and the other Br the apex. The set of basal ligands are not coplanar. Bis(N-β-diethylaminoethyl-5-chlorosalicylaldiminato)nickel(II) is the first example of a high-spin, five-coordinated nickel(II) complex, whose structure has been described by X-ray analysis.

Five-coordinated complexes of transition metals have been found to have square-pyramidal or trigonal-bipyramidal structures. Among the factors determining the stability of square-pyramidal or trigonal-bipyramidal configurations are: ligand–ligand repulsions, the type of metal–ligand bond, crystal-field stabilization energy (CFSE), crystal packing forces, steric effects.

We have already mentioned that, as far as ligand–ligand repulsions are concerned, a square-pyramidal configuration with L_{base}–M–L_{ap} $\simeq$ 100° is only slightly less stable than the trigonal-bipyramidal configuration. On the other hand, it has been shown[19] that for nickel(II) complexes, with this type of ligands, CFSE favors the square-pyramidal arrangement by 10 kcal/mole. CFSE effects should predominate in high-spin complexes, thus stabilizing the square-pyramidal configuration. Anyhow, the present structure does not constitute any definite proof in favor of this hypothesis, since the steric requirements of the ligand molecule determine essentially the distribution of the donor atoms about the metal.

Acknowledgment. We wish to thank the Research Computer Laboratory of the University of Washington for free time on the 7090. P. L. O. wishes to thank Professor E. C. Lingafelter for his kind hospitality. Financial support of the Italian Consiglio Nazionale delle Ricerche is gratefully acknowledged.

[19] M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

Intermediates in the Conversion of π- to σ-Allylic Complexes of Palladium(II)[1]

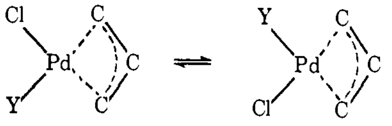
Kermit C. Ramey and Gary L. Statton

Contribution from the Atlantic Refining Company, Research and Development Division, Glenolden, Pennsylvania. *Received May 12, 1966*

Abstract: The temperature dependence of the nmr spectra of a number of allylic complexes of palladium yielded information on the intermediates in the conversion of π to σ complexes. The results are interpreted in terms of a number of processes including ligand exchange (as shown in eq 1) and π to σ equilibration (eq 2), which may be followed by a head-over-tail equilibration (eq 3).

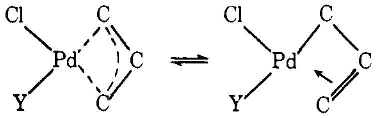
The allylic complexes of transition metals have been studied by a variety of techniques, including X-ray,[2] infrared,[3,4] and nmr.[1,4–8] Nevertheless, the structure of the intermediates in the conversion of π- to σ-allylic complexes and the mechanism by which the conversion takes place are not well understood. Most of the results have been based on nmr spectra as obtained at room temperature.

In a recent communication[1] we reported on the temperature dependence of the nmr spectra of some allylic complexes of palladium. The results for the triphenylphosphine adduct of methallylpalladium(II) chloride indicated that the system was involved in a number of equilibrations and the spectra were interpreted in terms of two equilibrating π structures which were followed by a π to σ equilibration. In this report the temperature dependence of the nmr spectra of a number of allylic complexes of palladium was studied in detail and the results are interpreted in terms of a number of processes including: ligand exchange



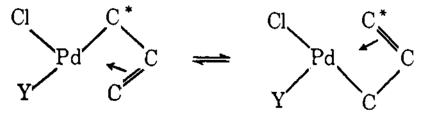
(1)

and π to σ equilibration



(2)

which may be followed by a head-over-tail equilibration



(3)

where Y = DMSO-d_6, $(Ph)_3As$, and $(Ph)_3P$.

Experimental Section

The nmr spectra were obtained with solutions containing approximately 10% of complex in solution in either $CDCl_3$ or o-$C_6H_4Cl_2$. A Varian HA-100 spectrometer equipped with a variable-temperature probe and accessories was used. The chemical shifts are reported in τ units.

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[1] For part I see G. L. Statton and K. C. Ramey, *J. Am. Chem. Soc.*, **88**, 1327 (1966).

(2) J. M. Rowe, *Proc. Chem. Soc.*, **66** (1962).

(3) H. P. Fritz, *Chem. Ber.*, **94**, 1217 (1961).

(4) H. C. Dehm and J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4429 (1960).

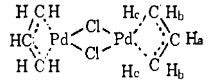
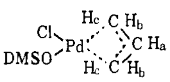
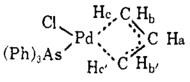
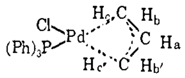
(5) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963).

(6) B. L. Shaw and N. Sheppard, *Chem. Ind.* (London), 517 (1961).

(7) D. W. Moore, H. B. Jonassen, T. B. Joyner, and A. J. Bertrand, *ibid.*, 1304 (1960).

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

Table I. Nmr Parameters of Allylic Palladium(II) Complexes

Predicted structure	Solvent	Temp, °C	Chemical shifts τ values					Coupling constants, cps
			a	b	c			
	$CDCl_3$	35	4.58	5.89	6.95			$J_{ab} = 6.8$ $J_{ac} = 11.8$ $J_{bc} < 1.0$
	$CDCl_3$	−20[a]	4.19	5.71	6.57			$J_{ab} = 6.7$ $J_{ac} = 11.6$
					bc			
	$CDCl_3$	70[b]	4.35		6.30			$J_{ab} = J_{ac} = 9.7$
			a	b	b′	c	c′	
	$CDCl_3$	−50[c]	4.50	5.30	6.75	6.35	7.17	$J_{ab} = 6.0$ $J_{ab'} = 6.0$ $J_{ac} = 13.5$ $J_{ac} \mp 11.5$
			a	bb′	cc′			
	$CDCl_3$	30[a]	4.57	6.00	6.73			
			a		bb′cc′			
	$CDCl_3$	70[b]	4.59		6.41			$J_{ab} = J_{ab'} = 9.7$ $J_{ac} = J_{ac'} = 9.7$
			a	b	b′	c	c′	
	$CDCl_3$	−30[c]	4.42	5.31	6.93	6.30	7.18	$J_{ab} = 7.0$ $J_{ab} \mp 6.0$ $J_{ac} = 13.5$ $J_{ac'} = 12.0$ $J_{bP} = 7.0$ $J_{cP} = 10.0$
			a	bb′	cc′			
	o-$C_6H_4Cl_2$	90[a]	4.67	6.11	7.10			
			a	bb′cc′				
	o-$C_6H_4Cl_2$	140[b]	4.66	6.63				$J_{ab} = J_{ab'} =$ $J_{ac} = J_{ac'} = 9.4$

[a] Cl and Y ligands are involved in an exchange process. [b] Two or more equilibrations; ligand exchange, π to σ, and head-over-tail. [c] Ligands are not involved in an exchange process.

Allylpalladium chloride was synthesized from Na_2PdCl_4 and allyl alcohol by the method of Moiseev, *et al.*,[9] and the phosphine and arsine derivatives were synthesized by the procedure of Powell, *et al.*[8]

Anal. Calcd for allyl(chlorotriphenylphosphine)palladium(II), $C_{21}H_{20}ClPPd$: C, 56.7; H, 4.7. Found: C, 56.9; H, 4.7.

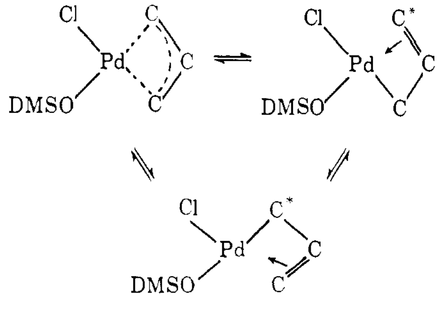
Anal. Calcd for allyl(chlorotriphenylarsine)palladium(II), $C_{21}H_{20}AsClPd$: C, 51.5; H, 4.1. Found: C, 51.3; H, 4.0.

Results and Discussion

Allyl Complexes of Palladium(II) Chloride. The nmr spectrum of allylpalladium(II) chloride in solution in $CDCl_3$ is shown in Figure 1a, and consists of three resonances which correspond to the a, b, and c protons as depicted in Table I. The spectrum is consistent with the structure proposed on the basis of an X-ray diffraction study[2] which indicates that the allyl part of the molecule is situated at an angle of 124° from the Pd–Cl plane. The nmr parameters are listed in Table I, and they are in fair agreement with previous reports.[4,10] The spectrum of the product obtained by the addition of 1 mole of DMSO-d_6/mole of Pd is shown in Figure 1b. The latter spectrum was interpreted by Chien and Dehm[11] in terms of the following equilibration.

$$Pd—CH_2—CH{=}\overset{*}{C}H_2 \rightleftharpoons Pd—\overset{*}{C}H_2—CH{=}CH_2$$

Additional information concerning the equilibration is obtained from the temperature dependence of the nmr spectrum of the allylpalladium(II) chloride–DMSO-d_6 adduct in solution in $CDCl_3$, and the results are shown in Figure 2. The spectra clearly show that the over-all process is not only that of a head-over-tail equilibration, but that a number of processes are taking place. One possibility is that of a π to σ equilibration which may be followed by a head-over-tail process



The spectrum of the low-temperature species which shows that the *cis* protons are equivalent and that the *trans* protons are equivalent does not appear to be consistent with the above process, if the structure is that of a square-planar type which is the predominant type that has been reported for complexes of the type $(ligand)_2MRX$ and $(ligand)_2MR_2$, where M is either nickel, palladium, or platinum. For a square-planar type structure the terminal protons, either *cis* or *trans*, would not be expected to be equivalent. The equiva-

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(9) I. I. Moiseev, E. A. Fedorskaya, and Ya. K. Syrkin, *Zh. Neorg. Khim.*, 4, 2641 (1959).

(10) M. L. H. Green and P. L. I. Nagy, *Advan. Organometal. Chem.*, 1, 332 (1964).

(11) J. C. W. Chien and H. C. Dehm, *Chem. Ind.* (London), 745 (1961).

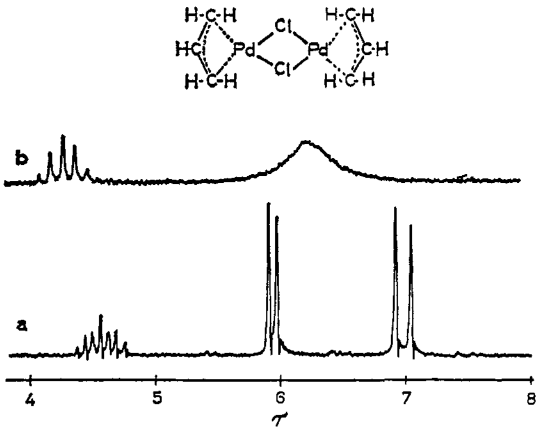


Figure 1. Nmr spectra of allylpalladium(II) chloride: (a) in solution in $CDCl_3$; (b) in solution in $CDCl_3$ to which has been added 1 mole of DMSO-d_6/mole of Pd.

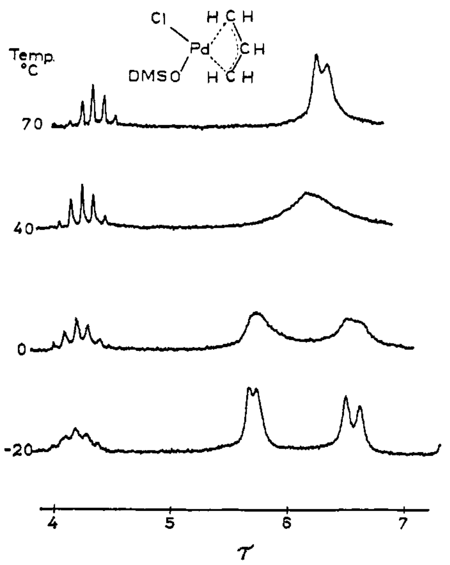
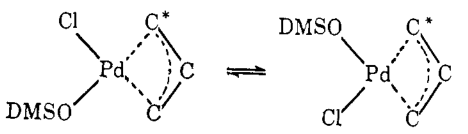


Figure 2. Temperature dependence of the nmr spectrum of the system consisting of allylpalladium(II) chloride in solution in $CDCl_3$ to which has been added 1 mole of DMSO-d_6/mole of Pd.

lence of the two *cis* protons and the two *trans* protons would, however, be consistent with a tetrahedral-type structure, although this appears to be somewhat improbable. A more reasonable explanation would be that the low-temperature species is of the square-planar type and that it is involved in still yet another equilibration. One distinct possibility is that of an exchange between the Cl and DMSO-d_6 ligands as depicted below.



This exchange of ligands is indicated not only by the sensitivity of the system to the concentration of DMSO-d_6, but also by the shift of ~20° in temperature at which the two peaks coalesce in going from a solution of the complex in pure DMSO-d_6 to one containing 1 mole of DMSO-d_6/mole of Pd.

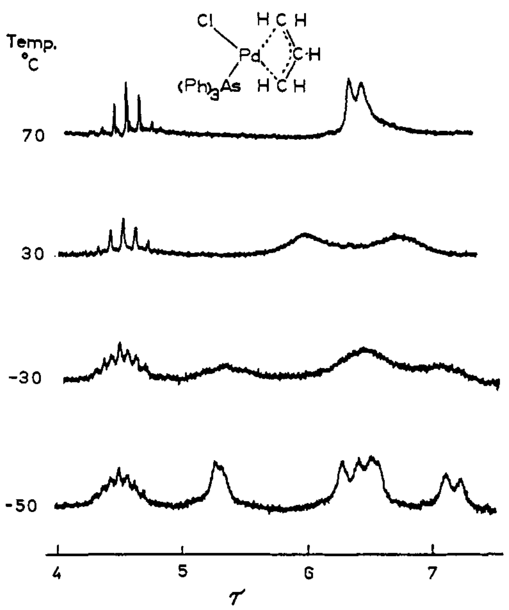


Figure 3. Temperature dependence of the nmr spectrum of the $(Ph)_3As$ adduct of allylpalladium(II) chloride in solution in $CDCl_3$.

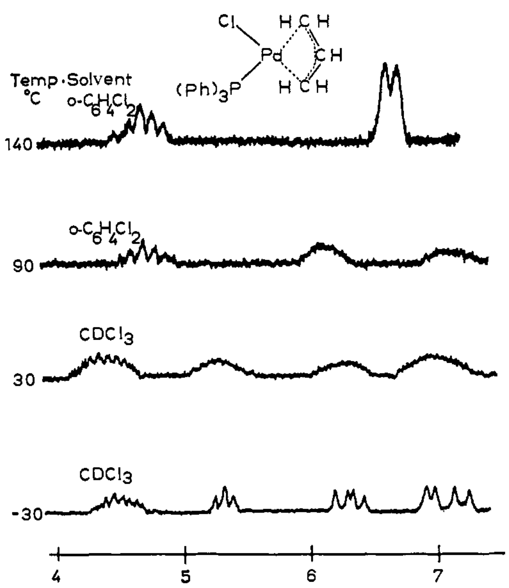
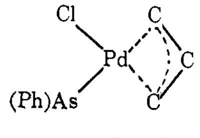


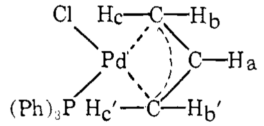
Figure 4. Temperature dependence of the nmr spectrum of the $(Ph)_3P$ adduct of allylpalladium(II) chloride in solution in $CDCl_3$ and in o-$C_6H_4Cl_2$.

In order to shed some light on the above process, the triphenylarsine adduct of allylpalladium(II) chloride was prepared and the temperature dependence of the nmr spectrum of the product in solution in $CDCl_3$ is shown in Figure 3. Unlike that for the DMSO-d_6 adduct, the spectrum of the low-temperature species shows five distinct resonances and the nmr parameters are listed in Table I. The spectrum of the triphenylarsine adduct as obtained at −50° appears to correspond to the following structure in which the Cl and $(Ph)_3As$ ligands are not involved in an exchange process. As the temperature is increased the resonance



of the terminal protons first broadens; then the *cis* protons and the *trans* protons converge into two broad bands at about 30°. This change is attributed to the exchange of the Cl and $(Ph)_3As$ ligands which occurs at a higher temperature than that for the Cl-DMSO-d_6 exchange. As the temperature is further increased the two broad bands coalesce into a sharp doublet, and this is attributed to the π to σ equilibration which may be followed by a head-over-tail equilibration.

Further evidence for the proposed equilibrations was obtained from the $(Ph)_3P$ adduct of allylpalladium(II) chloride, and the temperature dependence of the nmr spectrum of the product is shown in Figure 4. Again the spectrum of the low-temperatue species shows five resonances. An assignment of the resonances to the four terminal b,c and b′,c′ protons, as depicted in the following structure, was made on the basis that the *trans* couplings $J_{P-H_b \text{ or } P-H_c}$ are expected to be larger than the *cis* couplings $J_{P-H_{b'} \text{ or } P-H_{c'}}$.[12] As the temperature is increased, the resonances for the terminal protons broaden, but the two *cis* protons and the two *trans* protons do not converge at 60°, which is about the upper limit for the system. The spectrum of the complex in solution in o-$C_6H_4Cl_2$, as obtained at 90 and 140°, shows that the complex is undergoing similar transitions as was observed for the DMSO-d_6 and $(Ph)_3As$ adducts.



Further proof for the ligand-exchange process was obtained by the addition of the allylpalladium(II) chloride dimer to a solution of the triphenylphosphine–allylpalladium(II) chloride adduct in $CDCl_3$. The spectrum of the mixture at 30° yielded sharp resonances for the dimer which was superimposed upon the broad bands of the triphenylphosphine adducts' resonances. Upon heating to 70°, the spectrum indicated that the species interact. The sharp resonances of the dimer first broaden and then converge with the broader bands for the adduct. Upon cooling to 30°, the sharp resonances reappear and the spectrum corresponds to the original mixture. The spectrum of the allylpalladium(II) chloride dimer in $CDCl_3$ did not change significantly over the corresponding temperature range 30–70°.

Although nmr spectra are sensitive to exchange processes, the mechanisms deduced from the spectra are certainly not unambiguous. A second mechanism which could explain, at least in part, the temperature dependence of the nmr spectra of the DMSO-d_6, $(Ph)_3As$, and $(Ph)_3P$ adducts of allylpalladium(II) chloride is that of a rotational process which has been postulated for the temperature dependence of the nmr spectrum of π-$C_6H_5CH_2Mo(CO)_2C_5H_5$.[13] Rotation of the allyl group by 180° seems somewhat improbable primarily because of the steric interaction of proton a (Table I). Furthermore, a detailed analysis of the systems involved, particularly that for the DMSO-d_6 adduct, shows that the sharp doublet as observed at the higher temperatures does not fall midway between that of the *cis* and the *trans* resonances as observed at the lower temperatures.

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(12) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1625 (1964).

(13) R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

Boron Heterocycles. III. The Effect of Borane Lewis Acid on Apparent Base Strength. New Examples of Base Strength Reversal[1,2]

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Contribution from the Evans Laboratory of Chemistry, Ohio State University, Columbus, Ohio.

Received December 27, 1965

Abstract: A study of adducts of several Lewis acids including boron heterocycles containing terminal B–H bonds has led to the conclusion that the relative base strength with respect to a reference acid depends, principally, upon the strength of the acid and not necessarily upon supplementary π-type bonding involving d orbitals on phosphorus or sulfur ligand atoms. Homogeneous displacement reactions, vapor density studies, and qualitative kinetic observations suggest the apparent relative base strengths with respect to acid strength as shown in sequence 3. Results from the BH_3 system fully confirm earlier work.[3] It is believed that the order of base strength depends upon the strength of the σ bond formed between boron and the donor atom, and, as the acid becomes increasingly stronger, the tendency to reverse the normal order of base strength increases so that $P > N$ and $S > O$. Nmr spectroscopy has proved to be useful in examining equilibrium distributions of adducts in solution.

Earlier work in this laboratory has shown that $\underline{SCH_2CH_2SB}HN(CH_3)_3$ is much more stable with respect to dissociation than $\underline{OCH_2CH_2OB}HN(CH_3)_3$.[2] This is consistent with observations made on the boron halides, that as one proceeds from BF_3 to BCl_3 to BBr_3

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(1) Presented before the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(2) Part I: S. H. Rose and S. G. Shore, *Inorg. Chem.*, **1**, 744 (1962); part II: B. Z. Egan, S. G. Shore, and J. E. Bonnell, *ibid.*, **3**, 1024 (1964).

(3) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).