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## "Mixed-Ligand" Bis-Monodentate Phosphorus Donor Ligand Complexes of Palladium(II), $LL'PdCl_2$ . A Comprehensive Investigation<sup>1</sup>

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A large series of complexes of the type *cis*- $LL'PdCl_2$ , where L and L' are combinations of phosphines, phosphites, phosphonites, phosphinites, triethylarsine, and piperidine, have been synthesized and characterized by decomposition points, electronic and infrared spectroscopy, and <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The "mixed-ligand" complexes are in equilibrium with their symmetrical counterparts in solution. When both ligands are phosphorus donors, they are at least as thermodynamically stable and kinetically more inert in solution than the symmetric complexes. The equilibrium position is dependent upon the nature of the ligands but seemingly solvent and temperature independent. Total disproportionation is observed in solution for some arsine and all piperidine complexes. The phosphorus-phosphorus coupling constants, <sup>2</sup>J<sub>PP</sub>, are related to Tolman's electronic parameters in a parabolic way, consistent with current theories of spin-spin coupling. This allows prediction of coupling constants and discussion of line shapes for the [X<sub>n</sub>A]<sub>2</sub> spin systems.

### Introduction

There has been considerable recent interest<sup>3-13</sup> in the mechanisms of the *cis*-*trans* isomerization of square-planar complexes of the type  $ML_2X_2$  (M = Pd, Pt; X = uninegative anion; L = monodentate phosphorus ligand). Three different mechanisms have been proposed for this isomerization involving three different intermediates.<sup>3-13</sup> These intermediates are of the types  $ML_2L'X_2$ ,  $[ML_2L'X]^+X^-$ , and  $MLL'X_2$ .<sup>10,11</sup>

We have recently described a general synthesis of the compounds  $MLL'X_2$ .<sup>14</sup> Now that these compounds are available, an assessment can be made as to their viability as intermediates in the isomerization mechanism.

There also is considerable current interest in the measurement of phosphorus-phosphorus coupling in the NMR spectra of transition metal-phosphorus ligand complexes. This interest is both of theoretical value for bonding arguments and of utilitarian value for its relationship to structural determination of these complexes in solution.<sup>15-23</sup>

A number of complexes of the type  $[L(am)PdCl_2]$  have been reported<sup>24-27</sup> where am is either piperidine or *p*-toluidine and L is a phosphorus donor or triethylarsine. It was concluded on the basis of dipole moment measurements in benzene that they all possessed the *trans* geometry.<sup>27</sup> We anticipated on the basis of our observations on  $L_2PdX_2$  complexes<sup>10-12,28-31</sup> that these solutions might contain in fact equilibrium mixtures of both the *cis* and *trans* isomers.

For these reasons we have prepared and characterized a series of complexes of the type  $PdLL'Cl_2$  where L and L' are combinations of phosphines, phosphinites, phosphonites, phosphites, triethylarsine, and piperidine. Their characterization, magnetic resonance spectra (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H}), and solution behavior are reported herein.

### Experimental Section

**A. Reagents and Physical Measurements.** Chemicals were reagent grade and used as received or synthesized by standard literature methods or as described below. All solvents, when necessary, were dried by standard procedures and stored over Linde 4-Å molecular sieves for at least 2 days prior to use. All reactions involving preparation of the complexes were carried out under nitrogen. Melting points were determined on a Meltemp apparatus and are uncorrected.

Infrared spectra were recorded on a Beckman IR-12 spectrometer as Nujol mulls between CsBr plates in the low-frequency region (650-200  $cm^{-1}$ ).

Electronic spectra were recorded on a Cary 14 spectrophotometer as  $CHCl_3$  solutions in 1-cm quartz cells.

The <sup>1</sup>H spectra were recorded at 100 MHz on a Jeolco 4H-100 spectrometer equipped with a V-6040 variable-temperature controller. The <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Varian XL-100-15 spectrometer in Fourier transform mode with deuterium pulse lock as previously described.<sup>28</sup> Proton and carbon chemical shifts are relative to internal TMS while the phosphorus chemical shifts are relative to external 85%  $H_3PO_4$  (capillary). Solvents were

spectroscopic grade and used as received from the manufacturer after a routine check for purity. Samples for NMR spectra were prepared as previously described.<sup>29</sup> Spectra were recorded and followed as a function of time to ensure equilibration. The ratios of "mixed-ligand" to symmetric species were determined by <sup>31</sup>P{<sup>1</sup>H} NMR spectra recorded on solutions prepared from  $LL'PdCl_2$  after they stood at room temperature for 30 min.

**B. Synthesis. 1. Ligands.** The ligands piperidine, trimethyl phosphite, triphenyl phosphite and triphenylphosphine were purchased commercially and purified. Other phosphines and triethylarsine were prepared by standard Grignard reactions and purified by vacuum distillation. Phosphites, phosphonites, and phosphinites were prepared by alcoholysis reactions and purified by vacuum distillation.

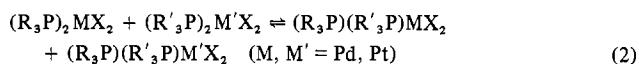
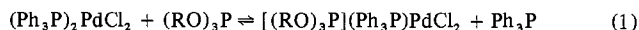
**2. "Mixed-Ligand" Palladium(II) Complexes.** The general method for preparation of these complexes has been discussed elsewhere.<sup>14</sup> The following synthesis for dichloro(dimethylphenylphosphine)(dibenzyl phenylphosphonite)palladium(II) is typical.

To a solution containing 0.1130 g (0.25 mmol) of dichlorobis(dimethylphenylphosphine)palladium(II) in 25 ml of chloroform stirring under nitrogen was added a solution containing 0.2052 g (0.25 mmol) of dichlorobis(dibenzyl phenylphosphonite)palladium(II) in 25 ml of chloroform. The solution was stirred overnight and reduced to dryness. Light yellow crystals of dichloro(dimethylphenylphosphine)(dibenzyl phenylphosphonite)palladium(II) were obtained in nearly quantitative yield (0.300 g, 99%); mp 72-74 °C. They were recrystallized from  $CH_2Cl_2$  by addition of petroleum ether to incipient precipitation. The mixed-ligand complexes with piperidine and triethylarsine were prepared in the same manner as the phosphorus mixed-ligand complexes.

Each of the symmetric complexes  $PdL_2Cl_2$  were analytically pure (new complexes will be described elsewhere), and since elemental analyses could not distinguish between  $PdLL'Cl_2$  and a 1:1 mixture of  $PdL_2Cl_2$  and  $PdL'L_2Cl_2$ , no elemental analyses were obtained for the mixed-ligand complexes. Decomposition points agreed with those of previously reported and analyzed complexes.<sup>27</sup>

### Results and Discussion

Mixed-ligand complexes of the type  $MLL'X_2$  have previously been detected in solution.<sup>10,15,16</sup> Attempts to prepare them by bridge-splitting reactions of dimeric palladium complexes failed,<sup>17</sup> even though this same reaction was successful with amines and with the platinum analogues.<sup>24-27</sup> During the course of our study of the catalyzed isomerization mechanism of  $L_2PdX_2$  complexes we discovered that reactions 1 and 2 produce mixed-ligand complexes.



The generality of these reactions has now been investigated for M = Pd and we find that reaction 1 occurs when the excess ligand is a phosphite, a phosphonite, or a phosphinite. Reaction 2 occurs when the ligands are phosphines, phosphonites, phosphinites, triethylarsine, and piperidine. It thus appears to

Table I. Physical Properties of the Complexes *cis*-LL'<sub>2</sub>PdCl<sub>2</sub>

| No. | L <sup>a</sup>         | L'                     | Color         | Dec pt, °C | Electronic spectra |                        | Ir $\nu_{\text{PdCl}}$ , cm <sup>-1</sup> | <sup>1</sup> H NMR <sup>b</sup> |               |                       |               |
|-----|------------------------|------------------------|---------------|------------|--------------------|------------------------|---|---------------------------------|---------------|-----------------------|---------------|
|     |                        |                        |               |            | $\nu$ , kK         | $\epsilon \times 10^4$ |   | $\delta(\text{CH}_3)$           | <i>J</i> , Hz | $\delta(\text{CH}_2)$ | <i>J</i> , Hz |
| 1   | Me <sub>2</sub> PPh    | BzOPPh <sub>2</sub>    | Lt yellow     | 121-123    | 30.5               | 1.3                    | 275, 317                                  | 1.91                            | 12.5          | 4.22                  | 7.0           |
| 2   | Me <sub>2</sub> PPh    | (BzO) <sub>2</sub> PPh | Yellow        | 72-74      | 29.9               | 1.2                    | 272, 315                                  | 1.81                            | 11.8          | 5.13 <sup>e</sup>     | 7.2           |
|     |                        |                        |               |            |                    |                        |   |                                 |               | 4.51                  | 10.8          |
| 3   | Me <sub>2</sub> PPh    | (BzO) <sub>3</sub> P   | Lt yellow     | 77-78      | 31.8               | 0.87                   | 285, 303                                  | 1.71                            | 11.3          | 5.10                  | 8.8           |
| 4   | Me <sub>2</sub> PPh    | (MeO) <sub>3</sub> P   | Lt yellow     | 131-132    | 31.6               | 0.90                   | 270, 295                                  | 3.71                            | 11.9          |                       |               |
|     |                        |                        |               |            |                    |                        |   | 1.99                            | 11.9          |                       |               |
| 5   | Me <sub>2</sub> PPh    | BzPPh <sub>2</sub>     | Lt yellow     | 165        | 30.0               | 3.0                    | 282, 345                                  | 1.52                            | 12.1          | 4.21                  | 11.9          |
| 6   | Me <sub>2</sub> PPh    | Bz <sub>2</sub> PPh    | Yellow        | 158        | 29.5               | 1.3                    | 274, 309                                  | 1.74                            | 13.8          | 3.55                  | <sup>e</sup>  |
| 7   | Me <sub>2</sub> PPh    | Bz <sub>3</sub> P      | Lt yellow     | 131        | 30.5               | 1.6                    | 290, 310                                  | 1.72                            | 11.3          | 3.23                  | 11.3          |
| 8   | (MeO) <sub>3</sub> P   | Ph <sub>3</sub> P      | White         | 181-183    | 29.5               | 0.95                   | 285, 303                                  | 3.58                            | 12.5          |                       |               |
| 9   | (MeO) <sub>3</sub> P   | (PhO) <sub>3</sub> P   | White         | 147-148    | 32.5               | 0.64                   | 275, 317                                  | 3.45                            | 15.6          |                       |               |
| 10  | (MeO) <sub>3</sub> P   | (BzO) <sub>3</sub> P   | Yellow-orange | 65         | 32.3               | 1.0                    | 298, 309                                  | 3.79                            | 15.0          | 5.17                  | 8.4           |
| 11  | (MeO) <sub>3</sub> P   | Et <sub>3</sub> As     | White         | 126-129    | 30.0               | 0.25                   | 278, 301                                  | 3.85                            | 13.1          |                       |               |
| 12  | (MeO) <sub>2</sub> PPh | BzOPPh <sub>2</sub>    | Lt yellow     | 113        | 33.2               | 1.1                    | 268, 313                                  | 3.52                            | 13.1          | 4.86                  | 6.3           |
| 13  | (MeO) <sub>2</sub> PPh | (BzO) <sub>2</sub> PPh | Yellow        | 60-62      | 33.3               | 1.2                    | 296, 330                                  | 3.21                            | 17.5          | 4.91 <sup>d</sup>     | 12.3          |
|     |                        |                        |               |            |                    |                        |   |                                 |               | 4.36                  | -9.8          |
|     |                        |                        |               |            |                    |                        |   |                                 |               | 5.19                  | 9.4           |
| 14  | (MeO) <sub>2</sub> PPh | (BzO) <sub>3</sub> P   | Lt yellow     | 146        | 31.6               | 1.1                    | 278, 301                                  | 3.52                            | 13.1          |                       |               |
| 15  | (MeO) <sub>2</sub> PPh | BzPPh <sub>2</sub>     | Lt yellow     | 174        | 30.6               | 1.1                    | 265, 297                                  | 3.60                            | 10.6          | 3.20                  | 12.5          |
| 16  | (MeO) <sub>2</sub> PPh | Bz <sub>2</sub> PPh    | Lt yellow     | 167        | 29.9               | 0.95                   | 275, 308                                  | 3.68                            | 13.1          | 3.29                  | 14.4          |
| 17  | (MeO) <sub>2</sub> PPh | Bz <sub>3</sub> P      | White         | 156        | 32.1               | 1.2                    | 275, 303                                  | 3.78                            | 13.5          | 3.39                  | 12.5          |
| 18  | (MeO) <sub>2</sub> PPh | Et <sub>3</sub> As     | Lt yellow     | 126-127    | 30.8               | 0.37                   | 270, 301                                  | 3.85                            | 13.1          |                       |               |
| 19  | Ph <sub>3</sub> P      | (BzO) <sub>3</sub> P   | Lt yellow     | 128-130    | 29.3               | 2.5                    | 297, 322                                  |                                 |               | 4.79                  | 7.5           |
| 20  | Ph <sub>3</sub> P      | Bz <sub>3</sub> P      | Yellow        | 238-241    | 29.4               | 5.8                    | 272, 298                                  |                                 |               | 3.35                  | 6.9           |
| 21  | Ph <sub>3</sub> P      | (PhO) <sub>3</sub> P   | Lt yellow     | 208-210    | 29.4               | 1.3                    | 305, 350                                  |                                 |               |                       |               |
| 22  | (PhO) <sub>3</sub> P   | (BzO) <sub>3</sub> P   | White         | 121-124    | 32.1               | 0.95                   | 305, 330                                  |                                 |               | 4.49                  | 7.5           |
| 23  | (PhO) <sub>3</sub> P   | Bz <sub>3</sub> P      | Lt yellow     | 158-160    | 29.6               | 1.2                    | 303, 328                                  |                                 |               | 3.37                  | 12.5          |
| 24  | MeOPPh <sub>2</sub>    | Et <sub>3</sub> As     | Lt yellow     | 151        | 29.4               | 0.64                   | 290, 313                                  | 3.68                            | 12.7          |                       |               |

<sup>a</sup> Me = CH<sub>3</sub>, Bz = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, Ph = C<sub>6</sub>H<sub>5</sub>, Et = C<sub>2</sub>H<sub>5</sub>. <sup>b</sup> Resonances reported for PR groups only; all doublets unless otherwise noted.  
<sup>c</sup> ABX system, *J*<sub>AB</sub> = 11.0 Hz. <sup>d</sup> ABX system, *J*<sub>AB</sub> = 13 Hz. <sup>e</sup> Overlapping ABX and [ABX]<sub>2</sub> spin systems; no calculations attempted.

Table II. <sup>31</sup>P{<sup>1</sup>H} NMR Data for Equilibrium Mixtures of the Complexes *cis*-LL'<sub>2</sub>PdCl<sub>2</sub> and L<sub>2</sub>PdCl<sub>2</sub>

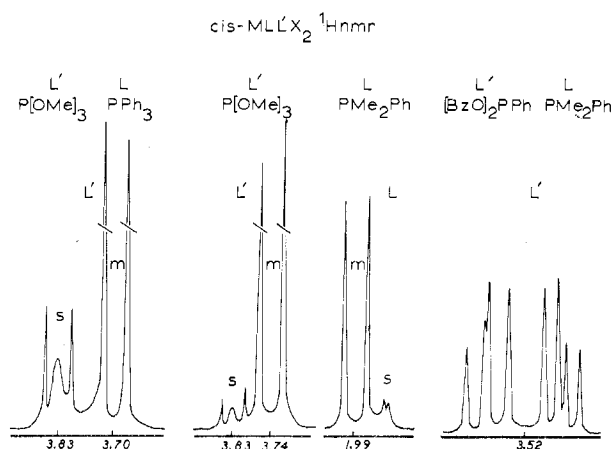
| No. | L                      | L'                     | - $\delta(\text{L})$        |        | - $\delta(\text{L}')$        |        | <sup>2</sup> <i>J</i> <sub>PP</sub> , Hz | LL' <sub>2</sub> PdCl <sub>2</sub> :<br>L <sub>2</sub> PdCl <sub>2</sub> total |
|-----|------------------------|------------------------|-----------------------------|--------|------------------------------|--------|--|--|
|     |                        |                        | Symmetrical                 | Mixed  | Symmetrical                  | Mixed  |  |  |
| 1   | Me <sub>2</sub> PPh    | BzOPPh <sub>2</sub>    | -2.50 (trans)<br>5.98 (cis) | 8.78   | 110.71                       | 109.45 | 20                                       | 2.5 ± 10%  |
| 2   | Me <sub>2</sub> PPh    | (BzO) <sub>2</sub> PPh |                             | 7.72   |                              | 117.73 | 20.4                                     | ∞ <sup>a</sup>   |
| 3   | Me <sub>2</sub> PPh    | (BzO) <sub>3</sub> P   |                             | 9.53   |                              | 94.29  | 21.7                                     | ∞ <sup>a</sup>   |
| 4   | Me <sub>2</sub> PPh    | (MeO) <sub>3</sub> P   |                             | -10.00 |                              | 97.35  | 22.6                                     | ∞ <sup>a</sup>   |
| 5   | Me <sub>2</sub> PPh    | BzPPh <sub>2</sub>     | -2.47 (trans)<br>6.0 (cis)  | 5.65   | 13.46 (trans)<br>20.25 (cis) | 28.64  | 0  | 0.12   |
| 6   | Me <sub>2</sub> PPh    | Bz <sub>2</sub> PPh    | -2.47 (trans)<br>5.90 (cis) | 6.96   | 14.14 (trans)                | 32.52  | 7  | 0.16   |
| 7   | Me <sub>2</sub> PPh    | Bz <sub>3</sub> P      | -2.47 (trans)<br>6.07 (cis) | 7.65   | 0.55 (trans)<br>9.46 (cis)   | 28.40  | 8  | 0.21   |
| 8   | (MeO) <sub>3</sub> P   | Ph <sub>3</sub> P      | 97.55                       | 94.19  | 23.27                        | 35.31  | 29.9                                     | 2.5  |
| 9   | (MeO) <sub>3</sub> P   | (PhO) <sub>3</sub> P   |                             | 93.82  |                              | 89.46  | 64.4 (AB)                                | ∞ <sup>a</sup>   |
| 10  | (MeO) <sub>3</sub> P   | (BzO) <sub>3</sub> P   | 97.55                       | 97.33  | 92.70                        | 92.68  | 77.5 (AB)                                | 1.4  |
| 11  | (MeO) <sub>3</sub> P   | Et <sub>3</sub> As     | 96.79                       | 100.74 |                              |        |  | 9.5  |
| 12  | (MeO) <sub>2</sub> PPh | BzOPPh <sub>2</sub>    | 113.43                      | 113.80 | 110.71                       | 110.70 | 40 (AB)                                  | 1.8  |
| 13  | (MeO) <sub>2</sub> PPh | (BzO) <sub>2</sub> PPh | 113.43                      | 112.40 | 116.10                       | 116.83 | 50 (AB)                                  | 1.3  |
| 14  | (MeO) <sub>2</sub> PPh | (BzO) <sub>3</sub> P   | 113.38                      | 113.63 | 92.71                        | 94.76  | 60.8                                     | 2.0  |
| 15  | (MeO) <sub>2</sub> PPh | BzPPh <sub>2</sub>     | 113.46                      | 118.09 | 30.42                        | 30.58  | 30.2                                     | 4.7  |
| 16  | (MeO) <sub>2</sub> PPh | Bz <sub>2</sub> PPh    | 113.36                      |        | 14.16                        |        |  | 0 <sup>b</sup>   |
| 17  | (MeO) <sub>2</sub> PPh | Bz <sub>3</sub> P      | 113.48                      |        | 32.77                        | 32.77  | ?  | <sup>c</sup>   |
| 18  | (MeO) <sub>2</sub> PPh | Et <sub>3</sub> As     | 113.53                      | 109.90 |                              |        |  | 0.45   |
| 19  | Ph <sub>3</sub> P      | (BzO) <sub>3</sub> P   | 23.26                       | 35.94  | 92.76                        | 91.35  | 28.7                                     | 2.6  |
| 20  | Ph <sub>3</sub> P      | Bz <sub>3</sub> P      | 23.26                       | 20.20  | 19.26                        | 20.20  | <6                                       | 0.5 <sup>c</sup>   |
| 21  | Ph <sub>3</sub> P      | (PhO) <sub>3</sub> P   | 23.24                       | 35.05  | 83.46                        | 82.14  | 28.4                                     | 2.0  |
| 22  | (PhO) <sub>3</sub> P   | (BzO) <sub>3</sub> P   | 72.42                       |        | 83.52                        |        |  | 0 <sup>b</sup>   |
| 24  | MeOPPh <sub>2</sub>    | Et <sub>3</sub> As     | 112.55                      | 116.16 |                              |        |  | 0.71   |
| 25  | Ph <sub>3</sub> P      | (EtO) <sub>3</sub> P   | 23.21                       | 36.07  | 92.66                        | 89.06  | 31                                       | 4.7  |
| 26  | (PhO) <sub>3</sub> P   | MeOPPh <sub>2</sub>    | 78.39                       | 98.17  | 112.57                       | 111.42 | 30                                       | 0.13   |

<sup>a</sup> All mixed. <sup>b</sup> All symmetric. <sup>c</sup> Intermediate exchange occurring.

be a general reaction. The physical and spectral properties of the compounds isolated are given in Tables I and II.

**A. Proton Nuclear Magnetic Resonance.** It has been shown for the X<sub>n</sub>AA'X'<sub>n</sub> spin systems of complexes of the type (R<sub>3</sub>P)<sub>2</sub>PdX<sub>2</sub>, where R = methyl, alkaryl, *O*-methyl, or *O*-alkaryl, that the appearance of the R resonance in the <sup>1</sup>H

NMR is determined by the magnitude of <sup>2</sup>*J*<sub>PP</sub>.<sup>33</sup> When the two phosphorus nuclei are mutually *cis*, <sup>2</sup>*J*<sub>PP</sub> is generally<sup>21</sup> less than 80 Hz and the methyl or methylene resonance will be a doublet or "filled-in" doublet depending upon whether <sup>2</sup>*J*<sub>PP</sub> is nearer 0 or 80 Hz, respectively. If the two phosphorus nuclei are mutually *trans*, then <sup>2</sup>*J*<sub>PP</sub> is generally<sup>21</sup> 500 Hz or greater



**Figure 1.** The 100-MHz  $^1\text{H}$  NMR spectra of  $\text{CDCl}_3$  solutions of three  $\text{LL}'\text{PdCl}_2$  complexes showing differing ratios of mixed-ligand (m) and symmetric (s) species. The  $\text{CH}_2$  resonance of  $[(\text{BzO})_2\text{PPh}][\text{Me}_2\text{PPh}]\text{PdCl}_2$  exemplifies the ABX spin system (A, B =  $^1\text{H}$ , X =  $^{31}\text{P}$ ) and was analyzed as such.

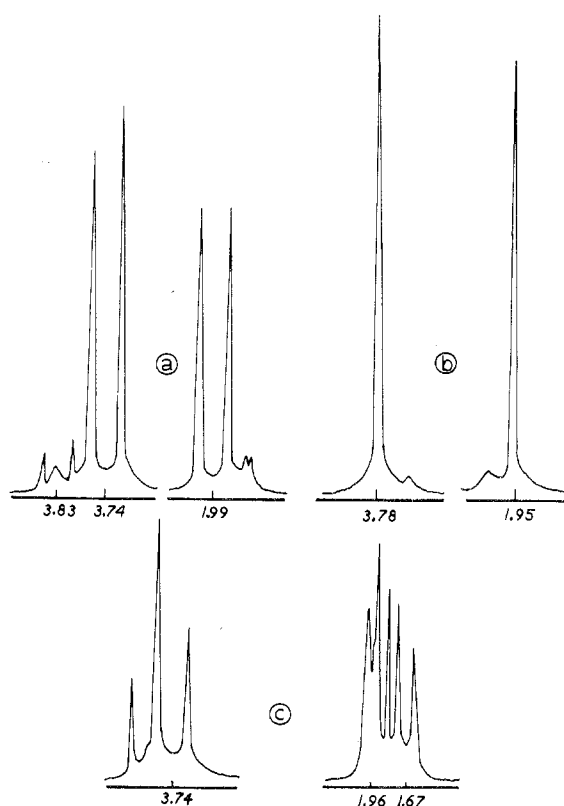
and the methyl or methylene resonance will be a 1:2:1 triplet. Under uncommonly favorable circumstances  $^2J_{\text{PP}}$  can be measured directly.<sup>15,16,21</sup> Because of the paucity<sup>21</sup> of data on  $^2J_{\text{PP}}$  for palladium complexes, the validity of the generalizations as to the magnitudes quoted above is somewhat uncertain.

The spin system of the  $(\text{R}_3\text{P})(\text{R}'_3\text{P})\text{PdCl}_2$  complexes is  $\text{X}_n\text{AMY}_n$  or  $\text{X}_n\text{ABY}_n$  where X, Y =  $^1\text{H}$  and A, B, M =  $^{31}\text{P}$ . These spin systems are amenable to  $\text{ABX}_n$  or  $\text{AMX}_n$  subspectral analysis<sup>16</sup> because  $J_{\text{XY}}$  should be approximately zero, an assumption which has proven to be valid<sup>32</sup> for the complexes belonging to the  $\text{X}_n\text{AA}'\text{X}'_n$  (in this case  $J_{\text{XX}'} = 0$ ) spin system. Thus, from a simple first-order analysis, the proton resonance for the methyl or methylene group of the mixed-ligand complexes should be a doublet for the cis isomers and a 1:1:1:1 doublet of doublets<sup>15,16</sup> for the trans isomers.

Using the above arguments, it is evident from the data in Table I and Figure 1 that the  $(\text{R}_3\text{P})(\text{R}'_3\text{P})\text{PdCl}_2$  complexes are cis in solution.

Anions such as  $\text{Br}^-$  and  $\text{I}^-$  favor the trans geometry<sup>15,16</sup> and the rate of formation of the trans isomer via reaction 2 when  $\text{X}^- = \text{Br}^-$  or  $\text{I}^-$  is very slow<sup>15,16,34</sup> as shown by monitoring the reaction with  $^1\text{H}$  or  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.

Since we had previously shown that solvent and temperature greatly affected the solution geometry of the  $(\text{R}_3\text{P})_2\text{PdCl}_2$  complexes,<sup>10-12,28,29,31</sup> we anticipated similar behavior for the  $(\text{R}_3\text{P})(\text{R}'_3\text{P})\text{PdCl}_2$  complexes. This is not the case. The  $^1\text{H}$  NMR spectra of all of the  $\text{LL}'\text{PdCl}_2$  complexes in the solvents  $\text{C}_6\text{D}_6$ ,  $\text{CDCl}_3$ , *sym*- $\text{C}_2\text{H}_2\text{Cl}_4$ , *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ , and nitrobenzene remained unchanged over the temperature range of 0–95 °C where attainable. Spectra were run in nitrobenzene at room temperature and at 95 °C after the samples had been held at 95 °C for 2 days. The spectra were nearly identical before and after heating although some minor line broadening was noted. Thus, neither isomerization nor redistribution of the mixed-ligand complexes occurred under these conditions. Catalyzed isomerization<sup>4-6,11,28</sup> was attempted by the addition of excess phosphine to an equilibrium mixture of the symmetric and mixed-ligand complexes. The addition of excess ligand (Figure 2) caused ligand exchange to occur for all species as well as isomerization of the symmetric species from cis to trans. It did not, however, catalyze isomerization of the mixed-ligand complexes. These data, in conjunction with the fact that reaction 2 leads to mixed-ligand complexes, suggest that the mixed-ligand complexes are, in general, thermodynamically more stable and/or kinetically more inert than the symmetric complexes. Consequently, the cis mixed-ligand complexes are

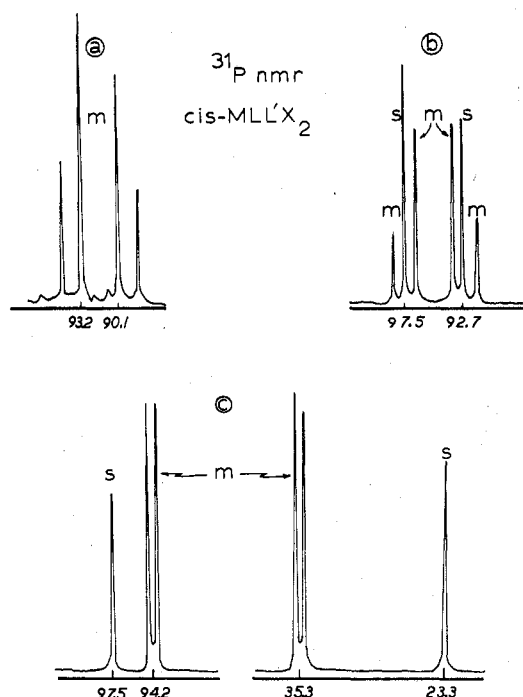


**Figure 2.** The 100-MHz  $^1\text{H}$  NMR spectra of catalyzed isomerization of  $[(\text{CH}_3\text{O})_3\text{P}](\text{Me}_2\text{PPh})\text{PdCl}_2$  in  $\text{CDCl}_3$  with a trace of  $\text{P}(\text{OMe})_3$ : (a) without catalyst the solution is primarily all mixed-ligand species; (b) addition of a trace of  $\text{P}(\text{OCH}_3)_3$  causes rapid ligand exchange; (c) after  $1/2$  h the  $\text{CH}_2\text{O}$  region shows more symmetric and some excess ligand and mixed-ligand complexes while the  $\text{CH}_3$  region shows "mixed-ligand", some excess ligand, and both the cis and trans symmetric complexes.

for the most part *not* viable intermediates in the cis–trans isomerization pathway for the symmetric complexes. The trans mixed-ligand complexes, on the other hand, may be.

For all the cis mixed-ligand complexes the  $\text{PCH}_3$  and  $\text{PCH}_2$  resonances are doublets with  $^2J_{\text{PH}} = 6.9$ – $12.5$  Hz. Thus  $^4J_{\text{PH}}$  is essentially zero. This implies for the cis symmetric complexes with the  $\text{X}_n\text{AA}'\text{X}'_n$  spin system where the doublet separation is formally  $|^2J_{\text{PH}} + ^4J_{\text{PH}}|$  that the splitting is essentially  $^2J_{\text{PH}}$ .<sup>30</sup> Similarly, the  $\text{POCH}_2$  and  $\text{POCH}_3$  resonances are doublets with  $^3J_{\text{PH}} = 6.3$ – $17.5$  Hz and  $^5J_{\text{PH}}$  is essentially zero. Likewise, then, in the cis symmetric phosphite, phosphinite, or phosphonite complexes the doublet separation is essentially  $^3J_{\text{PH}}$ . This implies, in turn, that since  $|^nJ_{\text{PH}} + ^{n+2}J_{\text{PH}}|$  is uniformly larger<sup>11,12,28-30</sup> in cis complexes than in trans complexes,  $^nJ_{\text{PH}}$  and  $^{n+2}J_{\text{PH}}$  have opposite signs in the trans complexes.

**B. Phosphorus-31 NMR.** The  $^{31}\text{P}\{^1\text{H}\}$  NMR data are given in Table II and representative spectra are shown in Figure 3. This study was undertaken to determine directly  $^2J_{\text{PP}}$  and to measure the equilibrium between the mixed-ligand and symmetric complexes (eq 2) in solution. It has been shown<sup>21</sup> that  $^2J_{\text{PP}}$  for cis "virtually coupled" systems is less than 100 Hz. Our values range from 0 to 77.5 Hz suggesting that all of the complexes possess the cis geometry as concluded from the  $^1\text{H}$  NMR data. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra are examples of either AB or AX spin systems for the mixed-ligand complexes depending upon the similarity of the individual ligands. Four complexes were analyzed as AB systems, namely,  $[(\text{MeO})_2\text{PPh}][(\text{BzO})_2\text{PPh}]\text{PdCl}_2$ ,  $[(\text{MeO})_3\text{P}][(\text{PhO})_3\text{P}]\text{PdCl}_2$ ,  $[(\text{MeO})_2\text{PPh}][\text{BzOPPh}_2]\text{PdCl}_2$ , and  $[(\text{MeO})_3\text{P}][(\text{BzO})_3\text{P}]\text{PdCl}_2$ , the rest being AX systems.



**Figure 3.** <sup>31</sup>P NMR spectra of three *cis*-MLL'<sup>1</sup>X<sub>2</sub> complexes in CDCl<sub>3</sub> showing a change in the mixed (m):symmetric complex (s) ratio with change in basicity and size of ligand: (a) L = P(OMe)<sub>3</sub>, L' = P(OPh)<sub>3</sub>, all "mixed ligand", AB spin system; (b) L = P(OMe)<sub>3</sub>, L' = P(OBz)<sub>3</sub>, primarily "mixed ligand", AB spin system; (c) L = P(OMe)<sub>3</sub>, L' = PPh<sub>3</sub>, mixed and symmetric species, AX spin system.

The solutions contain varying amounts of symmetric and mixed-ligand complexes. The relative amounts are a function of the ligands involved. The relative integrated intensities of the respective resonances provide a measure of the equilibrium constants of reaction 2 (Figures 1 and 3). For complexes **16** and **22**, only the symmetric complexes are present in solution. For complexes **2-4** and **9**, only the mixed-ligand complexes are present in solution. For most complexes with triethylarsine and for all with piperidine, disproportionation of the mixed-ligand complex to symmetric complexes appears more rapid and complete than for most organophosphorus-organophosphorus mixed-ligand complexes (*vide infra*). Thus, by varying the ligands both extremes are obtained. Where both types of complexes are present, the ratios of LL'-PdCl<sub>2</sub>:L<sub>2</sub>PdCl<sub>2</sub> total vary from 0.12 to 4.38. The <sup>31</sup>P{<sup>1</sup>H} NMR of the complex (Ph<sub>3</sub>P)(Bz<sub>3</sub>P)PdCl<sub>2</sub><sup>20</sup> deserves special comment.

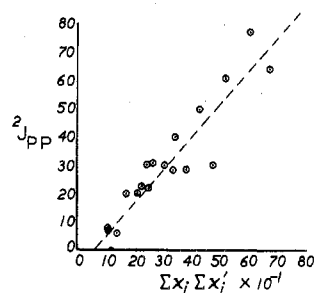
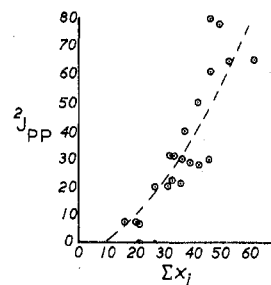
This spectrum contains three <sup>31</sup>P resonances, one attributable to each of the symmetric species and one *singlet* attributable to the mixed-ligand species. Since phosphorus-hydrogen coupling is present in the <sup>1</sup>H NMR of this complex and since the <sup>31</sup>P resonance of (Bz<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> is not at its normal position and that of (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> is, it is concluded that this complex is undergoing intermediate exchange. As J<sub>PH</sub> = 6.9 Hz, an upper limit of 43.4 s<sup>-1</sup> can be placed on the exchange rate. Further, it appears that the exchange is that of tribenzylphosphine and not triphenylphosphine. This is the only complex for which exchange was noted. Thus all other complexes exchange at a slower rate. Since the (R<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> complexes usually isomerize faster than this, these data reaffirm the conclusions from the <sup>1</sup>H NMR data that the *cis* mixed-ligand species are not likely isomerization intermediates.

As noted above <sup>2</sup>J<sub>PP</sub> varies considerably among the mixed-ligand complexes. Assuming that <sup>2</sup>J<sub>PP</sub> is dominated by Fermi contact effects,<sup>21</sup> its magnitude should be affected by the electronegativity of the substituents bound to phos-

**Table III.** Tolman's Substituent Constants Σχ<sub>1</sub> for Phosphorus Ligands

| Ligand                 | Σχ <sub>1</sub> <sup>a</sup> | Ligand              | Σχ <sub>1</sub> <sup>a</sup> |
|------------------------|------------------------------|---------------------|------------------------------|
| (PhO) <sub>3</sub> P   | 29.1                         | Me <sub>2</sub> PH  | 13.5                         |
| (BzO) <sub>3</sub> P   | 26.1                         | Ph <sub>3</sub> P   | 12.9                         |
| (MeO) <sub>3</sub> P   | 23.1                         | BzPPh <sub>2</sub>  | 12.1                         |
| (BzO) <sub>2</sub> PPh | 21.7                         | Bz <sub>2</sub> PPh | 11.3                         |
| (EtO) <sub>3</sub> P   | 20.4                         | MePPh <sub>2</sub>  | 11.2                         |
| (MeO) <sub>2</sub> PPh | 19.7                         | Bz <sub>3</sub> P   | 10.5                         |
| BzOPPh <sub>2</sub>    | 17.3                         | Me <sub>2</sub> PPh | 9.5                          |
| MeOPPh <sub>2</sub>    | 16.3                         | Me <sub>3</sub> P   | 7.8                          |

<sup>a</sup> Taken as the algebraic sum of χ<sub>1</sub> given by C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2953 (1970). The value of the BzO group was estimated 3.5 (Bz) + 5.2 (given as the average difference between X<sub>OR</sub> and X<sub>R</sub>).

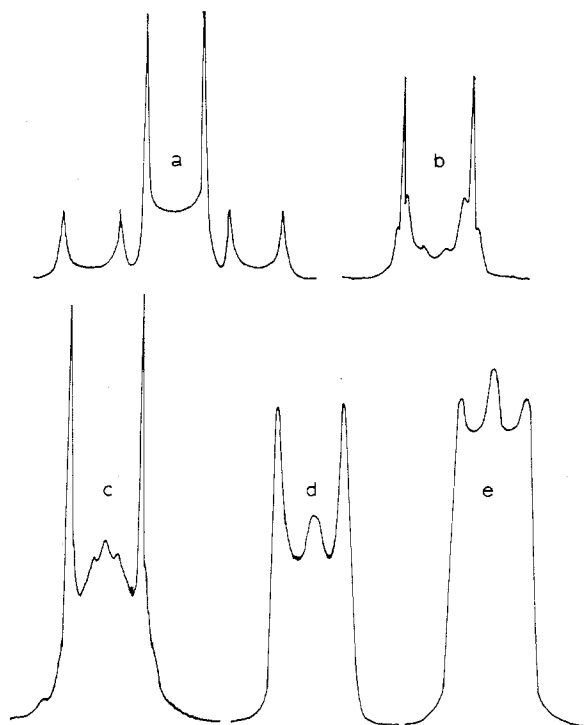


**Figure 4.** (Top) Plot of <sup>2</sup>J<sub>PP</sub> vs. Σχ<sub>1</sub> for LL'/PdCl<sub>2</sub> complexes generally obeying eq 3 with a least-squares best fit of <sup>2</sup>J<sub>PP</sub> = 0.519Σχ<sub>1</sub> + 0.015Σ(χ<sub>1</sub>)<sup>2</sup> - 5.85. (Bottom) Plot of <sup>2</sup>J<sub>PP</sub> vs. Σχ<sub>1</sub>Σχ'<sub>1</sub> for LL'/PdCl<sub>2</sub> complexes with a least-squares fit of <sup>2</sup>J<sub>PP</sub> = 0.1179Σχ<sub>1</sub>Σχ'<sub>1</sub> - 7.018.

phorus via the (Sp|δrp|Sp) terms in eq 3 which represents the

$${}^2J_{PP'} \propto - (Sp|\delta(rp)|Sp)(Sp'|\delta(rp')|Sp) \sum_R^{occ} \sum_I^{unocc} (E_h - E_I)^{-1} C_{kP} C_{lP} C_{kP'} C_{lP'} \quad (3)$$

square of the s electron density at the phosphorus nucleus. As a test of this hypothesis, Tolman's substituent constants, χ<sub>1</sub><sup>35</sup> (Table III), were used as a measure of the phosphorus electron density and plotted vs. <sup>2</sup>J<sub>PP</sub> in Figure 4. Clearly, the general form of eq 3 is obeyed suggesting that this is a rational approach. A change in s electron density, however, coincides with a change in hybridization and consequently angle changes as well. This suggests that there should be steric contributions to <sup>2</sup>J<sub>PP</sub>. Thus, deviations in this correlation occur where steric interactions begin to compete with electronic effects. Nonetheless, the correlation allows the prediction of <sup>2</sup>J<sub>PP</sub> for *cis*-(R<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> type complexes. For example, it predicts <sup>2</sup>J<sub>PP</sub> = 50-56 Hz vs. 80 Hz measured<sup>21</sup> for [(CH<sub>3</sub>O)<sub>3</sub>P]<sub>2</sub>PdCl<sub>2</sub> and <sup>2</sup>J<sub>PP</sub> = 1-6 Hz vs. 8 Hz measured<sup>21</sup> for [(CH<sub>3</sub>)<sub>3</sub>P]<sub>2</sub>PdCl<sub>2</sub>. Moreover, the predicted value of <sup>2</sup>J<sub>PP</sub> = 14-18 Hz for [CH<sub>3</sub>OPPh<sub>2</sub>][MePPh<sub>2</sub>]PdCl<sub>2</sub> compares favorably with <sup>2</sup>J<sub>PP</sub> = 17 Hz found<sup>18</sup> for [Ph<sub>2</sub>PCH<sub>2</sub>OPPh<sub>2</sub>]PdCl<sub>2</sub> and 9 Hz found<sup>18</sup> for [Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>OPPh<sub>2</sub>]PdCl<sub>2</sub>. The data quoted



**Figure 5.** The 100-MHz  $^1\text{H}$  NMR spectra of the methyl or methoxy regions for five *cis*- $\text{L}_2\text{MX}_2$  complexes in  $\text{CDCl}_3$  that exhibit the various line shapes from a 1:1 doublet to "filled-in": (a)  $\text{L} = \text{Ph}_2\text{PMe}$ ,  $\text{M} = \text{Pt}$ ,  $\text{X} = \text{Cl}$ , simple 1:1 doublet; (b)  $\text{L} = (\text{MeO})_3\text{P}$ ,  $\text{M} = \text{Pt}$ ,  $\text{X} = \text{Cl}$ , beginning of filling-in;<sup>36</sup> (c)  $\text{L} = (\text{MeO})_2\text{PPh}$ ,  $\text{M} = \text{Pd}$ ,  $\text{X} = \text{Cl}$ ; (d)  $\text{L} = (4\text{-CH}_3\text{Ph})_2\text{PCH}_3$ ,  $\text{M} = \text{Pd}$ ,  $\text{X} = \text{N}_3$ , increased filling-in of doublet with increase in  $^2J_{\text{PP}}$  going from  $\text{X} = \text{Cl}$  to  $\text{N}_3$ ; (e)  $\text{L} = 4\text{-CH}_3\text{PhP}(\text{CH}_3)_2$ ,  $\text{M} = \text{Pd}$ ,  $\text{X} = \text{N}_3$ , "apparent" triplet due to more basic ligand compared to (d).

for similar platinum(II) complexes<sup>32</sup> do not produce a similar correlation and  $^2J_{\text{PP}}$  varies over the very limited range of 15.8–21.4 Hz for eight compounds. In addition, it can be said, using the theory developed by Harris<sup>33</sup> for the  $\text{X}_n\text{AA}'\text{X}'_n$  spin systems, that the  $^1\text{H}$  NMR of *cis* palladium(II)-bis(phosphine) complexes containing  $\alpha$  methyl or methylene groups will always be 1:1 doublets. Likewise, the  $^1\text{H}$  NMR of *cis* palladium(II)-bis(phosphorus donor) complexes containing  $\alpha$   $\text{OCH}_3$  or  $\text{OCH}_2$  groups will always be "filled-in" doublets. These resonances for *trans* complexes should always be 1:2:1 triplets. The same statements are probably also true for platinum(II) complexes. The types of  $^1\text{H}$  NMR line shapes for these complexes are exemplified in Figure 5. This is important as filled-in doublets could have been called triplets in the past and wrongly assigned the *trans* geometry.

**C. Carbon-13 NMR.** The  $^{13}\text{C}\{^1\text{H}\}$  data were obtained in order to corroborate the other data and to obtain information regarding values of various coupling constants. The data obtained for the piperidine complexes show that all disproportionate completely to the symmetric complexes in solution as previously suggested from the  $^{31}\text{P}\{^1\text{H}\}$  NMR. The spectra of the symmetric complexes will be reported elsewhere. The spin systems are of the type AX for monophosphorus ligand complexes and AMX (A,  $\text{M} = ^{31}\text{P}$ ;  $\text{X} = ^{13}\text{C}$ ) for bis(phosphorus ligand) complexes. The former should exhibit doublets regardless of geometry, and the latter, a doublet of doublets for the *trans* geometry and doublets for the *cis* geometry if  $J_{\text{PC}}$  parallels  $J_{\text{PH}}$ .<sup>15,16</sup> The spectrum shown in Figure 6 is typical and verifies the *cis* assignment. Other data are given in Table IV. Each of the piperidine complexes showed three resonances assignable to the piperidine carbons at  $\delta$  51.32, 27.45, and 23.62 as well as resonances characteristic only of the  $(\text{R}_3\text{P})_2\text{PdCl}_2$  complexes. It is concluded that these three

**Table IV.**  $^{13}\text{C}\{^1\text{H}\}$  NMR Data for Some *cis*- $\text{LL}'\text{PdCl}_2$  Complexes

| No. | L                          | L'                       | $\delta(\text{CH}_2)$                         | $J$ , Hz                                   | $\delta(\text{CH}_3)$                                  | $J$ , Hz                                       | $\delta(\text{C}_1)$                     | $J$ , Hz        | $\delta(\text{C}_{2,e})$                    | $J$ , Hz                       | $\delta(\text{C}_{3,s})$                    | $J$ , Hz                       | $\delta(\text{C}_4)$ | $J$ , Hz |
|-----|----------------------------|--------------------------|---|--|--|--|--|-----------------|---|--------------------------------|---|--------------------------------|----------------------|----------|
| 11  | $(\text{MeO})_3\text{P}$   | $\text{Et}_3\text{As}$   | 9.86  | 0  | 18.0   | 0  |  |                 |   |                                |   |                                |                      |          |
| 18  | $(\text{MeO})_2\text{PPh}$ | $\text{Et}_3\text{As}$   | 9.85  | 0  | 54.35 d<br>17.46                                       | 4.2  | 132.56                                   | 0               | 131.23 d                                    | 12.8                           | 128.66 d                                    | 128.67                         | 128.80 (OPh)         | 0 (OPh)  |
| 27  | $(n\text{-Bu})_3\text{P}$  | $\text{Et}_3\text{As}$   | 9.85 (As)<br>24.19 (P) <sup>a</sup><br>(12.9) | 0 (As)<br>21.54 (P) <sup>a</sup><br>(25.4) | 55.35 d<br>17.46 (As)<br>13.36 (P) <sup>a</sup><br>(2) | 8.0<br>0 (As)<br>13.15 (P) <sup>a</sup><br>(0) |  |                 |   |                                |   |                                | 125.80 (OPh)         | 0 (OPh)  |
| 21  | $\text{Ph}_3\text{P}$      | $(\text{PhO})_2\text{P}$ | 64.10 d                                       | 6.3  | 15.71 d  | 5.3  | 131.8 d (OPh)<br>137.77 d (Ph)<br>130.95 | 3.3<br>8.0<br>0 | 129.90 d (OPh)<br>134.53 d (Ph)<br>134.31 d | 4.0 (OPh)<br>24.3 (Ph)<br>11.5 | 120.95 d (OPh)<br>128.39 d (Ph)<br>128.16 d | 9.9 (OPh)<br>15.0 (Ph)<br>11.1 | 128.09 (Ph)          | 0 (Ph)   |
| 22  | $\text{Ph}_3\text{P}$      | $(\text{EtO})_2\text{P}$ |   |  |  |  |  |                 |   |                                |   |                                | 130.95               | 0        |

<sup>a</sup> These are the  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  carbons of *P-*n*-Bu*; coupling constants are in parentheses.

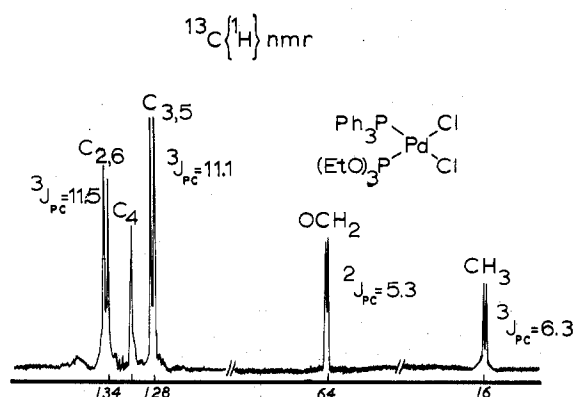


Figure 6. The 100-MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a  $\text{CDCl}_3$  solution of  $(\text{Ph}_3\text{P})[(\text{EtO})_3\text{P}]\text{PdCl}_2$  exhibiting phosphorus-methylene carbon coupling which is absent in the symmetric complex spectrum. Aromatic-region  $\text{C}_{2,6}$  and  $\text{C}_{3,5}$  doublets indicate cis geometry.

resonances represent *trans*-(pip)<sub>2</sub>PdCl<sub>2</sub>. These included complexes with Me<sub>2</sub>PPh, (MeO)<sub>2</sub>PPh, (MeO)<sub>3</sub>P, Et<sub>3</sub>P, (*n*-Bu)<sub>3</sub>P, and Bz<sub>3</sub>P. Since these phosphorus ligands span a range of size and basicity, it is concluded that although mixed-ligand species of the sort (pip)(R<sub>3</sub>P)PdCl<sub>2</sub> can be isolated in the solid state,<sup>24-27</sup> they completely disproportionate in solution. The <sup>31</sup>P NMR support this contention as only one resonance is observed and it occurs at the requisite chemical shift for the appropriate (R<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> complex. Thus, the conclusion that the (am)(R<sub>3</sub>P)PdCl<sub>2</sub> complexes are *trans* in benzene solution based upon dipole moments<sup>27</sup> is in error. The solutions instead contain *trans*-(R<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> and *trans*-(pip)<sub>2</sub>PdCl<sub>2</sub>. The same is true of the triethylarsine complexes with Et<sub>3</sub>P, (*n*-Bu)<sub>3</sub>P, Me<sub>2</sub>PPh, and Bz<sub>2</sub>PPh. On the other hand, the triethylarsine complexes with the methoxyphosphines are equilibrium mixtures in solution. Evidently disproportionation occurs unless both ligands are soft donors. Ligand size is also an important criterion for stability.

**D. Infrared and Electronic Spectra.** Assuming that the ligands are point charges, the *cis* geometry would possess C<sub>s</sub> symmetry, and the *trans*, C<sub>2</sub> symmetry. For each, two infrared-allowed  $\nu_{\text{PdCl}}$  frequencies are anticipated. These are listed in Table I but give no insight as to geometry.

Even though many of the solutions contain more than one species, only one electronic transition is observed in their electronic spectra. This is so despite the fact that many (R<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> complexes display two electronic transitions.<sup>7,8,30</sup> Thus, the electronic spectra offer few clues as to the species in solution.

The complexes are white or various shades of yellow, yet all possess the *cis* geometry in solution and, since they do not isomerize in solution, very likely possess the *cis* geometry in

the solid state as well. Consequently, for these species color is no criterion for geometry.

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**Registry No.** 1, 55481-11-3; 2, 55481-13-5; 3, 55481-15-7; 4, 55501-90-1; 5, 55501-89-8; 6, 58448-78-5; 7, 58448-79-6; 8, 58448-80-9; 9, 58448-81-0; 10, 58448-82-1; 11, 57739-00-1; 12, 55481-17-9; 13, 55481-18-0; 14, 55481-19-1; 15, 58448-83-2; 16, 58473-46-4; 17, 58448-84-3; 18, 58448-85-4; 19, 55481-21-5; 20, 55481-20-4; 21, 57738-96-2; 22, 55501-88-7; 23, 55481-22-6; 24, 58448-86-5; 25, 57738-95-1; 26, 58448-87-6; 27, 58448-88-7; <sup>31</sup>P, 7723-14-0.

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