# Organometallic Exchange Reactions. IX. Proton Magnetic Resonance Spectra of Allylpalladium Thiocyanate and Mixed Halide Dimers[1]

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**Abstract:** The nmr spectra of 2-methylallylpalladium thiocyanate and mixtures of 2-methylallylpalladium chloride and iodide have been investigated. The low-temperature spectra reveal that the thiocyanate dimer is bridged unsymmetrically, *i.e.*, as –SCN–, and provide evidence for the existence of the unsymmetrically bridged dimer, $(C_4H_7Pd)_2ICl$. A rapid exchange of the 2-methylallylpalladium groups by a second-order mechanism involving the bridges was observed in both systems. An intermediate for the exchange, $(C_4H_7PdX)_4$, is proposed.

The nmr spectra of $\pi$-allyl groups bonded to a transition metal in situations which lead to an unsymmetrical environment have recently been the subject of study.[2–9] The nmr spectrum of such an allyl group in the limit of slow exchange is an AGMPX type. With an increase in temperature the spectrum may be transformed to either an $AM_2X_2$ or $AX_4$ spectrum. The temperature dependence of the spectrum of the allyl group in compounds of the monomeric form $C_3H_5$–PdClL, where L is a phosphine or arsine, can be accounted for in part in terms of a dissociation of the ligand L, or reaction of the monomer with excess ligand L.[8]

The spectra of the allyl groups in bisallylrhodium chloride dimer have been discussed in terms of a $\sigma$–$\pi$ equilibrium or rotation about the C–C bond of the allyl group.[9] The authors conclude that neither of these modes of intramolecular rearrangement alone or together can give rise to the observed temperature dependence. They propose that bridge dissociation is a kinetically important process in equilibration.

There is presently very little information available on the kinetics of bridge rupture in systems of this kind. We have studied the proton resonance spectra of methallylpalladium thiocyanate dimer, and a mixture of methallylpalladium chloride and iodide. In the latter case a mixed dimer, $(CH_3C_3H_4)_2PdClI$, is present in addition to the parent components. Observation of the temperature dependences of the nmr spectra of these systems has provided quantitative information regarding the kinetics of bridge rupture. The palladium halide or pseudo-halide bridge systems are surprisingly labile in comparison with the bisallylrhodium chloride dimer bridge. In addition, we have shown that the exchange process involving the bridge is a second-order process.

## Experimental Section

Weighed quantities of the allylpalladium compounds were dissolved in chloroform or a mixture of 30% chloroform–70% methylene chloride. Solution samples were stored at Dry Ice temperature. Concentrations were generally in the range of 0.05 *M* in dimer. Measurements of the nmr spectra were made on a Varian A-60A or HA-100 spectrometer.

Methylallylpalladium chloride was synthesized by the method of Dent, Long, and Wilkinson.[10] The product was crystallized from methylene chloride and methanol and dried under vacuum. *Anal.* Calcd for $C_8H_{14}Pd_2Cl_2$: C, 24.38; H, 3.56; Cl, 18.03. Found: C, 24.95; H, 3.83; Cl, 17.64.

Methylallylpalladium iodide was prepared by adding a saturated solution of potassium iodide to a solution of methylallylpalladium chloride in acetone. Alternatively, methylallylpalladium chloride was distributed between chloroform and a saturated solution of aqueous potassium iodide. *Anal.* Calcd for $C_8H_{14}Pd_2I_2$: C, 16.65; H, 2.43; I, 44.02. Found: C, 17.02, 17.08; H, 2.73, 2.64; I, 47.8, 43.3. The thiocyanate was formed by a similar procedure. *Anal.* Calcd for $C_{10}H_{14}Pd_2S_2N_2$: C, 27.35; H, 3.14; N, 6.38; S, 14.60. Found: C, 27.68; H, 3.29; N, 6.14; S, 14.37.

The completeness of the metathesis reaction was checked by thin layer chromatography using 40% pentane–60% benzene on Eastman K-301-R silica gel plates. $R_f$ values for the chloride, iodide, and the thiocyanate are 0.37, 0.67, and 0.64, respectively. It was found that a mixture of the iodide and the chloride could be separated and that the iodide prepared by the above procedures contains no observable chloride.

## Analysis of the Data

Observed two-site spectra were compared with spectra calculated for various exchange rates, as previously described,[11] to obtain a value for the exchange parameter, $\tau_e$. An activation energy was calculated from a plot of log $(1/\tau)$ *vs.* $1/T$. The molecularity was determined from a plot of log rate *vs.* log concentration (*vide infra*).

The three-site spectra were compared to a series of calculated spectra. Theoretical line shapes were calculated using the classical Bloch equations as modified

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] W. B. Wise, D. C. Lini, and K. C. Ramey, *Chem. Commun.*, 463 (1967).

[3] K. Vrieze, P. Cosse, C. W. Hilbers, and A. P. Praat, *Rec. Trav. Chim.*, **87**, 769 (1967).

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

[5] K. C. Ramey and G. L. Statton, *J. Am. Chem. Soc.*, **88**, 4387 (1966).

[6] J. C. Barborak, L. Watts, and R. Pettit, *ibid.*, **88**, 1329 (1966).

[7] K. Vrieze, P. Cossee, A. P. Praat, and C. W. Hilbers, *J. Organometal. Chem.*, **11**, 353 (1968).

[8] K. Vrieze, C. Maclean, P. Crosse, and C. W. Hilbers, *Rec. Trav. Chim.*, **86**, 1077 (1966).

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

[10] W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.* 1585 (1964).

[11] K. C. Williams and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4134 (1966).

by McConnell.[12] For a site *a* exchanging with sites *b* and *c*, these are

$$\dot{u}_a + \Delta\omega_a v_a = -\frac{u_a}{T_{2a}} - \frac{u_a}{\tau_{ab}} - \frac{u_a}{\tau_{ac}} + \frac{u_b}{\tau_{ba}} + \frac{u_c}{\tau_{ca}}$$

$$\dot{v}_a - \Delta\omega_a v_a = -\frac{v_a}{T_{2a}} - \frac{v_a}{\tau_{ab}} - \frac{v_a}{\tau_{ac}} + \frac{v_b}{\tau_{ba}} + \frac{v_c}{\tau_{ca}} - \omega_1 M_z^a$$

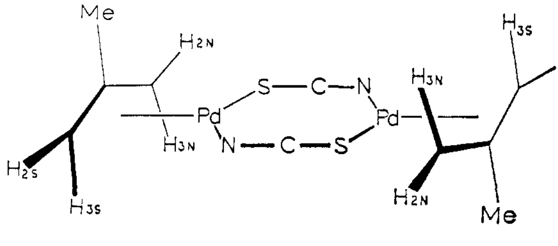
where *u* and *v* are the in-phase and out-of-phase magnetization, respectively, and $M_z$ is the magnetization in the direction of the large static field. The experimental spectra were obtained under slow passage conditions so $\dot{u}_a = \dot{u}_b = \dot{u}_c = \dot{v}_a = \dot{v}_b = \dot{v}_c = 0$. $M_z$ has been set equal to $M_0$ which corresponds to no radiofrequency saturation; *i.e.*, $M_0$ is not tipped away from the large static field. $T_{2a}$ is the transverse relaxation time for site *a*. $1/\tau_{jk}$ is the probability of a nucleus going from *j* to *k* in unit time. The frequency $\omega_1 = \gamma(H_1)$.

The first equation differs from the usual Bloch equations by the terms $(-u_a/\tau_{ab}) - (u_a/\tau_{ac})$, which account for the decrease of magnetization due to the transfer of nuclei from site *a* to *b* (or *c*), and by the terms $(u_b/\tau_{ba}) + (u_c/\tau_{ca})$, which measure the increase of magnetization due to the transfer of nuclei from *b* and *c*, respectively, to *a*.

Expressions for site *b* and *c* can be written in an analogous manner. These equations were solved, and the intensity, which is proportional to the sum of the out-of-phase magnetizations, $v_a + v_b + v_c$, was displayed as a function of frequency using a Calcomp plotter. These displays were compared to the experimental curves, to choose a best fit for the exchange rate variables. Values for the remaining required quantities are known, or could be estimated, from data for the individual pure components.

## Results and Discussion

Spectra for methylallylpalladium thiocyanate in chloroform are displayed in Figure 1. From the low-temperature spectra it appears that the structure for the compound is[13,14]



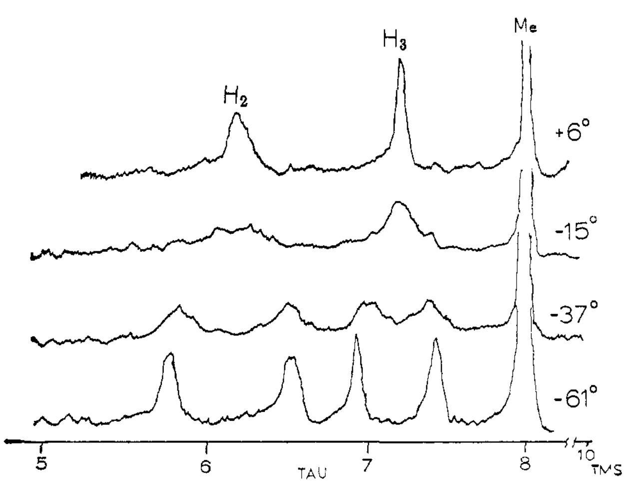


Figure 1. ¹H magnetic resonance spectra at 60 MHz of methylallylpalladium thiocyanate dimer in methylene chloride.

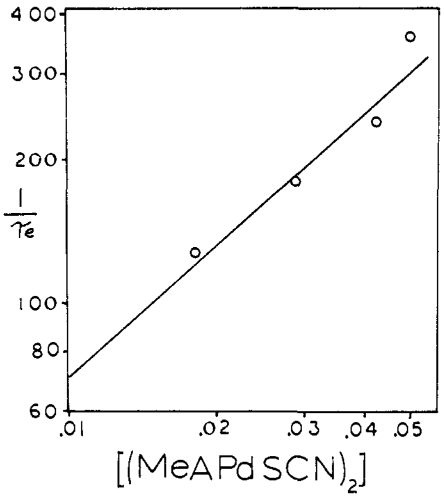


Figure 2. Log $(1/\tau_e)$ *vs.* log $[(CH_3C_3H_4PdSCN)_2]$.

The pair of lines at low field are assigned as $H_2$.[15] The broader line of each pair, at $\tau$ = 6.45 and 7.37, is assigned to the proton *trans* to nitrogen, since nitrogen ($I$ = 1) might be expected to exhibit a certain amount of coupling, albeit not resolved, with the *trans* protons.[16]

With an increase in temperature the spectrum partially collapses. The two $H_3$ protons become equivalent, as do the two $H_2$ protons. Since the $AM_2X_2$ type of spectrum seen here at +6° is well established for allylpalladium systems, the assignment of the low-temperature lines to $H_2$ and $H_3$ doublets is quite reliable. The collapse of the $H_3$ and $H_2$ doublets at about −15° (Figure 1) cannot reaonably be thought to occur as a result of any process involving just the allyl–metal bonding. It must therefore reflect a process occurring in the bridge which renders the allyl group symmetrical, *e.g.*, a dissociative process.

$$(CH_3C_3H_4PdSCN)_2 \rightleftharpoons 2CH_3C_3H_4PdSCN$$

The temperature dependence of the spectrum in the region of the $H_3$ proton lines was treated in terms of a simple two-site, uncoupled spin-exchange system. The

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(12) H. M. McConnell, *J. Chem. Phys.*, 28, 430 (1958).

(13) Although the structure is shown with a center of symmetry, as found in the solid state for the chloride dimer,[14] the relative orientation of the allyl groups (*i.e.*, *syn* or *anti*) in solution is not known and is not reflected in any of the considerations presented here.

(14) (a) A. E. Smith, *Acta Cryst.*, 18, 331 (1965); (b) W. E. Oberhansli and L. F. Dahl, *J. Organometal. Chem.*, 3, 43 (1965).

(15) E. O. Fisher and H. Werner, "Metal Complexes," Elsevier Publishing Co., New York, N. Y., 1966, p 177.

(16) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

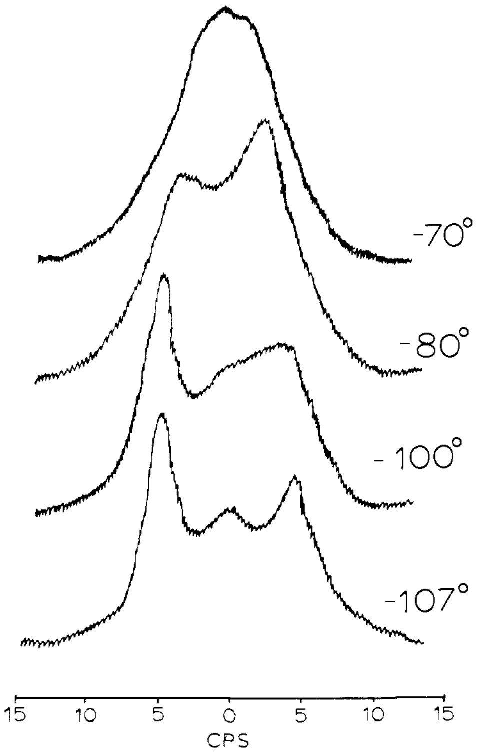

Figure 3. $^1$H magnetic resonance spectra at 100 MHz of the $CH_3$ groups in a methylallylpalladium chloride and iodide mixture in 30% chloroform–70% methylene chloride.

Arrhenius energy was computed to be 6.8 kcal/mole; $\Delta S^{\ddagger}$ was evaluated as $-19$ eu. The effect of concentration variation on line width in the slow exchange region at $-15°$ was studied at 100 MHz. The results indicate that the exchange is concentration dependent. A least-squares fit of log $(1/\tau)$ *vs.* log (dimer concentration) over a 2.5-fold concentration range gave a slope of 0.91 (Figure 2). Similar results, yielding a slope of 0.97, were obtained from a second study, using a different sample of thiocyanate, at $-37°$ and observing the protons at 60 MHz. *The result indicates that the rate is second order in dimer.*

Let $[D_i]$ represent the concentration of protons at chemical site $i$ in the dimer. Clearly, $[D_i]$ is proportional to [D], the dimer concentration. Following the usual development, we have

$$\frac{1}{\tau_i} = \frac{1}{[D_i]}\,\frac{d[D_i]}{dt} = k[D_i]^{N-1} = k'[D]^{N-1}$$

experimentally, $1/\tau_i \propto [D]$. Therefore, the exchange process itself is second order in dimer.

The spectra of mixtures of methylallylpalladium chloride and iodide in 30% chloroform–70% methylene chloride were examined as a function of temperature. The 100-MHz spectra in the region of the methyl group absorptions appear as shown in Figure 3. The absorptions for the methyl groups of iodide and chloride dimers were assigned from the spectra of the pure components. The central line is assigned to the methyl groups of the mixed dimer, $CH_3C_3H_4PdClIPdC_3H_4CH_3$. The low-field absorption is due to the chloride dimer.

The mixed dimer is presumably formed in the equilibrium

$$[CH_3C_3H_4PdCl]_2 + [CH_3C_3H_4PdI]_2 \rightleftharpoons 2(CH_3C_3H_4Pd)_2ICl$$

This is similar to the mixed bridge in $(CH_3)_2AlBrClAl(CH_3)_2$ observed by low-temperature nmr in mixtures of dimethylaluminum chloride and bromide.[17] From the relative areas under the methyl absorptions in the slow exchange limit at $-108°$, the equilibrium constant for the above reaction is estimated to be 1.0. On the basis of a random distribution of halide between the possible bridging sites, the equilibrium constant should be 4.0. The discrepancy between the purely statistical and observed values corresponds to a free-energy difference of only about 0.5 kcal/mole. Apparently the difference in size of chlorine and iodine does not produce a large strain in the bridge. These results are of interest in connection with exchanges of halides in species of the form RMX, where R is an alkyl, M is a metal such as Hg,[18] and X is a halide or pseudo-halide. In these systems, the bridge structure may be an intermediate in exchange of the X groups.

The exchange process in this mixed system was observed to stop only near the limit of low-temperature capability and in the face of solubility limitations, so the spectra of the methylene protons were not observed under very good conditions. Nevertheless, it seems quite certain that new absorptions due to methylene protons of the mixed dimer do not appear at chemical shifts which are intermediate between those for the chloride and iodide dimers. Apparently, the $H_2$ and $H_3$ protons of the mixed dimer are influenced by one of the two bridging groups more than the other, so that the chemical shifts of these protons appear at the same chemical shift as for the pure components. It is not clear whether it is the halide *cis* or *trans* to the $CH_2$ moiety which is of primary importance in determining its chemical shift.

As the temperature is increased the methyl absorptions coalesce to two lines and then to one, as shown in Figure 3. These spectra were analyzed and fitted to calculated spectra for variations in both temperature and concentration. Although a precise fitting is difficult because of the number of variables involved, certain general conclusions can be drawn unambiguously. The observed spectra are quite clearly concentration dependent. *The inverse exchange times are directly proportional to concentration, indicating that the exchanges are second order.* Over a 38° temperature range and a fourfold dilution, a satisfactory fit was obtained with the following assumed parameters.

| Exchange pair | $H^{\ddagger}$ | $S^{\ddagger}$ |
|---|---|---|
| $I_2$–ICl | 5.3 | $-16.6$ |
| $Cl_2$–ICl | 6.1 | $-16.8$ |
| $Cl_2$–$I_2$ | $\infty$ | $-\infty$ |

A comparison of calculated and observed spectra is shown in Figure 4 for a series in which concentration is

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[17] E. A. Jeffrey, T. Mole, and J. K. Saunders, *Australian J. Chem.*, 21, 649 (1968).

[18] L. L. Murrell and T. L. Brown, *J. Organometal. Chem.*, 13, 301 (1968).

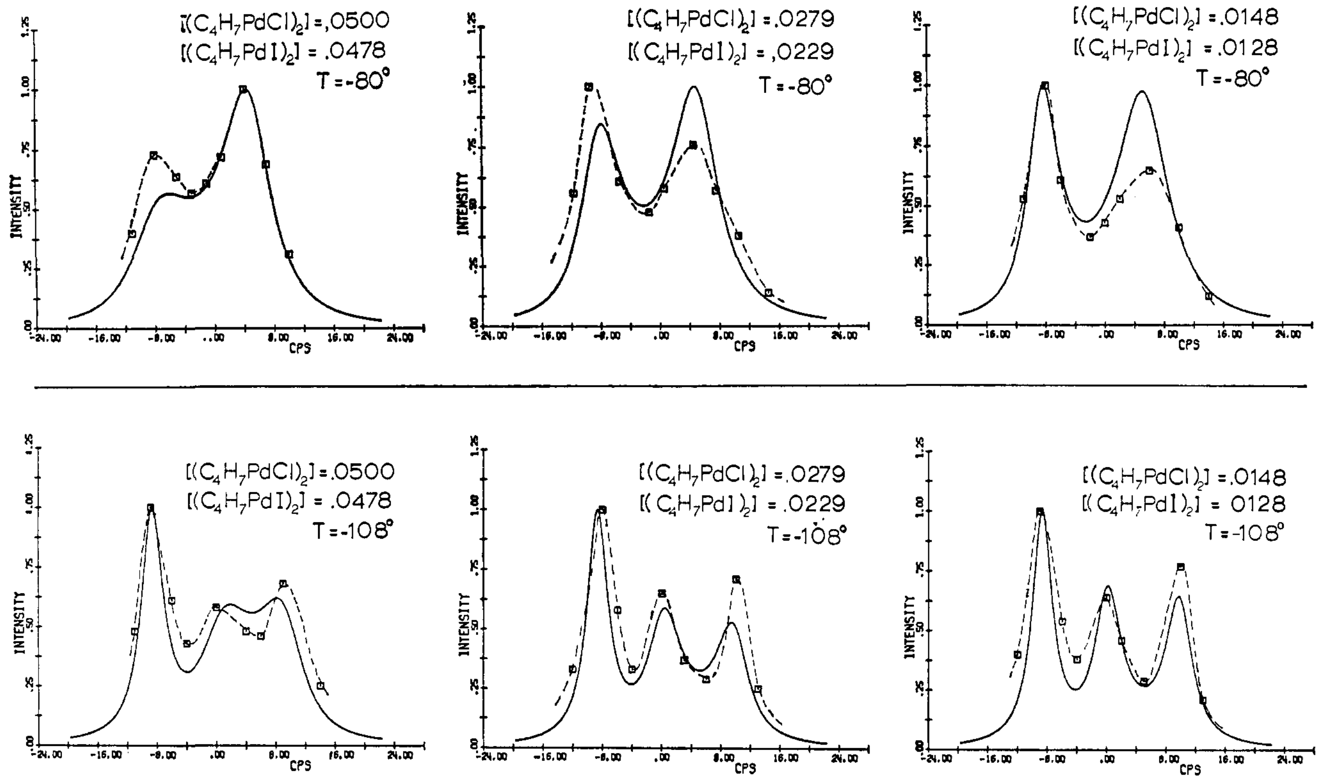
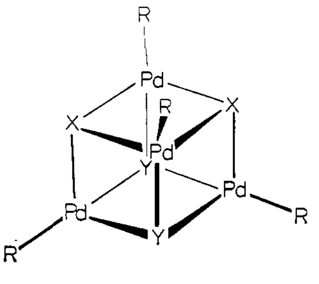


Figure 4. Comparison of calculated and observed spectra for $[CH_3C_3H_4PdCl]_2$ and $[CH_3C_3H_4PdI]_2$ in 30% chloroform–70% methylene chloride. The continuous line represents the calculated spectrum; the dotted line and squares represent the observed spectrum.

varied at two different temperatures. Since the iodide dimer and chloride dimer peaks are furthest apart, the spectra are fairly insensitive to this exchange. Thus the satisfactory fit with the above values does not mean that $(CH_3C_3H_4PdCl)_2$ and $(CH_3C_3H_4PdI)_2$ do not exchange but only that they exchange relatively slowly. In effect, the exchanges of the iodide–chloride dimer with the iodide and chloride dimers dominate the spectra.

The thiocyanate and mixed halide dimer systems provide useful complementary information regarding the exchange processes. It would certainly be quite reasonable to suppose that the exchange process occurring in the thiocyanate dimer is a simple dissociation of the dimer, since this would effectively erase the distinction between the atoms bonded opposite the two $CH_2$ groups of the allyl. Rotation of the entire $\pi$-bonded allyl group in the plane normal to the Pd–allyl bond axis would also effect the observed exchange, but this is an unlikely possibility in view of the observation[19] that the allyl group in allylpalladium thioacetylacetone retains asymmetry to temperatures above 5°, in the absence of Lewis bases.[19a] The concentration dependence of the exchange rate also rules out these possibilities, since they involve only a first-order dependence on dimer concentration. On the other hand, the concentration dependence data in the mixed halide system are not very helpful in assessing the reaction pathway, since even a dissociation process would not lead to first-order kinetics if the rates of dissociation of the three species involved differed by only a little. This raises the question of whether there is in fact any rupture of bridge bonds at all. Two dimers might come together to form a transition state in which there is somehow an opportunity for the SCN groups to turn over, but without actual rupture of the bridge bond. The data for the mixed halide systems clearly require a bridge bond rupture, however, since the exchange of methyl groups between the three sites can occur only by transfer from one kind of dimer to the other.

Although the spectra in the thiocyanate system are observed in a higher temperature interval than for the mixed system, the activation energies and entropies are very similar for both systems. It is reasonable to suppose that the exchanges occur by a similar pathway. We propose that the exchange proceeds by a bimolecular process involving the interaction of two dimers to form an intermediate tetramer of the form



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[19] S. J. Lippard and S. M. Morehouse, private communication.

[19a] Note Added in Proof. This conclusion is supported also by the results communicated recently by J. W. Faller, M. J. Incorvia, and M. E. Thomsen, *J. Am. Chem. Soc.*, 91, 518 (1969).

The thiocyanate groups in this intermediate are presumed to bond only through sulfur. Since the intermediate can dissociate to dimers in any one of three equivalent ways, the bridging groups are effectively transferred between allylpalladium moieties. There is some precedent (for example, in the $(CH_3)_3PtCl$ tetramer[20] and in the $Et_3AsCuI$ tetramer[21]) for a species of the type proposed as intermediate.

The presumed bridge dissociation in bisallylrhodium chloride dimer occurs at a much slower rate than the exchanges observed in the present work. Since we have shown that the exchange occurs in the course of a second-order process, presumably associative, it is reasonable to surmise that the great difference in rates in the two types of systems is due to the nonavailability of an associative pathway for the rhodium system. Rhodium is six-coordinate in bisallylrhodium chloride dimer. Typically, six-coordinate systems do not readily undergo an increase in coordination number. A first-order bridge dissociation is thus the lowest pathway available. The four-coordinate palladium complexes, by contrast, easily enter into an associative interaction to effect the exchange. Thus, the very rapid exchange kinetics and the second-order nature of the process are accounted for.

Finally, it should be noted that in solutions containing both $\pi\text{-}C_3H_5PdClP(C_6H_5)_3$ and $(\pi\text{-}C_3H_5PdCl)_2$, the collapse of the allyl spectrum to an $AX_4$ type in the phosphine-containing monomer appears to occur through a second-order process, first order in each of the compounds present.[7] Although the nature of the intermediate in this case is not clear, the results show clearly that the dimer species enters into a bimolecular interaction of this type without the occurrence of intermolecular allyl group exchange. In this particular system, evidence of intermolecular allyl group exchange is observed at temperatures on the order of +60 to +80°.

(20) R. E. Rundle and J. H. Sturdivant, *J. Am. Chem. Soc.*, **69**, 1561 (1947).

(21) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).