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Notes

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The System $PdX_2(PMe_3)_2$ and PMe_3 in CH_2Cl_2 Solution As Studied by Phosphorus-31 Nuclear Magnetic Resonance

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We have reported recently[1] that the identity of the species present in dichloromethane solutions of PtX_2L_2 and L (L = PMe_3, PEt_3, P-*n*-Bu_3, P-*p*-tol_3) are *cis*- and *trans*-PtX_2L_2, $[PtXL_3]^+$ (X = Cl, Br), PtI_2L_3, and $[PtXL_4]^+$ (X = Cl, Br, I; L = PMe_3). Variable-temperature ^{31}P NMR showed that intermolecular phosphine exchange occurs between $[PtClL_3]^+$, $[PtClL_4]^+$, PtI_2L_3, and free L. These species are either tetragonal planar or square pyramidal, and there was no evidence of any intramolecular process interconverting the positions of the phosphines. We concluded that the cis-trans isomerization of PtX_2L_2 catalyzed by L proceeds by the double displacement mechanism originally proposed by Basolo and Pearson[2] and not by pseudorotation of a five-coordinate intermediate.[3]

We report now the results of a ^{31}P NMR study of the corresponding palladium(II) complexes as well as a comparison of the geometries and phosphine exchange mechanisms of five-coordinate MX_2L_3 and $[MXL_4]^+$ (M = Ni, Pd, Pt; L = PMe_3; X = Cl, Br, I).

Results and Discussion

1. Studies of $PdX_2(PMe_3)_2$ and PMe_3 in Dichloromethane Solution. Identification of the Species Present. The synthesis,[4] IR,[5] and ^{1}H NMR[6] spectral properties of *cis*- and *trans*-PdX_2L_2 are well established. Cis-trans thermal isomerization occurs in solution when a trace of L is added and the equilibrium thermodynamic parameters have been determined in various solvents for PdX_2L_2 (L = PPh_2Me, $PPhMe_2$; X = Cl, OCN,[7] N_3[8]). One complex with three bonded phosphines, $PdCl_2(PPhMe_2)_3$, was found by X-ray analysis[9] to have a distorted square-pyramidal geometry. No complexes with four bonded phosphines have been characterized so far, except $[HPd(PEt_3)_4]^+$.[10]

We have prepared a series of solutions of $PdX_2(PMe_3)_2$ and PMe_3 and compared their ^{31}P NMR spectra with those of known PdX_2L_2 and $[PdXL_3]^+$ complexes. The identity of the species present in dichloromethane solution is given in Table I. On the NMR time scale, a fast intermolecular exchange between $[PdX(PMe_3)_n]^+$ (n = 3, 4) and free PMe_3 is observed at room temperature. The $^{31}P\{^1H\}$ FT NMR spectra were recorded at the low-temperature slow-exchange limit, and the spectral data are summarized in Table II. The "tris" species are formulated as five-coordinate $PdX_2(PMe_3)_3$ (X = Cl, Br, I) since the ^{31}P NMR spectrum of $PdX_2(PMe_3)_2 + PMe_3$ (1:1) is different from that of $[PdX(PMe_3)_3]PF_6$ (e.g., Figure 1). The ^{31}P triplet of $PdX_2(PMe_3)_3$ (X = Br, I) appears at higher field than the ^{31}P doublet with a $^2J(P,P)$ coupling constant much smaller than that of the corresponding $[PdX(PMe_3)_3]^+$ complexes (Table II). This pattern is quite similar to those of NiX_2L_3 (X = Cl, Br, I; L = PMe_3, $P(OMe)_3$) which were shown by Meier et al.[12] to have a trigonal-bipyramidal geometry with two axial L ligands. The same respective positions of axial and equatorial phosphite signals were observed by Meakin and Jesson[13] in the ^{31}P NMR spectrum of the trigonal-bipyramidal $[Pd(P(OMe)_3)_5]^{2+}$ ion. In contrast, there is an inversion of the NMR pattern of $PdCl_2(PMe_3)_3$ with respect to that of the preceding "tris" species with a $^2J(P,P)$ coupling constant now close to that of a quadratic arrangement of three

Table I. The System $PdX_2(PMe_3)_2$ and PMe_3 in CH_2Cl_2 Solution

starting complex	$[PMe_3]_{added}/[Pd]$	species in solution
trans-$PdCl_2L_2$	trace[b]	*cis*-$PdCl_2L_2$ (>99%)
cis-PdX_2L_2 (X = Br, I)	trace[b]	*trans*-PdX_2L_2 (>99%)
PdX_2L_2 (X = Cl, Br, I)[a]	1[c]	PdX_2L_3 (>99%)
PdX_2L_2 (X = Cl, Br, I)[a]	≥2[c,d]	$[PdXL_4]^+$ (>99%)

[a] Cis or trans. [b] At 30 °C. [c] At −90 °C. [d] At −155 °C in $CHClF_2$.

Table II. ^{31}P NMR Parameters for Trimethylphosphine Complexes of Palladium(II)

		δ(P)		
no.	complex[a]	trans to P	cis to P	^2J(P,P)
1a,b	*trans*- and *cis*-$PdCl_2L_2$	−2.1 s	−12.1 s	
2a	*trans*-$PdBr_2L_2$	−17.3 s		
3a	*trans*-PdI_2L_2	−11.0 s		
4	$[Pd_2Cl_2L_4](PF_6)_2$		10.5 s	
5	$[Pd_2Br_2L_4](PF_6)_2$		−8.1 s	
6	$[Pd_2I_2L_4](PF_6)_2$		2.9 s	
7	$PdCl_2L_3$[b]	−6.6	−5.3	21
8	$[PdClL_3]PF_6$[b]	−7.5	−4.8	26
9	$PdBr_2L_3$	−8.0 d	−17.1 t	10
10	$[PdBrL_3]PF_6$	−4.2 d	−6.5 t	24
11	PdI_2L_3	−14.5 d	−34.2 t	4
12	$[PdIL_3]PF_6$[b]	−15.8	−14.6	22
13	$[PdClL_4]Cl$	−15.9 s		
14	$[PdBrL_4]Br$	−18.1 s		
15	$[PdIL_4]I$	−20.9 s		

[a] In CD_2Cl_2 for **1-3**, **7-15**, in acetone-d_6 for **4-6**; at 30 °C for **1-6**, at −90 °C for **7-15**. Chemical shifts are in ppm relative to external H_3PO_4 (62.5%) and are correct to ±0.1; a negative sign indicates a shift to higher field relative to the reference. Coupling constants are in Hz and are correct to ±2 Hz. [b] Second-order spectrum at 36.43 MHz. The AB_2 spin system was simulated by the program ITRCAL.[11]

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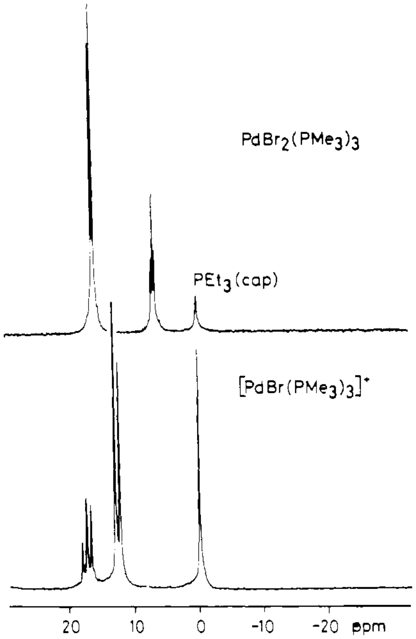
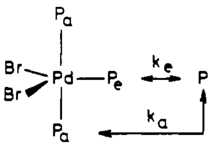


Figure 1. $^{31}P\{^1H\}$ FT NMR spectra in CD_2Cl_2 at -90 °C of (a) $PdBr_2(PMe_3)_3$ or a mixture of *trans*-$PdBr_2(PMe_3)_2$ and PMe_3 (1:1) and (b) $[PdBr(PMe_3)_3]^+$.

Scheme I



phosphines and one chlorine atom. We thus propose a trigonal-bipyramidal geometry with two axial PMe_3 for $PdBr_2(PMe_3)_3$ and $PdI_2(PMe_3)_3$ in solution and a distorted square-pyramidal structure for $PdCl_2(PMe_3)_3$, as found in the solid state for $PdCl_2(PPhMe_2)_3$.[9]

The $^{31}P\{^1H\}$ NMR spectrum of a mixture of $PdX_2(PMe_3)_2$ and PMe_3 (1:2) in CD_2Cl_2 at -90 °C presents a singlet. The species formed should be formulated as $[PdX(PMe_3)_4]^+$ (X = Cl, Br, I) since the chemical shift changes when the nature of X is varied. The spectrum in $CHClF_2$ down to -155 °C does not show any change either of the multiplicity or of the line width. Thus, it is unlikely that this singlet results from a fast exchange between chemically nonequivalent phosphines. Indeed, for the corresponding $[NiX(PMe_3)_4]^+$ complexes the rate of the exchange process can be reduced to a frequency that is low on the NMR scale at -110 °C, and Pd(II) complexes are known to be more inert toward exchange reactions than the corresponding Ni(II) complexes.[2]

2. Dynamic Processes Involving $PdBr_2(PMe_3)_3$ and $[PdX(PMe_3)_4]^+$ (X = Cl, Br). The temperature dependence of the $^{31}P\{^1H\}$ FT NMR spectrum of $PdBr_2(PMe_3)_3$ in dichloromethane indicates that a fast exchange of phosphine takes place at room temperature. This process is intermolecular as shown by the following evidence: (i) The addition of a trace of $Pd_2X_4(PMe_3)_2$[14] to a solution of the corresponding $PdX_2(PMe_3)_3$ (X = Cl, Br, I) complex in dichloromethane blocked the phosphine exchange at 30 °C. This was due to bridge splitting of the dimer removing traces of free PMe_3 from the solution. (ii) The spectrum of a 6.1 × 10^{-2} M solution of $PdBr_2(PMe_3)_3$ in CD_2Cl_2–CH_2Cl_2 (1:2) was taken at various temperatures corresponding to the slow-exchange domain (Figure 2). Simulation by the program EXCHNG[15] required two rate constants to fit these spectra. (See Scheme I.) Meier et al.[12] have shown that the fitting procedure for $NiX_2(PMe_3)_3$ (X = Cl, Br, I) requires only one parameter. They found that the phosphine exchange mechanism is intramolecular and proceeds via a four-coordinate intermediate, $NiX_2(PMe_3)_2$, by dissociation of an axial phosphine of the trigonal-bipyramidal $NiX_2(PMe_3)_3$. If the phosphine-exchange process of $PdBr_2(PMe_3)_3$ was intramolecular, i.e., a Berry-type pseudorotation or a process similar to that of $NiX_2(PMe_3)_3$, one fitting parameter would be sufficient, since dissociation of an equatorial phosphine does not lead to site exchange.[12]

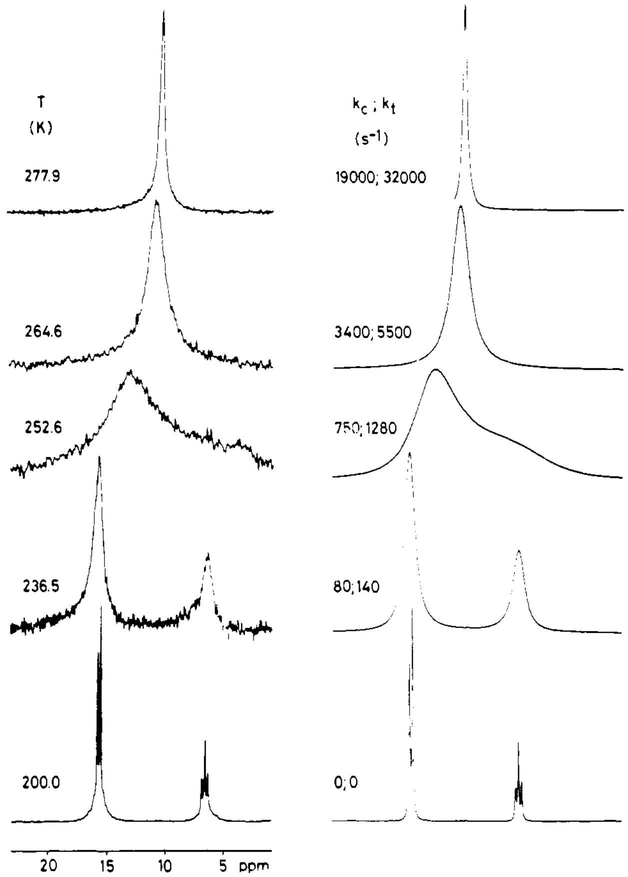


Figure 2. Experimental and calculated $^{31}P\{^1H\}$ FT NMR spectra for the intermolecular exchange of L in $PdBr_2(PMe_3)_3$ as a function of temperature in CD_2Cl_2–CH_2Cl_2 (1:2) ([Pd] = 6.1 × 10^{-2} M).

Table III. Activation Parameters for the Phosphine-Exchange Process Involving $PdBr_2(PMe_3)_3$ in CD_2Cl_2[a]

k_{250}, s^{-1}	ΔG^*_{250}, kcal/mol	ΔH^*,[b] kcal/mol	ΔS^*, eu
$k_a = 950$	11.2 ± 0.1	16.7 ± 0.5	22 ± 2
$k_e = 530$	11.4 ± 0.1	16.8 ± 0.5	22 ± 2

[a] [Pd] = 6.1 × 10^{-2} M. The temperature range examined was 230–300 K; $k_a/k_e = 1.8 \pm 0.2$ for this temperature range. [b] Calculated from $\ln(k/T) = \ln(k_B/h) + \Delta S^*/R - \Delta H^*/RT$. Alignment coefficients are 0.998 and 0.999.

The residence times of the phosphine on a complexed site (τ_{compl}), on site P_e (triplet; $\tau_{P_e} = 1/k_e$), and on site P_a (doublet; $\tau_{P_a} = 2/k_a$) are related by

$$1/\tau_{compl} = -d[PdBr_2L_3]/dt[PdBr_2L_3] = (k_2^a + k_2^e)[L] = k_a + k_e$$

The values of k_a and k_e calculated from an exchange matrix

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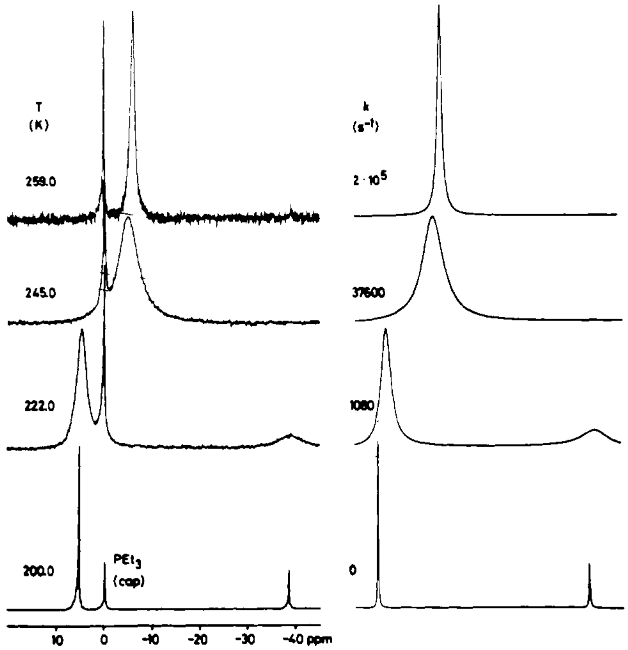

Figure 3. Experimental and calculated $^{31}P\{^1H\}$ FT NMR spectra for the intermolecular exchange between $[PdBr(PMe_3)_4]^+$ and free PMe_3 (1:0.85) as a function of temperature in CD_2Cl_2–CH_2Cl_2 (1:2) ([Pd] = 6.1×10^{-2} M, PEt_3 as external reference).

for six sites[16] are reported in Table III. The activation parameters related to k_a and k_e are equal. The two distinct NMR processes correspond to a single chemical process, i.e., equilibrium 2, where $k_2 = k_1K_1K_2 = {}^3/_4K_1(k_2{}^a + k_2{}^e)$. The

$$PdBr_2(PMe_3)_3 \rightleftarrows [PdBr(PMe_3)_3]^+ + Br^- \qquad K_1 << 1 \quad (1)$$

$$[PdBr(PMe_3)_3]^+ + L \underset{k_1}{\overset{k_2}{\rightleftarrows}} [PdBr(PMe_3)_4]^+ \qquad K_2 >> 1 \quad (2)$$

rate-determining step for the exchange of phosphine is equilibrium 2 since the observed ratio k_a/k_e is equal to the statistical ratio of 2. Effectively, $k_a/k_e = 1.8 \pm 0.2$ over the temperature range studied. Equilibrium 1 is present since the addition of increasing amounts of $[NBu_4]Br$ to $[PdBr(PMe_3)_3]PF_6$ gradually shifts the $^{31}P\{^1H\}$ NMR spectrum to that of $PdBr_2(PMe_3)_3$, the equilibrium constant K_1 being $(1.32 \pm 0.06) \times 10^{-3}$ M at −70 °C (a fast exchange of Br^- ion is still taking place between the four- and the five-coordinate complexes at that temperature since only one doublet and one triplet are observed). The square-pyramidal $[PdBr(PMe_3)_4]^+$ ion is also observed as a stable species in solutions of $PdBr_2(PMe_3)_2$ containing an excess of PMe_3 or is observed by adding 1 equiv of PMe_3 to $[PdBr(PMe_3)_3]PF_6$.

Direct evidence for the exchange process related to k_1 (eq 2) is provided as follows. Variable-temperature $^{31}P\{^1H\}$ FT NMR spectra of a solution of $[PdX(PMe_3)_4]^+$ (X = Cl, Br) were taken and simulated by the program EXCHNG by using an exchange matrix for two sites (Figure 3). The results are reported in Table IV, and the positive entropies of activation are indicative of a dissociative mechanism. Indeed, the rate of exchange $k_{obsd} = {}^1/_4\tau_{compl}$ is independent of the concentration of added PMe_3 (Figure 4). Thus the exchange pathway is clearly the dissociation of one phosphine from $[PdX(PMe_3)_4]^+$ (k_1 path of eq 2). In conclusion, $PdX_2(PMe_3)_3$ complexes are to be considered as stereochemically rigid, and this study contradicts the postulated isomerization mechanism of PdX_2L_2 through pseudorotation of a five-coordinate PdX_2L_3 intermediate.[3]

Table IV. Activation Parameters for the Exchange of $[PdX(PMe_3)_4]^+$ (X = Cl, Br) and PMe_3 in CD_2Cl_2

k_{220}, s^{-1}	ΔG^*_{220}, kcal/mol	ΔH^*,[a] kcal/mol	ΔS^*, eu
	$[PdClL_4]^+$		
24 100	8.3 ± 0.1	14.7 ± 0.3	29 ± 1
	$[PdBrL_4]^+$		
660	9.9 ± 0.1	16.2 ± 0.7	28 ± 3

[a] The temperature range examined is 190–250 for $[PdClL_4]^+$ and 210–260 K for $[PdBrL_4]^+$; the alignment coefficient of ln (kT^{-1}) vs. T^{-1} is 0.999 and 0.997.

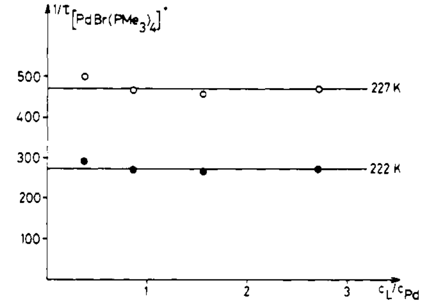

Figure 4. $1/\tau_{compl}$ vs. c_{PMe_3} for the exchange between $[PdBr(PMe_3)_4]^+$ and free PMe_3 in CD_2Cl_2–CH_2Cl_2 (1:2) ($c_{Pd} = 6.1 \times 10^{-2}$ M).

3. Geometries and Phosphine-Exchange Mechanisms of MX_2L_3 and $[MXL_4]^+$ (M = Ni, Pd, Pt; L = PMe_3; X = Cl, Br, I). The summary presented in Table V is based on Meier's et al. results for M = Ni[12] and on our results for Pd (this work) and Pt.[1] The proposed geometries in the solid state are based on the X-ray crystal structure determinations of $NiBr_2(PMe_3)_3$,[17] $[NiBr(PMe_3)_4]BF_4$,[18] $PdCl_2(PPhMe_2)_3$,[9] and $[PtCl(PMe_3)_3]Cl$.[1]

All Ni complexes are trigonal bipyramidal and stereochemically nonrigid. The intramolecular phosphine exchange in these species occurs through different mechanisms: a Berry pseudorotation in $[NiXL_4]BF_4$, a dissociative D mechanism in NiX_2L_3, and an associative interchange I_a in $[NiXL_4]X$. The trigonal-bipyramidal geometry is less favored for Pd and not observed for Pt. PdX_2L_3 complexes are either trigonal bipyramidal (X = Br, I) or distorted square pyramidal (X = Cl), and those species, as well as PtI_2L_3 (SP), are in equilibrium with tetragonal planar $[MXL_3]^+$ ions in dichloromethane solutions. The $[MXL_4]^+$ (M = Pd, Pt) ions are square pyramidal, and the intermolecular phosphine exchange in these species proceeds by a dissociative D mechanism ($[PdXL_4]X$, eq 5 (Table V)) or by two parallel pathways ($[PtXL_4]X$, eq. 5 and 6 (Table V)). "PtX_2L_3" (X = Cl, Br) complexes are definitely four-coordinate tetragonal planar in CH_2Cl_2 solutions. None of the Pd and Pt complexes are to be considered as stereochemically nonrigid, since the intermolecular phosphine exchange in these species is always rapid relative to the rate of intramolecular rearrangement. There is no evidence that a Berry-type pseudorotation is a low activation energy process in MX_2L_3 (M = Pd, Pt). Thus, there is still no unambiguous proof for the mechanism proposed by Haake[19] and Louw[3] for the cis–trans isomerization of PtX_2L_2 catalyzed by L.

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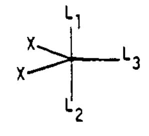
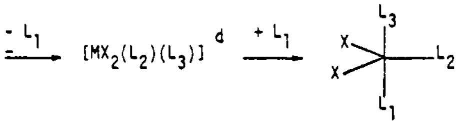
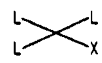
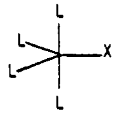
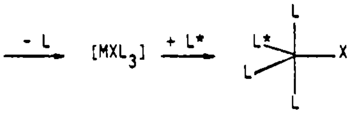
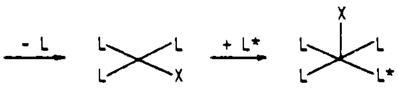
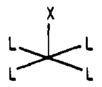
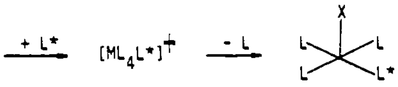
Table V. Geometries and Phosphine Exchange Mechanisms of MX_2L_3 and $[MXL_4]^+$ (M = Ni, Pd, Pt; L = PMe_3)

		geometry in		
M	X	soln (CH_2Cl_2)[a]	solid state	phosphine exchange mechanism
			"MX_2L_3"	
Ni	I		same	in absence of free L: intramolecular, dissociative r.d.s.  (3) in presence of L: see $[NiXL_4]^+$
	Br			
	Cl			
Pd	I	[b]		in absence of L: no exchange at r.t. in presence of L: intermolecular, see $[PdXL_4]^+$
	Br	[b]		
	Cl	distorted SP[b]	same	
Pt	I	SP [b]	?	
	Br	 [c]	same	
	Cl			
			$[MXL_4]^+$	
Ni	I		same	in absence of L: intramolecular, Berry pseudorotation (B) [e] in presence of L: two exchange pathways, i.e. (B) and (4)  (4)[e]
	Br			
	Cl			
Pd	I			in absence of L: no intramolecular process observed in presence of L: intermolecular, dissociative r.d.s.  (5)
	Br			
	Cl			
Pt	I		?	in absence of L: no intramolecular process observed in presence of L: two exchange pathways, i.e. (5) and (6)  (6)
	Br			
	Cl			

[a] The energy difference between the trigonal bipyramid and the square pyramid (SP) is low. Likewise, the crystal structure of $[PtCl(PMe_3)_3]Cl$ shows that the ion has a slight tetrahedral distortion. Thus the proposed geometries have to be understood as being those in closest agreement with the observed NMR parameters. [b] In equilibrium with $[MXL_4]^+$. [c] Five-coordinate MX_2L_3 were not observed in solution. [d] The intermediate may be any $MX_2(L_2)(L_3)$ species of C_{2v} symmetry.[12] [e] With BF_4^- as counterion. When X^- is the counterion, faster exchange rates are observed, and the phosphine exchange proceeds by an associative interchange I_a.[12]

Experimental Section

Spectroscopic Measurements. The techniques used have been described previously.[1]

Preparation of Complexes. All reactions were carried out in an atmosphere of nitrogen. Solvent and trimethylphosphine were transferred on vacuum lines. PMe_3[20] and the following complexes were prepared as reported in the literature: **1–3**,[4] **4–6**,[14] and **8**, **10**, and **12**.[6] E. Manzer (Mikrolabor, ETH Zürich) carried out the microanalyses.

For compounds **7**, **9**, and **11**, $PdX_2(PMe_3)_2$ (X = Cl, Br, I) was dissolved in the minimum amount of dichloromethane, and 1 equiv of PMe_3 was added. The volume was reduced to a few milliliters, and diethyl ether was added. The products precipitated out as yellow microcrystalline powders, yield 32–40%. Anal. Calcd for $C_9H_{27}Cl_2P_3Pd$ (**7**): C, 22.66; H, 6.71. Found: C, 22.76; H, 6.77. Calcd for $C_9H_{27}Br_2P_3Pd$ (**9**): C, 21.86; H, 5.50. Found: C, 21.77; H, 5.44. Calcd for $C_9H_{27}I_2P_3Pd$ (**11**): C, 18.37; H, 4.62. Found: C, 18.19; H, 4.54.

Complexes **13–15** were observed in solution only.

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Registry No. **1a**, 20136-11-2; **1b**, 20136-10-1; **2a**, 23627-41-0; **2b**, 21258-97-9; **3a**, 20136-12-3; **3b**, 76420-80-9; **4**, 76391-56-5; **5**, 76391-57-6; **6**, 76391-58-7; **7**, 68391-72-0; **8**, 76391-59-8; **9**, 76391-60-1; **10**, 76402-71-6; **11**, 76391-61-2; **12**, 76391-63-4; **13**, 76391-64-5; **14**, 76402-72-7; **15**, 76391-65-6.

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