Chemical Exchange in "Virtually Coupled" Systems. Metal-Ion-Induced Relaxation of Methyl-Phosphorus Coupling in Phosphine Complexes

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Abstract: Theoretical evidence is presented to show that AX coupling may be relaxed by chemical exchange in A′AX systems if A and A′ are strongly coupled. Analysis shows that one might expect to find chemical situations for methylphosphine complexes where the proton nmr pattern is a doublet, a "virtual-coupled" triplet, or a singlet depending on phosphorus–phosphorus coupling and ligand exchange. We present here some examples of phosphine complexes where A–X decoupling occurs and discuss the various causal mechanisms.

The important role of transition metal phosphine complexes in homogeneous catalysis[2] has prompted their considerable study in recent years. The discovery that nuclear magnetic resonance "virtual coupling" in bisphosphines is apparently related to the geometry of the complex has been important to solution structural work in this area. Thus, for example, it is possible to establish the solution geometry of bis(dimethylphenylphosphine)platinum(II) dihalide by nmr since the ^{31}P–^{31}P coupling constant is near zero in the *cis*-planar molecule but rather large in the *trans*-structured species.[3-5] The proton nmr pattern for the methyl groups on the *trans* phosphines resembles a "triplet" produced by coupling to two equivalent spin ½ phosphorus nuclei. Harris[6] has treated the coupling involved in the appropriate $X_nAAX'_n$ systems and has concluded that when $J_{AA'} \gg (J_{XA} - J_{XA'})$, "virtual coupling" will occur.

In studies of methyldiphenylphosphine adducts with sulfur ligand complexes,[7,8] we observed that the doublet expected for methyl protons coupled to the phosphorus atom at times was collapsed. With certain of the complexes, this collapse could be attributed to paramagnetism.[9,10] With others, it was possible to show that the chemical shift and the J_{P-CH_3} coupling were concentration dependent and that the formation of a singlet was due to averaging of coupling constants of the coordinated with the free phosphine. In the case of some *cis*-palladium complexes, however, neither of these explanations appeared appropriate. Instead it appeared as if a chemical exchange of the phosphine ligands from the diamagnetic complexes was producing the decoupling.

Employing the density matrix technique of Kaplan as described by Alexander,[11,12] we have investigated the nmr line shapes to be expected for an $X_nAA'X'_n$ system in which chemical exchange decoupling of AA′ occurs. This approximates the condition which can exist experimentally if magnetically coupled methylphosphine ligands undergo chemical exchange. In this paper we describe the details of the theoretical investigation and some experimental studies related to the decoupling of J_{P-CH_3} by each of the above mechanisms.

Experimental Section

Chemicals used in these studies are reported elsewhere. Spectral grade chloroform-*d* was the solvent of choice for most studies.

Proton nmr spectra in general were recorded on Varian A-60A and HA-100 spectrometers. The temperature dependence of the $PdL_2(S_2CO)$ spectrum, where $L = CH_3P(C_6H_5)_2$, was recorded at −10 and 60° using the standard Varian temperature control for the A-60A. Phosphorus-31 spectra were recorded on a Varian HR-60 instrument.

Computational work was performed on a Univac 1107 digital computer using FORTRAN programs.

Titration of a Palladium(II) Complex with a Phosphine. Varying amounts of bis(*p*-dithiocumato)palladium(II) and diphenylmethylphosphine were weighed into nmr tubes and approximately 1 ml of Spectrograde chloroform was added. The spectra were run on the Varian A-60A spectrometer at 50°. The upfield chemical shift of the methylphosphine protons from $CHCl_3$ (in cps) and J_{P-H} (in cps) were recorded as a function of the complex-to-phosphine molar ratio.

Theoretical Treatment of Nmr Spectra

The density matrix technique of Kaplan and Alexander for the treatment of nmr spectra with intermolecular exchange is discussed in some detail in the recent review by Johnson.[13] As an approximation to the situation encountered where two methylphosphine ligands are coupled through a metal and undergo chemical exchange with additional phosphine, we chose to consider first the XAA′ system.[14] The procedures used for this system with coupling constants J_{XA}, $J_{XA'}$ and $J_{AA'}$ necessitate the description of eight spin-state basis functions and density matrix elements (Table I) corresponding *to the allowed* ($m_k = m_l \pm 1$) *transitions* found by application of the I_+ operator (eq 1). Similar expressions for the X_2AA' system are given in Table II.

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(2) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

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(13) C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965).

(14) This is equivalent to ignoring XX′ coupling.

Table I. Spin-State Basis Functions and Matrix Elements for the XAA′ System

1	ααα	5	βαα
2	ααβ	6	βαβ
3	αβα	7	ββα
4	αββ	8	βββ

$$(1,5)^a \quad iC = \frac{1}{2\tau}(\rho_{26} - \rho_{15}) - i\rho_{15}\left(\Delta - \frac{N}{2}\right) - \rho_{15}/T_2{}^0$$

$$(2,6) \quad iC = \frac{1}{2\tau}(\rho_{15} - \rho_{26}) - i\rho_{26}\left(\Delta + \frac{L}{2}\right) - \rho_{26}/T_2{}^0 + \frac{i}{2}J(\rho_{27} - \rho_{36})$$

$$(3,7) \quad iC = \frac{1}{2\tau}(\rho_{48} - \rho_{37}) - i\rho_{37}\left(\Delta - \frac{L}{2}\right) - \rho_{37}/T_2{}^0 - \frac{i}{2}J(\rho_{27} - \rho_{36})$$

$$(4,8) \quad iC = \frac{1}{2\tau}(\rho_{37} - \rho_{48}) - i\rho_{48}\left(\Delta - \frac{N}{2}\right) - \rho_{48}/T_2{}^0$$

$$(2,7)^b \quad 0 = \rho_{27}\left(-\frac{1}{\tau} - \frac{1}{T_2{}^0} - i\Delta\right) + \frac{i}{2}J(\rho_{26} - \rho_{37})$$

$$(3,6)^b \quad 0 = \rho_{36}\left(-\frac{1}{\tau} - \frac{1}{T_2{}^0} - i\Delta\right) - \frac{i}{2}J(\rho_{26} - \rho_{37})$$

[a] Allowed transitions for X. A, A′ transitions neglected. [b] Forbidden but relevant. [c] $\Delta = \omega_X - \omega$, $N = J_{XA} + J_{XA'}$, $L = J_{XA} - J_{XA'}$, $C = C_{IJ} = (\omega r/2)(\rho_{II} - \rho_{JJ})$, τ = lifetime in site, $J = J_{AA'}$.

$$I(\omega) = \mathrm{Imag} \sum_\alpha P_\alpha \,\mathrm{Trace}\left[\rho^\alpha \sum_J I_{\alpha+}{}^J\right] \qquad (1)$$

In eq 1, $I(\omega)$ is the absorption of frequency ω, P_α is the fraction of molecules of type α, ρ^α is the density matrix, and $I_+ = I_x + iI_y$. Following ref 10–12, we may write eq 2 for the time derivative of the density matrix elements associated with transitions for which $\Delta m = +1$, and for exchange between identical sites. In eq 2 we have

$$\frac{d\rho_{kl}}{dt} = \frac{1}{\tau}\left(\frac{\partial \rho_{kl}}{\partial t}\right)_{\mathrm{exch}} - i\rho_{kl}\Big\{\sum_i (\omega_i - \omega)[(I_Z{}^i)_{kk} - (I_Z{}^i)_{ll}] + \sum_{i<j} J_{ij}(I_Z{}^iI_Z{}^j)_{kk} - (I_Z{}^iI_Z{}^j)_{ll}]\Big\} + \sum_{i<j} J_{ij}[\rho, I_+{}^iI_-{}^j + I_-{}^iI_+{}^j]_{kl} + i\omega_r(\rho_{kk} - \rho_{ll})\sum_i (I_x{}^i)_{kl}$$

$$\left[\frac{\partial \rho(k,\alpha;k'\alpha')}{\partial t}\right]_{\mathrm{exch}} = \frac{1}{\tau}\left[\delta(k,k')\sum_k \frac{\rho(k,\alpha;k,\alpha')}{N_{\mathrm{exch}}} + \delta(\gamma,\gamma')\sum_\gamma \frac{\rho(k,\gamma';k'\gamma)}{N_{\mathrm{non}}} - \rho(k,\alpha;k'\alpha')\right] \qquad (2)$$

followed the nomenclature of Alexander[12] as used by Johnson,[13] and k, k' and γ, γ' are the spin states of the exchanging and nonexchanging portions, respectively, primes indicating states after exchange. N_{exch} and N_{non} are the dimensions of the exchanging and nonexchanging spin space, and τ is the lifetime in the site. The exchanging unit is considered to be A′. Using the above equations, expressions are obtained for the time derivatives of the density matrix elements associated with the allowed transitions and the forbidden transitions coupled by the nonsecular terms. This leads to 15 equations (12 allowed, 3 "forbidden") which may be readily set up for computer solution, the absorption being given by eq 1.

Of the 12 matrix elements associated with allowed transitions, 4 correspond to X spin flips. These determine the calculated X spectrum to 1 part in 10^6 (if the resonance frequency of the A nuclei is considered to be well removed from that of the X nucleus). The four equations for the allowed X transition matrix elements, together with the two relevant forbidden transitions, are given in Table I.

As discussed by Harris[6,15] the incorporation of additional X nuclei leads to an increase in the number of possible transitions. This effect on the spectrum is particularly significant under conditions of no chemical exchange when $J_{AA'} \sim (J_{XA} - J_{XA'})$. To examine the generality of the conclusions found for the XAA′ fragment under chemical exchange, we have also examined the calculated X spectrum for X_2AA'. To do this a set of 24 equations must be solved (Table II).

The equations for the density matrix elements of the allowed transitions in the X_2AA' system are of exactly the same form as those given above for XAA′, and the modification lies in the addition of terms in the coupling constants J_{AX} and $J_{AX'}$ into the diagonal elements of the forbidden transition density matrix equations. This is true for any number of X nuclei incorporated, and, in principle, there is no difficulty extending the present calculations. The matrices would, however, become very large. The only significant changes would be for the conditions noted above, thus giving no additional information on the effects of exchange. The full number of X nuclei must be included, though, if the calculated line shapes are to be used for the determination of exchange rates from experimental spectra.

For the nonexchange situation the calculated X transitions for $X_{2n}AA'$ are the same as those for $X_nAA'X'_n$ if $J_{XX'} = 0$.[15] Thus the commutator $[\rho', H]$ terms are independent of the ordering of the nuclei. This equivalence will still hold under chemical exchange conditions, though the exchange terms will now couple a larger number of density matrix terms. For the nonexchange situation the ratio $L/J_{AA'}$ is sufficient to define the effects on the spectrum of AA′ coupling.[13] With chemical exchange, however, J_{XA}, $J_{XA'}$, $J_{AA'}$, and τ are each signifi-

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[15] R. K. Harris, *Inorg. Chem.*, 5, 701 (1966).

Table II. Basic Functions and Density Matrix Equations for X_2AA'

Spin Functions

1	αααα	5	αααβ	9	ααβα	13	ααββ
2	αβαα	6	αβαβ	10	αββα	14	αβββ
3	βααα	7	βααβ	11	βαβα	15	βαββ
4	ββαα	8	ββαβ	12	βββα	16	ββββ

Density Matrix Equations

(1,2) $iC = \frac{1}{2\tau}(\rho_{56} - \rho_{12}) - i\rho_{1,2}(\Delta + N/2) - \rho_{1,2}/T_2{}^0$

(1,3) $iC = \frac{1}{2\tau}(\rho_{57} - \rho_{13}) - i\rho_{1,3}(\Delta + N/2) - \rho_{1,3}/T_2{}^0$

(3,4) $iC = \frac{1}{2\tau}(\rho_{78} - \rho_{34}) - i\rho_{3,4}(\Delta + N/2) - \rho_{3,4}/T_2{}^0$

(2,4) $iC = \frac{1}{2\tau}(\rho_{68} - \rho_{24}) - i\rho_{2,4}(\Delta + N/2) - \rho_{2,4}/T_2{}^0$

(5,6) $iC = \frac{1}{2\tau}(\rho_{12} - \rho_{56}) - i\rho_{5,6}(\Delta + L/2) + \frac{i}{2}J(\rho_{5,10} - \rho_{9,6}) - \rho_{5,6}/T_2{}^0$

(5,7) $iC = \frac{1}{2\tau}(\rho_{13} - \rho_{57}) - i\rho_{5,7}(\Delta + L/2) + \frac{i}{2}J(\rho_{5,11} - \rho_{9,7}) - \rho_{5,7}/T_2{}^0$

(7,8) $iC = \frac{1}{2\tau}(\rho_{34} - \rho_{78}) - i\rho_{7,8}(\Delta + L/2) + \frac{i}{2}J(\rho_{7,12} - \rho_{11,8}) - \rho_{7,8}/T_2{}^0$

(6,8) $iC = \frac{1}{2\tau}(\rho_{24} - \rho_{68}) - i\rho_{6,8}(\Delta + L/2) + \frac{i}{2}J(\rho_{6,12} - \rho_{10,8}) - \rho_{6,8}/T_2{}^0$

(9,10) $iC = \frac{1}{2\tau}(\rho_{13,14} - \rho_{9,10}) - i\rho_{9,10}\left(\Delta - \frac{L}{2}\right) + \frac{L}{2}J(\rho_{9,6} - \rho_{5,10}) - \rho_{9,10}/T_2{}^0$

(9,11) $iC = \frac{1}{2\tau}(\rho_{13,15} - \rho_{9,11}) - i\rho_{9,11}\left(\Delta - \frac{L}{2}\right) + \frac{L}{2}J(\rho_{9,7} - \rho_{5,11}) - \rho_{9,11}/T_2{}^0$

(11,12) $iC = \frac{1}{2\tau}(\rho_{15,16} - \rho_{11,12}) - i\rho_{11,12}\left(\Delta - \frac{L}{2}\right) + \frac{L}{2}J(\rho_{11,8} - \rho_{7,12}) - \rho_{11,12}/T_2{}^0$

(10,12) $iC = \frac{1}{2\tau}(\rho_{14,16} - \rho_{10,12}) - i\rho_{10,12}\left(\Delta - \frac{L}{2}\right) + \frac{L}{2}J(\rho_{10,8} - \rho_{6,12}) - \rho_{10,12}/T_2{}^0$

(13,14) $iC = \frac{1}{2\tau}(\rho_{9,10} - \rho_{13,14}) - i\rho_{13,14}\left(\Delta - \frac{N}{2}\right) - \rho_{13,14}/T_2{}^0$

(13,15) $iC = \frac{1}{2\tau}(\rho_{9,11} - \rho_{13,15}) - i\rho_{13,15}\left(\Delta - \frac{N}{2}\right) - \rho_{13,15}/T_2{}^0$

(15,16) $iC = \frac{1}{2\tau}(\rho_{11,12} - \rho_{15,16}) - i\rho_{15,16}\left(\Delta - \frac{N}{2}\right) - \rho_{15,16}/T_2{}^0$

(14,16) $iC = \frac{1}{2\tau}(\rho_{10,12} - \rho_{14,16}) - i\rho_{14,16}\left(\Delta - \frac{N}{2}\right) - \rho_{14,16}/T_2{}^0$

(5,10) $0 = \rho_{5,10}\left[-\frac{1}{\tau} - i\left(\Delta - \frac{L}{2}\right)\right] + \frac{i}{2}J(\rho_{5,6} - \rho_{9,10}) - \rho_{5,10}/T_2{}^0$

(9,6) $0 = \rho_{9,6}\left[-\frac{1}{\tau} - i\left(\Delta + \frac{L}{2}\right)\right] - \frac{i}{2}J(\rho_{5,6} - \rho_{9,10}) - \rho_{9,6}/T_2{}^0$

(5,11) $0 = \rho_{5,11}\left[-\frac{1}{\tau} - i\left(\Delta - \frac{L}{2}\right)\right] + \frac{i}{2}J(\rho_{5,7} - \rho_{9,11}) - \rho_{5,11}/T_2{}^0$

(9,7) $0 = \rho_{9,7}\left[-\frac{1}{\tau} - i\left(\Delta + \frac{L}{2}\right)\right] - \frac{i}{2}J(\rho_{5,7} - \rho_{9,11}) - \rho_{9,7}/T_2{}^0$

(7,12) $0 = \rho_{7,12}\left[-\frac{1}{\tau} - i\left(\Delta + \frac{L}{2}\right)\right] - \frac{i}{2}J(\rho_{7,8} - \rho_{11,12}) - \rho_{7,12}/T_2{}^0$

(11,8) $0 = \rho_{11,8}\left[-\frac{1}{\tau} - i\left(\Delta - \frac{L}{2}\right)\right] - \frac{i}{2}J(\rho_{7,8} - \rho_{11,12}) - \rho_{11,8}/T_2{}^0$

(6,12) $0 = \rho_{6,12}\left[-\frac{1}{\tau} - i\left(\Delta + \frac{L}{2}\right)\right] - \frac{i}{2}J(\rho_{6,8} - \rho_{10,12}) - \rho_{6,12}/T_2{}^0$

(10,8) $0 = \rho_{10,8}\left[-\frac{1}{\tau} - i\left(\Delta - \frac{L}{2}\right)\right] - \frac{i}{2}J(\rho_{6,8} - \rho_{10,12}) - \rho_{10,8}/T_2{}^0$

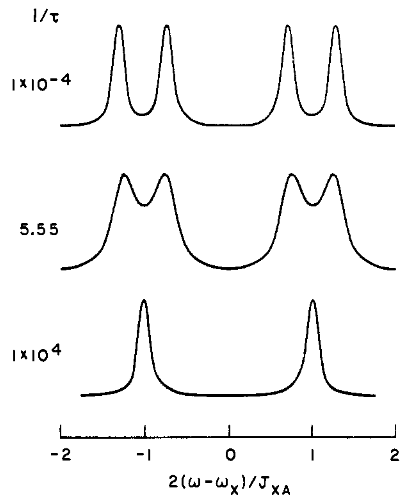

Figure 1. Calculated X nmr spectrum for the XAA′ system; $R = 0$, $S = 3.33$.

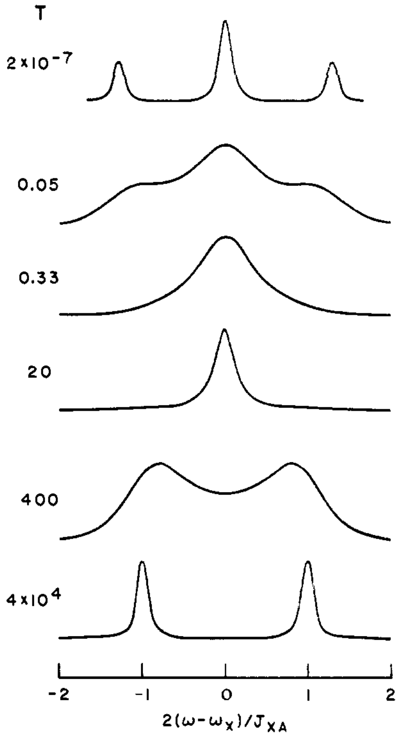

Figure 2. Calculated X nmr spectrum of XAA′ system; $R = 5$, $S = 3.33$.

cant in that they relate to the coupling of the density matrix expressions. Thus to characterize the calculated spectra we will use

$$R = J_{AA'}/J_{XA} \qquad S = J_{XA}/J_{XA'} \qquad \frac{1}{2\pi}T = (J_{AA'}\tau)^{-1}$$

In Figures 1–3 the calculated X spectra (XAA′ and X_2AA' give essentially identical results) are presented for three values of the ratio $J_{XA}/J_{AA'}$ at various exchange rates for a fixed value of $J_{XA}/J_{XA'}$.

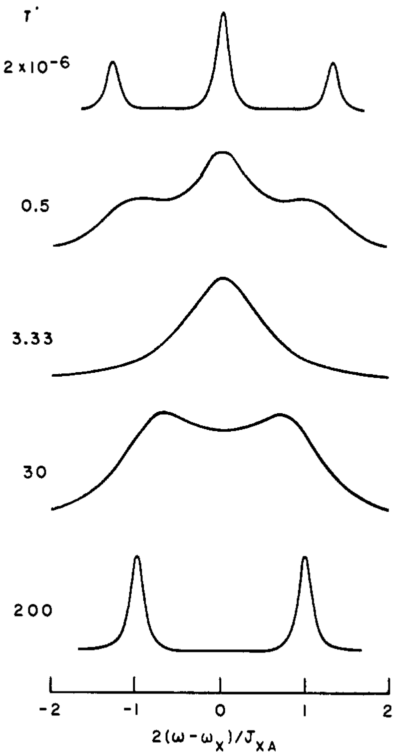

Figure 3. Calculated X nmr spectrum of XAA′ system; $R = 50$, $S = 3.33$.

Experimental Results

A chloroform solution of $Pd(S_2CO)(PCH_3(C_6H_5)_2)_2$ gives a methyl proton nmr spectrum at room temperature typical of a "virtually coupled" system, *i.e.*, a 1:2:1 "triplet" indicative of appreciable P–P coupling (Figure 4). Addition of a small increment of phosphine ligand collapses the "triplet" to a singlet. The "triplet" can be restored by cooling and collapsed again by warming.

The nmr spectrum of *cis*-$Pd(PCH_3(C_6H_5)_2)_2Cl_2$ in $CDCl_3$ containing excess phosphine also shows a collapsed "triplet" (Figure 5). This same solution shows a ^{31}P nmr spectrum which suggests the absence of first-order paramagnetism.

The methyl proton nmr behavior for the $Ni(PCH_3(C_6H_5)_2)_2Cl_2$ system is considerably different from that observed for the palladium complex. Here one observes effects due to first-order paramagnetism, namely a collapse of the coupling, shifting of peak positions, and broadening. This type of system has been studied previously by Horrocks.[9] It is worthwhile pointing out that only trace quantities of nickel(II) are necessary to produce a collapse of the doublet expected for the pure methyldiphenylphosphine. In fact, we and others[16] have observed that distilled phosphine placed into an nmr tube by means of a metallic syringe may give a singlet spectrum, but using a glass syringe the normal doublet is obtained.

A different phenomenon produces the singlet which may be observed for the methyl resonance when methyldiphenylphosphine is allowed to react with bis(dithiocu-

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(16) Professor A. L. Ternay first pointed out this observation to us. Our observations of methyl singlets were obtained using a Hamilton syringe.

Table III. Nuclear Magnetic Resonance Titration of Bis(dithiocumato)palladium(II) with Methyldiphenylphosphine

CH_3Ph_2P, moles ($\times 10^5$)	$Pd(S_2CC_6H_4C_3H_7)_2$, moles ($\times 10^5$)	Molar ratio complex/ phosphine	J_{P-CH_3},[a] cps	Δ,[b] cps
2.88[c] ± 0.05	5.17[c] ± 0.05	1.79	−10.6 ± 0.1	302.0 ± 0.2
4.21	4.88	1.16	−10.4 ± 0.1	303.0 ± 0.2
5.19	3.65	0.70	−6.8 ± 0.1	311.8 ± 0.2
7.87	2.37	0.33	−1.4 ± 0.1	325.2 ± 0.2
10.8	0.633	0.059	+2.8 ± 0.1	335.8 ± 0.2
9.30	0.00	0.00	+3.4 ± 0.1	337.1 ± 0.2

[a] Coupling constant for the methyl protons in Ph_2MeP. [b] Upfield shift of methyl protons in Ph_2MeP from $CHCl_3$. [c] Error ~0.05 mole in each measurement.

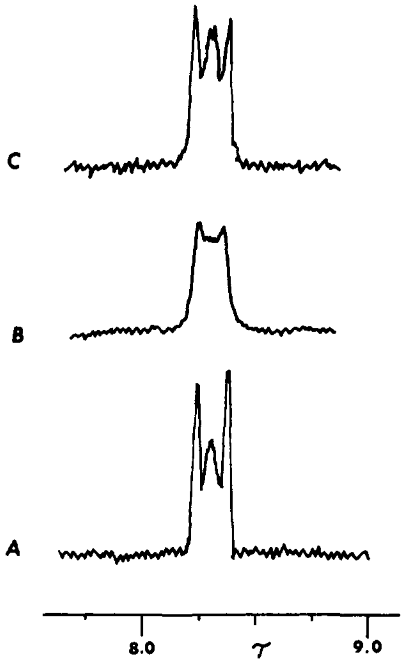

Figure 4. Proton nuclear magnetic resonance spectrum of $[CH_3P(C_6H_5)_2]_2PdS_2CO$: (A) complex in chloroform-*d*; (B) phosphine excess ~0.01 mole % at 60°; (C) solution B at −10°.

mato)palladium(II) in chloroform. At a phosphine-to-metal ratio of ~4.0, the doublet associated with the 1:1 adduct, $J_{P-CH_3} \sim 10.6$ cps, is collapsed (Table III). However, in this case the coupling constant decreases with increased phosphine and the chemical shift also changes correspondingly from the value associated with the 1:1 adduct to that of the free phosphine (Figure 6). Averaging of free and coordinated phosphine is indicated.

Discussion of Experimental Results

Prior to this study, to our knowledge only two mechanisms had been observed and theoretically characterized whereby a metal ion appeared to relax a coupling associated entirely with a ligand. The first of these, namely a spin-lattice (T_1) relaxation, has been well documented in the literature and is generally associated with the presence of paramagnetic (first-order paramagnetism) metal ions. This is the situation observed when nickel(II) salts are dissolved in phosphines. Paramagnetism likely is the cause of the relaxation observed in phosphine adducts with nickel(II) 1,1-dithiol complexes. Recently[10] Randall and Shaw suggested that temperature-independent paramagnetism (TIP, second-order paramagnetism) may also cause the J_{P-CH_3} coupling to relax. These authors have suggested TIP to be the cause of decoupling observations they observed with some phosphine complexes of second- and third-row transition elements, where large TIP values are known for the complexes. However, it is not apparent that chemical exchange averaging of "virtually coupled" phosphines can be eliminated as a mechanism for relaxation of the P–H coupling in the complexes of Chatt, *et al.*[17]

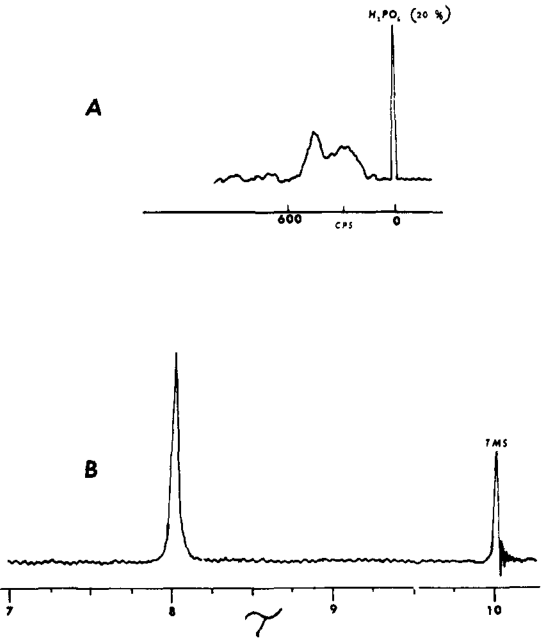

Figure 5. Nmr spectrum of $[CH_3P(C_6H_5)_2]PdCl_2$ in chloroform-*d* with slight excess of phosphine: (A) ^{31}P resonance; (B) proton resonance.

Cullingworth, *et al.*,[18] recently presented an example of chemical exchange averaging which leads to the apparent loss of J_{P-CH_3} coupling. They showed that the exchange of free phosphine with phosphine coordinated to trialkylaluminum leads to chemical shift and coupling constant changes which parallel the formation of a 1:1 adduct. The observed J_{P-CH_3} passes through zero in going from the value associated with the complex to that of the free phosphine. This indicates that the phosphine coordinated to the metal and the free phosphine have opposite

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(17) J. Chatt, G. J. Leigh, D. M. P. Mingos, R. W. Randall, and D. Shaw, *Chem. Commun.*, 419 (1968).

(18) A. R. Cullingworth, A. Pidcock, and J. D. Smith, *ibid.*, 89 (1966).

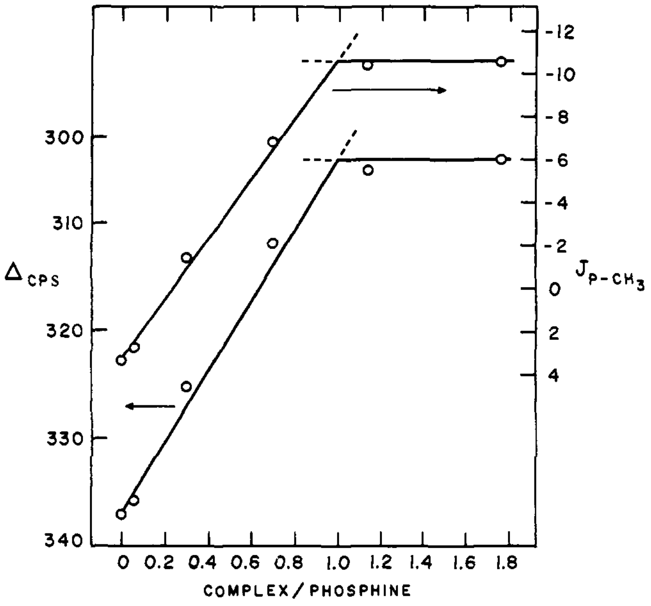

Figure 6. Chemical shift and J_{P-CH_3} coupling constant changes with the metal-to-ligand ratio for the reaction of $CH_3P(C_6H_5)_2$ with bis(dithiocumato)palladium(II) in $CHCl_3$ at 50°.

J_{P-CH_3} coupling constants. Since the dimethylphenylphosphine has been shown to have a positive $^{19}J_{P-CH_3}$ coupling constant, this coupling constant in the coordinated phosphine must be negative.

An entirely analogous situation exists for the reaction of bis(dithiocumato)palladium(II) with methyldiphenylphosphine (Figure 6). The 1:1 adduct appears to have a negative $^{19}J_{P-CH_3}$ coupling constant of ~10.6 cps which averages with the free phosphine constant of ~ +3.4 cps when the phosphine is present in excess. Near the Pd/P ratio of 0.25, the methyl signal of the phosphine appears as a singlet.

The loss of J_{P-CH_3} coupling in the L_2PdS_2CO and L_2PdCl_2 systems with a slight excess of phosphine present cannot be attributed to either of the mechanisms described above. First- or second-order paramagnetism is not found for planar palladium(II) complexes. Also, the absence of chemical shift changes in the spectra appears to rule it out. The observation of phosphorus-31 resonance in the L_2PdCl_2 complex (Figure 5) also tends to rule out paramagnetic relaxation.[20] No ^{31}P resonance could be observed in the paramagnetic nickel(II) systems.

An averaging of coupling constants also is eliminated as a decoupling mechanism since uncoordinated phosphine is not present in sufficient quantity (< 10 mole % excess) to be averaged with the complex producing a singlet. Furthermore, chemical shifts would occur if averaging of coordinated and uncoordinated phosphine were taking place. No changes were observed in the resonance frequency for the collapsed signal compared with the signals of the coordinated phosphines.

Under conditions of chemical exchange, it occurred to us that in a XA–M–A′X′ system, where XA and X′A′ are identical, spin exchange of A with A′ might occur by means of coupling through the metal. In *trans*-L_2MX_2 complexes A–A′ coupling (A = phosphorus) is known to be large; hence spin exchange seemed possible. In the L_2PdS_2CO complex described here, the A–A′ coupling must also be appreciable since the methyl resonance observed appears as a "virtually coupled" triplet. Using the treatment of Harris[6,15] as a model for the L_2M complexes and considering L exchange, it was possible to show that AX decoupling could indeed arise from A–A′ exchange.[21]

Discussion of Theoretical Treatment

For both the XAA′ and X_2AA' systems, the results obtained by the Kaplan–Alexander density matrix treatment[11,12] for the X transitions under zero exchange are the same as those given by Harris.[6,15] Since the conclusions for the $X_{2n}AA'$ system are the same as for the XAA′ system except where indicated, we will discuss the calculated spectra only for the latter.

Under conditions of no exchange with $J_{AA'} = 0$, when ω is in the region of the lowest frequency X transition, the only matrix element that makes a significant contribution is ρ_{48} (Table I). Under these conditions eq 1 is equivalent to a Bloch equation and reduces to Lorentzian form centered at $\omega_X - (J_{XA} + J_{XA'})/2$. Similarly, for the other lines when $J_{AA'}$ becomes significantly greater than L the spectrum (Figures 1 and 2) shows the virtually coupled 1:2:1 triplet pattern. It may be noted that when there is an odd number of X nuclei there will be a pair of forbidden transitions ($J_{AA'} = 0$) at $\omega = \omega_X$. For XAA′, the mixing when $J_{AA'} \neq 0$, of ρ_{26} and ρ_{37} together with the elements associated with the forbidden transitions gives intensity to these latter transitions. This may be contrasted to $X_{2n}AA'$.[6] However, for $L/J_{AA'} < \sim 0.2$ the spectra for both odd and even numbers of X nuclei approach equivalence, giving the 1:2:1 triplet pattern. For the intermediate region where $J_{AA'} \sim 0 \rightarrow 2L$ a more complicated pattern is seen (see Figure 1, ref 15). The number of lines is now a function of the number of X nuclei.

For the chemical exchange situation the calculated spectrum will depend on J_{XA}, $J_{XA'}$, $J_{AA'}$, and τ. Ratios of these parameters were defined previously. We have not derived an analytical solution for $I(\omega)$ in terms of these parameters, analogous to that given by Alexander;[12] for complex situations this will not be readily possible. However, with rapid computer solution available for a wide range of parametric values, useful results describing the behavior were obtained semiempirically.

For a description of the spectrum under fast exchange conditions the significant ratio is $R = J_{AA'}/J_{XA}$ (corresponding to Alexander's J/δ, where δ is the chemical shift). A range of 11–15 can be given to R appreciably below which a transition from slow to fast exchange brings about

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[19] W. McFarlane, *Chem. Commun.*, 58 (1967). We assume J_{P-CH_3} in $CH_3P(C_6H_5)_2$ also is positive.

[20] M. Cohn and T. R. Hughes, *J. Biol. Chem.*, **237**, 176 (1962).

[21] A referee has suggested that this result is "intuitive" for the A′AX system since "with large $J_{A'A}$ the exchange of A′ will increase the spin-lattice relaxation rate of A. In the vicinity of τ, $J_{A'X} \sim 1$, the relaxation process will be most efficient, A will relax at its maximum rate, and the A–X coupling will be almost completely averaged out." The large AA′ coupling is then similar in kind to the large nucleus–electron coupling in paramagnetic systems, and the effect of exchange is qualitatively the same as in the more common paramagnetic systems. A. Abragam ("Principles of Nuclear Magnetism," Oxford University Press, New York, N. Y., 1961) calls this a scalar relaxation of the first kind.

collapse of the spectrum to a doublet (Figures 1 and 2) and above which it collapses to a singlet (Figure 3). This corresponds to the behavior shown by two interacting nuclei under weak and strong coupling, respectively.[12] The result above is essentially independent of the value of $J_{XA'}$, assuming this to be of the same order of magnitude as J_{XA}. The features of the nonexchange spectrum, however, are strongly determined by the value of L, as is necessarily the appearance of the spectrum for rates intermediate between slow and fast exchange (Figures 1 and 2). Qualitatively this result is indicative of the averaging out of the X coupling to the exchanging nucleus, which occurs in all cases irrespective of the value of $J_{AA'}$. The coupling of the density matrix elements by $J_{AA'}$ then effectively operates between transitions located at $\omega_X - J_{XA}$ and $\omega_X + J_{XA}$, hence the significance of $J_{AA'}/J_{XA}$. Thus for fast exchange and R small $\rho_{15} \approx \rho_{26}$ and $\rho_{37} \approx \rho_{48}$, while for R large all matrix elements are strongly coupled and $\rho_{15} \approx \rho_{26} \approx \rho_{37} \approx \rho_{48}$. This leads to a single line centered at ω_X.

For the case where fast exchange gives a singlet a further increase in the exchange rate, to a fast exchange limit, leads to a breakup of the singlet and formation of a doublet in the same positions as for weak coupling, fast exchange (Figure 3). This then corresponds to strong coupling of ρ_{15} to ρ_{26}, and ρ_{37} to ρ_{48}. While the value of $J_{XA'}$ is not significant in determining the appearance of the fast exchange spectrum, an increase in $J_{XA'}$ leads to increase in the spectrum line width for fixed exchange rate. This would be small, however, if $J_{XA'}$ went from a value, say, of $J_{XA/2}$ to J_{XA}.

These results will be valid irrespective of the number of X nuclei included as the requirement is that pairs of lines on either side of ω_X be strongly coupled. This conclusion will always be true in a multi-X situation as the various density matrix elements must, of necessity, be considered in sets of six that are analogous to the equations listed above for the XAA′ case. In the case of the fast exchange doublet any line width increase could be offset by an increase in exchange rate. For the fast exchange singlet, however, if $J_{XA'}$ became very large a sharp singlet might not be formed and a significant rate increase would lead only to a doublet. But this latter situation does not appear to be physically probable.

The A spectrum also may be calculated by methods parallel to those given above. It should be noted that the results for $X_{2n}AA'$ and $X_nAA'X_n'$ are not equivalent, in general, under either exchange or nonexchange conditions. Consider, for example, the results of exchange on XAA′. For no exchange and $L/J_{AA'} < 1$ the A spectrum is the expected doublet. For rapid exchange, for situations in which the X spectrum collapses from a triplet to a doublet, the A spectrum passes from a doublet to a "triplet," again corresponding to the averaging of the coupling of the exchanging A′. For situations in which the X spectrum collapses to a singlet the A spectrum also gives a singlet since the matrix elements for both exchanging and nonexchanging A are coupled. This result should be true for both $X_{2n}AA'$ and $X_nAA'X_n'$ as well.

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