMSO	+15°–+70°[e]	5
$\left[\text{ > PdCl}\right]_2$	DMSO	~15°	c
$\left[\text{ > PdCl}\right]_2$	$CDCl_3$ + $(CH_3)_2S$ (2:1)	~35°[e]	c
$> \text{PdCl}(P(C_6H_5)_3)$	$CDCl_3$	~60°	c
$< \text{Mn(CO)}_4$	C_6H_6[f]	>180°	c
$< \text{Mn(CO)}_4$	DMSO[g]	>120°	c
$Zn(C_3H_5)_2$	THF	~ −100°	2

[a] Values in parentheses refer to molar ratio of solvents to Pd; also excess = >10:1 solvent:Pd ratio. [b] The complexities of these spectra often make the term coalescence ambiguous; consequently, the temperatures quoted are probably accurate to ±20°. > and < implies coalescence was not observed. In the case of crotyl complexes, coalescence refers to the *syn* and *anti* protons b and c. In the methallyl, it refers to the coalescence of all four *syn* and *anti* protons. [c] This work. [d] An irreversible decomposition to Pd metal leaves free chloride. [e] Depends on concentration of basic solvent over the range studied here. [f] Temperature above the boiling points achieved by use of sealed tubes. [g] Decomposition results at or above these temperatures.

$$1/2\left[\left(\text{ < Pd–Cl}\right)_2\right] + \text{B: } \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left(\text{Pd} \overset{Cl}{\underset{B}{<}}\right) \qquad K_1 \qquad (1)$$

$$\left(\text{ < Pd} \overset{Cl}{\underset{B}{<}}\right) + \text{B: } \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{ } /\!\!\!\!\diagdown\!\!\!\diagup\!\!\!-\text{PdClB}_2 \qquad K_2 \qquad (2)$$

methyl sulfide it lies to the left, but there are implications that the equilibrium 2 does exist, albeit K_2 is small.

Reference to several representative complexes in Table II indicates that a basic ligand is necessary to produce a dynamic allyl spectrum in palladium allyls. Allyl palladium chloride shows the resolved peaks attributed to a static π-allyl until it begins to decompose. Furthermore, π-allylmanganese tetracarbonyl, even in DMSO solution, never shows signs of imminent collapse up to the decomposition point. In fact, the rarely observed coupling between the *syn* and *anti*[8–11] protons is quite evident at a temperature of 160° (Figure 1).

(8) *syn* and *anti* (for example, c and b, respectively, in Table III) define placement relative to the substituent on the central carbon atom, as previously defined.[9] Coupling of *syn* and *anti* protons has apparently been previously observed only in 2-chloroallylpalladium complexes.[10,11] The splitting suggests that the first-order coupling constants J_{AB} and J_{AB}' are both equal to 1.2 cps. Though it is not certain, comparison with published AA'BB'X spectra indicate that a second-order interpretation is not necessary.

(9) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

(10) M. S. Lupin and B. L. Shaw, *Tetrahedron Letters*, 883 (1964).

(11) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, **2**, 325 (1964).
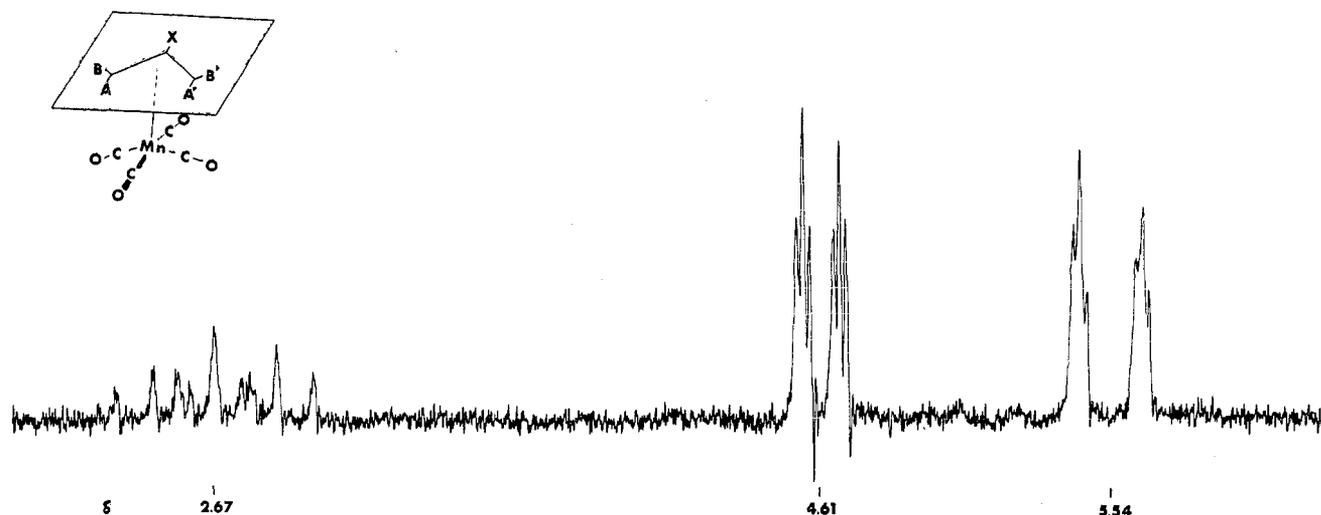
Figure 1.—The nmr spectrum of π-allylmanganese tetracarbonyl at 160°. The chemical shifts are given as ppm above the solvent benzene. They are assigned as follows: X, 2.67 ($\tau \sim 5.3$); B, 4.61 ($\tau \sim 7.2$); A, 5.54 ($\tau \sim 8.2$). The splittings are indicative of the following coupling constants (cps): $J_{AB} = J_{A'B'} = J_{A'B} = J_{AB'} = 1.2$; $J_{AX} = J_{A'X} = 12.0$; and $J_{BX} = J_{B'X} = 7.0$.

TABLE III

NMR PARAMETERS OF ALLYL AND METHALLYL PALLADIUM COMPLEXES IN CDCl₃[a]

R	Temp, °C	Chemical shift, τ					Coupling constants, cps				
		a	b*	c*	d	e	J_{ab}	J_{ad}	J_{bP}	J_{cP}	J_{aP}
CH₃	−20	8.05	6.41	5.48	7.21	7.15			10	6	
CH₃	+60		(bd) 6.81		(ce) 6.28						
CH₃	140			($\sim$6.5)							
H	−50	4.42	6.38	5.30	7.27	7.08	12	12	11	$\sim$7	$\sim$1–4
H	+70	4.5	Broad	5.5	Broad		10				0
H	+100	4.5		6.7			(10)				

[a] The methallyl data are taken from the original work of Statton and Ramey;[5] however, for comparison and consistency with Table IV, the labeling of protons here has been altered, but the assignment of the protons to a given resonance remains the same.

TABLE IV

NMR PARAMETERS OF CDCl₃ SOLUTIONS OF CROTYLPALLADIUM CHLORIDE IN THE PRESENCE OF BASIC LIGANDS

B	B:Pd	Temp, °C	Chemical shift, τ					Coupling constants, cps				
			a	b	c	d	e	J_{ab}	J_{ac}	J_{ad}	J_{de}	J_{eP}
(CH₃)₂S	2:1	−30	4.77	7.32	6.38	6.13	8.68	12.0	6.8	12.3	6.5	
(CH₃)₂S	2:1	+120	4.83	6.83		6.18	8.63		9.6	10.3	6.2	
DMSO	2:1	0	4.44	6.88	5.92	5.81	8.46	12	7	12	7	
DMSO	>20:1	90	4.34	6.37		5.73	8.50		10	10	6	
P(C₆H₅)₃	1:1	0	4.67	7.32	7.14	5.55	8.18	12	7	...	6	7
P(C₆H₅)₃	1:1	90	4.72	7.26		5.67	8.28		9	12	6	$\sim$0

Equilibria 1 and 2 involving these basic ligands could produce the spectral changes observed with increasing temperature merely by an increase in rate constants k_1, k_{-1}, k_2, and k_{-2}. A π-allyl form could be 99% predominant and, though not required, no appreciable increase in the concentration of any components would be necessary, for the small percentages of the remaining species would provide the pathways for averaging of environments. The somewhat more complex temperature dependence of the triphenylphosphine adduct of methallylpalladium(II) chloride can be rationalized by the following equilibria without resorting to an

equilibration of structures "intermediate between π- and σ-methallyl with carbon atoms only weakly bonded to the palladium."[6]
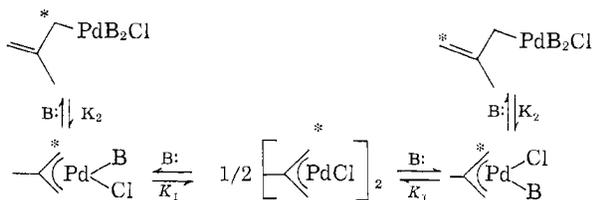
More complex equilibria or the specific details of particular pathways might be envisaged, but an effective switching of base and halogen, as in the k_1 equilibria, would produce the observed $ABCDX_3 \rightarrow A_2B_2X_3$ coalescence. Equilibria involving a σ-methallyl (K_2) suggests a rationale for 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((C₆H₅)₃P)₂Cl₂. 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 CH₂ 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 structures¹⁸⁻²¹ 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 resurrections⁵,⁶,¹⁸ of localized double bonds in π-allylic complexes. Indeed, to describe⁶ the rather small distortion of the C₃H₅Pd geometry from the symmetrical form it has in [C₃H₅PdCl]₂ to that¹⁸ which it has in C₃H₅PdClP-(C₆H₅)₃ as a complete change to the extreme

$$C=C\text{----}C$$
$$\diagdown \quad \diagup$$
$$Pd$$
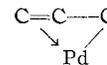
form seems very unwise. Such a bond structure is actually geometrically impossible, because if the Pd lies in a suitable position to form a decent μ bond, it is far away from the right location to form a σ bond to an sp³ orbital of the other carbon atom and *vice versa*. The definite but relatively small dissymmetry which results from the presence of two different ligands, Cl and P(C₆H₅)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 C₃H₅Pd 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.

(24) Fellow of the F. Giordani Foundation, Rome, 1965–1966.

DEPARTMENT OF CHEMISTRY   F. A. COTTON
MASSACHUSETTS INSTITUTE OF TECHNOLOGY   J. W. FALLER[23]
CAMBRIDGE, MASSACHUSETTS 02139   A. MUSCO[24]

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