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## Notes

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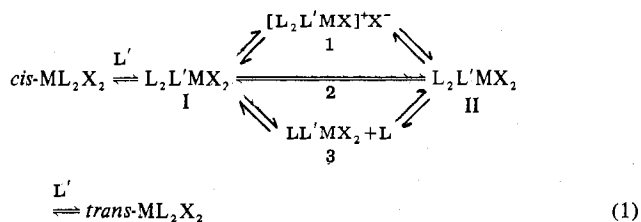
### Palladium (II)-Cyanide-Phosphine Complexes<sup>1</sup>

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Recent investigations<sup>3-14</sup> of the geometrical isomerization of complexes of the type  $L_2PdX_2$  have indicated that the isomerization process is associative, proceeding through pentacoordinate transition states (I and II) according to eq 1. Each of the three pathways (1, 2, and 3) occurs under



various conditions and the conditions favoring each have been delineated.<sup>9</sup> The least studied pathway is fluxional rotation<sup>15</sup> (pathway 2) and it should dominate in nonpolar solvents when L and L' are small and have nearly the same basicity, with X being a strongly coordinating anion. In some investigations<sup>3-5</sup> of catalyzed isomerizations the lack of L and L' interchange was taken to imply that any mechanistically important pentacoordinate species cannot have a regular geometry but must be distorted in such a way that L and L' can never become equivalent. It is apparent then that more information is needed regarding the solution behavior of pentacoordinate palladium complexes.

To date there have been few pentacoordinate complexes of palladium(II) with monodentate ligands reported.<sup>16-21</sup> Except for the ligand<sup>21</sup>  $C_6H_5CH_2P(CH_3)_2$ , these all involve the sterically undemanding phosphole type ligands,<sup>16-20</sup> and still, each of these complexes is extensively dissociated in solution. Numerous studies with pentacoordinate nickel complexes have shown that pentacoordination is stabilized by strong field ligands.<sup>22</sup> The exact reasons are not yet clear but evidence is emerging which suggests that the relative stabilities of  $ML_2X_2$  and  $ML_3X_2$  complexes depend upon a subtle interplay of steric and electronic effects.<sup>23</sup>

Thus there are two possible approaches in seeking to stabilize pentacoordinate heteroleptic palladium(II) complexes of the type  $PdL_3X_2$ . One approach is to seek sterically undemanding

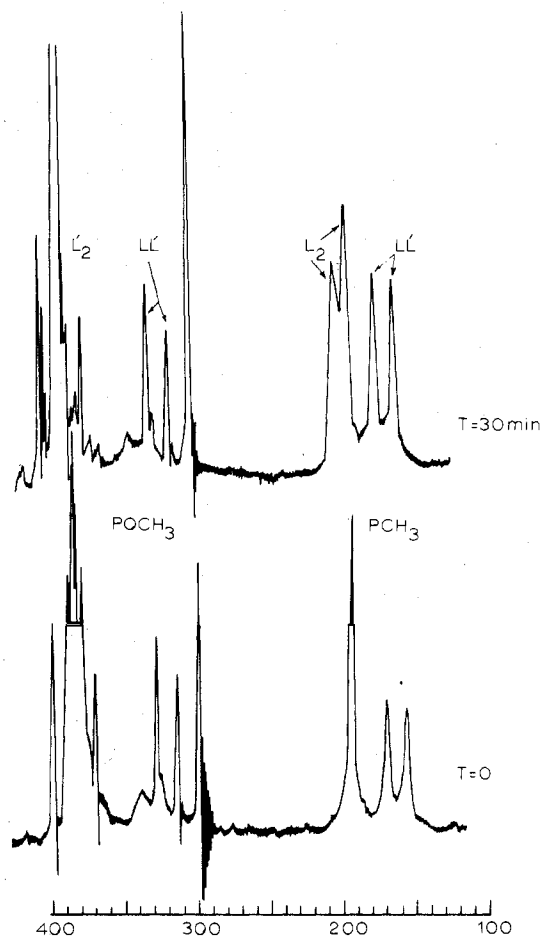


Figure 1. The 100-MHz <sup>1</sup>H NMR spectra in the methyl and methoxy regions for a  $CDCl_3$  solution containing an equimolar ( $1.25 \times 10^{-4}$  M each) mixture of  $[(CH_3)_2PC_6H_5]_2Pd(CN)_2$  and  $(CH_3O)_3P$  as a function of time. The numbers are chemical shifts in Hz from internal TMS.  $L_2 = [(CH_3O)_3P]_2Pd(CN)_2$ ,  $LL' = [ \{ (CH_3O)_3P \} \{ (CH_3)_2PC_6H_5 \} ] Pd(CN)_2$ , and  $L = [(CH_3)_2PC_6H_5]_2Pd(CN)_2$ .

ligands L and the other is to study strong-field anions X. The latter approach has been undertaken in this work by utilizing cyanide as the strong-field anion with a variety of phosphorus ligands L.

### Experimental Section

Chemicals used were reagent grade and used as received. 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 phosphines were conducted in a prepurified nitrogen

Table I. Physical Properties of the Complexes  $L_2Pd(CN)_2$ 

L	Mp, °C	Electronic spectra <sup>a</sup>		Ir spectra, cm <sup>-1</sup>		<sup>1</sup> H NMR <sup>b</sup>		<sup>31</sup> P NMR -δ (°P)
		ν, μm <sup>-1</sup>	10 <sup>4</sup> ε	ν <sub>C≡N</sub>	ν <sub>PdC</sub>	δ(CH <sub>3</sub> or CH <sub>2</sub> )	J, Hz	
Me <sub>2</sub> PPh	183	3.55	2.30	2136	500	2.00 t	7.5	-4.5
MePPh <sub>2</sub>	219	3.51	2.40	2130	507	2.32 t	6	7.6
BzPPh <sub>2</sub>	241	3.57	2.67	2126	509	4.13 t	8.0	21.1
Bz <sub>2</sub> PPh	252	3.72	2.10	2135	490	3.75 qt <sup>c</sup>	7.5	16.4
Bz <sub>2</sub> P	179	3.85	4.57	2130	474	3.46 t	6.3	15.1
MeOPPPh <sub>2</sub>	208	3.68	3.67	2132	497	3.79 t	15.6	116.2
(MeO) <sub>2</sub> PPh	172	3.98	2.19	2135	485	3.33 t	15.0	105.9
(MeO) <sub>3</sub> P	131	4.02	2.20	2145	539	3.88 t	15.2	95.7
BzOPPPh <sub>2</sub>	188	3.70	3.85	2135	495	4.99 t	15.1	110.4
(BzO) <sub>2</sub> PPh	168	4.03	1.97	2139	544	4.91 qt <sup>d</sup>	10.0	112.3
(BzO) <sub>3</sub> P	148	4.00	2.00	2143	498	4.95 t	15.0	102.5

<sup>a</sup> In CHCl<sub>3</sub> solution, all complexes are colorless. <sup>b</sup> Key: t, triplet; d, doublet; qt, quartet of triplets; J = <sup>n</sup>J<sub>PH</sub> + <sup>n+2</sup>J<sub>PH</sub>. <sup>c</sup> [ABX]<sub>2</sub> spin system: J<sub>AB</sub> = 0; ν<sub>A</sub> = 3.73 δ; ν<sub>B</sub> = 3.77 δ. <sup>d</sup> [ABX]<sub>2</sub> spin system: J<sub>AB</sub> = 12.5 Hz; ν<sub>A</sub> = 5.03 δ; ν<sub>B</sub> = 4.79 δ.

Table II. <sup>13</sup>C{<sup>1</sup>H} Data for CDCl<sub>3</sub> Solutions of the Complexes  $L_2Pd(CN)_2$ 

L <sup>a</sup>	δ(CH <sub>2</sub> or CH <sub>3</sub> ) <sup>a</sup>	J, <sup>b</sup> Hz	δ(CN)	J, <sup>c</sup> Hz	δ(C <sub>1</sub> )	J, <sup>b</sup>	δ(C <sub>2,6</sub> )	J, <sup>b</sup> Hz	δ(C <sub>3,5</sub> )	J, <sup>b</sup> Hz	δ(C <sub>4</sub> )	J
Me <sub>2</sub> PPh	16.73 t	10.3	132.5 t	25	132.05 s	0	131.1 s	0	129.1 s	0	d	
MePPh <sub>2</sub>	17.23 t	16.9	d	d	132.84 s	0	131.27 s	0	128.87 s	0	d	
Bz <sub>3</sub> P	32.39 t	19.6	132.9 t	22	127.44 s	0	130.17 s	0	128.99 s	0	127.44 s	0
Bz <sub>2</sub> PPh	32.86 t	20.2	131.0	d	Bz 131.47 s	0	130.33 s	0	128.71 s	0	127.38 s	0
					Ph 132.68 s	0	132.88 t	12	129.00 t	10	128.52 s	0
BzPPh <sub>2</sub>	37.50 t	20.2	132.5 t	10	Bz 131.4 s	0	133.59 s	0	128.32 s	0	127.13 s	0
					Ph 131.4 s	0	133.84 t	9.2	128.56 t	10.2	128.25 s	0
(BzO) <sub>3</sub> P	70.40 s	0	d	d	132.70 s	0	132.18 t	12.6	128.10 t	4.0	127.82 s	0
(BzO) <sub>2</sub> PPh	70.60 s	0	135.9 t	9	Bz 132.96 s	0	132.34 s	0	128.43 t	4.0	127.80 s	0
					Ph 133.16 s	0	132.87 t	14.0	128.71 t	13.2	128.17 s	0
BzOPPPh <sub>2</sub>	70.89 s	0	132.2	d	Bz 128.96 s	0	128.39 s	0	128.07 s	0	127.50 s	0
					Ph 128.96 s	0	128.71 t	3.0	128.07 s	0	127.50 s	0

<sup>a</sup> Key: Me, CH<sub>3</sub>; Ph, C<sub>6</sub>H<sub>5</sub>; Bz, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>; BzO, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O; t, triplet; s, singlet. <sup>b</sup> J = <sup>n</sup>J<sub>PC</sub> + <sup>n+2</sup>J<sub>PC</sub> for "virtually coupled" multiplet. <sup>c</sup> J for first-order triplet. <sup>d</sup> Not observed due to limited solubility and/or long relaxation time.

atmosphere. Melting points were determined on a Meltemp melting point apparatus and are uncorrected. Elemental analyses were performed by chemalytics, Inc., Tempe, Ariz. 85282, and satisfactory C, H, and N analyses were obtained for all complexes.

Infrared, electronic, and NMR spectra were obtained as described previously.<sup>12</sup> Proton and <sup>13</sup>C{<sup>1</sup>H} chemical shifts are relative to internal TMS. The <sup>31</sup>P{<sup>1</sup>H} chemical shifts are relative to external 85% H<sub>3</sub>PO<sub>4</sub> (capillary) with signals downfield of H<sub>3</sub>PO<sub>4</sub> being reported with negative shifts.

The ligands were prepared<sup>24</sup> by standard Grignard or solvolysis reactions and purified by vacuum distillation. The chloride complexes L<sub>2</sub>PdCl<sub>2</sub> were prepared by standard methods<sup>24</sup> and each of the cyano complexes was prepared from these by metathesis reactions with sodium cyanide. The physical properties of the complexes are listed in Table I.

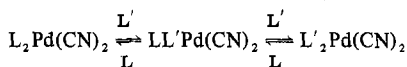
## Results and Discussion

All (R<sub>3</sub>P)<sub>2</sub>Pd(CN)<sub>2</sub> complexes exhibit single ν<sub>Pd-C</sub> vibrations in the solid state and the single ν<sub>C≡N</sub> vibrations both in the solid state and in chloroform solutions (both of which are required of a D<sub>2h</sub> trans geometry (Table I). Each of the complexes except [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]Pd(CN)<sub>2</sub> and [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]Pd(CN)<sub>2</sub> exhibits 1:2:1 triplets for the methyl or methylene resonances in its <sup>1</sup>H NMR spectrum, typical of the trans geometry<sup>13</sup> for the [X<sub>n</sub>A]<sub>2</sub> spin systems. Both [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]Pd(CN)<sub>2</sub> and [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]Pd(CN)<sub>2</sub> exhibit quartets of triplets for the methylene resonances in their <sup>1</sup>H NMR spectra, typical of the trans geometry for [ABX]<sub>2</sub> spin systems.<sup>25,26</sup> All phosphine complexes exhibited 1:2:1 triplets for their <sup>13</sup>C{<sup>1</sup>H} CH<sub>3</sub> or CH<sub>2</sub> resonances typical of the trans geometry for [A]<sub>2</sub>X spin systems.<sup>27</sup> In four cases (Table II) a 1:2:1 triplet was observed for the <sup>13</sup>C{<sup>1</sup>H} resonance of the cyanide carbon, consistent with the trans geometry and an A<sub>2</sub>X (A = <sup>31</sup>P, X = <sup>13</sup>C) spin system. The cis geometry should exhibit a doublet of doublets for the associated [A]<sub>2</sub>X spin system of the <sup>13</sup>C{<sup>1</sup>H} cyanide

carbon resonance since the two phosphorus-carbon coupling constants, <sup>2</sup>J<sub>PC</sub> and <sup>2</sup>J<sub>P'C</sub>, should be considerably different<sup>12,14</sup> and <sup>2</sup>J<sub>PP'</sub> should be small for the cis geometry.<sup>27,28</sup> All complexes exhibited single <sup>31</sup>P resonances, demonstrating the existence of a single species in solution. The <sup>31</sup>P chemical shifts are consistent with those anticipated for the trans geometry.<sup>29</sup> All of the phosphorus ester complexes exhibited singlets in their <sup>13</sup>C{<sup>1</sup>H} NMR spectra except for the cyanide carbon resonance of [(BzO)<sub>2</sub>PPh]<sub>2</sub>Pd(CN)<sub>2</sub>. These singlets are typical for the trans geometry in which algebraic cancellation of <sup>n</sup>J<sub>PC</sub> and <sup>n+2</sup>J<sub>PC</sub> has occurred in the [A]<sub>2</sub>X <sup>13</sup>C spin systems.<sup>30</sup>

Whenever the solutions contained even the slightest trace of excess phosphine, the <sup>1</sup>H NMR resonance of the methyl or methylene groups collapsed to a singlet indicative of rapid phosphine exchange.<sup>31-35</sup> This occurred for samples with excellent chemical analyses. Multiple recrystallizations, Pd(CN)<sub>2</sub>, or reactions<sup>36</sup> with CHCl<sub>3</sub> or CDCl<sub>3</sub> were necessary to remove this trace of excess phosphine. This is much more critical than for analogous chloride, azide, or bromide complexes. Similar behavior has been noted<sup>34</sup> for [(CH<sub>3</sub>)<sub>3</sub>P]<sub>2</sub>Ni(CN)<sub>2</sub> and excess ligand has been utilized to catalyze isomerizations in other systems.<sup>3-5,28,37</sup> Addition of a trace of (CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub> to a CDCl<sub>3</sub> solution of trans-[(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]Pd(CN)<sub>2</sub> collapsed the triplet methyl resonance to a singlet which remained a singlet even at -50 °C. Addition of more (CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub> to this solution caused the singlet to change to a doublet indicating that the exchange rate increases as the concentration of excess phosphine increases.<sup>33</sup> This is suggestive of an associative mode of exchange. When a trace of (CH<sub>3</sub>O)<sub>3</sub>P was added to a CDCl<sub>3</sub> solution of [(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]Pd(CN)<sub>2</sub>, geometric isomerization occurred with the concomitant formation of cis-[(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]Pd(CN)<sub>2</sub>.<sup>28,37</sup> The complex cis-[(CH<sub>3</sub>O)<sub>2</sub>P][(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]Pd(CN)<sub>2</sub> was also prepared by

the redistribution reaction which occurs upon mixing solutions of *trans*-[(CH<sub>3</sub>O)<sub>3</sub>P]<sub>2</sub>Pd(CN)<sub>2</sub> and *trans*-[(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>Pd(CN)<sub>2</sub> in equimolar amounts.<sup>28,37</sup> When a 1:1 mole ratio of (CH<sub>3</sub>O)<sub>3</sub>P was added to a solution of [(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>Pd(CN)<sub>2</sub> in CDCl<sub>3</sub> (Figure 1), the NMR spectra were consistent with the occurrence of the reactions



where L = (CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub> and L' = (CH<sub>3</sub>O)<sub>3</sub>P. Thus, at the instant at which (CH<sub>3</sub>O)<sub>3</sub>P was added, ligand substitution of (CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub> by (CH<sub>3</sub>O)<sub>3</sub>P occurred in a stepwise manner. Initially, there is a small concentration of free (CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub> and ligand exchange occurs at an intermediate rate between (CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub> and [(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>Pd(CN)<sub>2</sub> as shown by the singlet <sup>1</sup>H resonance in the methyl region. Slow exchange is observed between (CH<sub>3</sub>O)<sub>3</sub>P and [(CH<sub>3</sub>O)<sub>3</sub>P]<sub>2</sub>Pd(CN)<sub>2</sub> since there is loss of <sup>1</sup>H-<sup>31</sup>P coupling in the (CH<sub>3</sub>O)<sub>3</sub>P methyl resonance and the line shape for the [(CH<sub>3</sub>O)<sub>3</sub>P]<sub>2</sub>Pd(CN)<sub>2</sub> methyl resonance has changed. No exchange occurs with the "mixed-ligand" complex as doublets are observed in both the methoxy and methyl regions with the same coupling constants and chemical shifts as a solution containing only *cis*-[(CH<sub>3</sub>O)<sub>3</sub>P][(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>Pd(CN)<sub>2</sub>. Over a period of time (30 min) the concentrations of the "mixed-ligand" complex, free (CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>, and *trans*-[(CH<sub>3</sub>O)<sub>3</sub>P]<sub>2</sub>Pd(CN)<sub>2</sub> increase at the expense of [(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>Pd(CN)<sub>2</sub>. As this occurs, the rate of ligand exchange of [(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>Pd(CN)<sub>2</sub> increases as seen by the transition of the singlet <sup>1</sup>H methyl resonance into a doublet. Others<sup>16-21,31,34,38</sup> have isolated pentacoordinate complexes of the type L<sub>3</sub>MX<sub>2</sub> (M = Ni, Pd, Pt) and found that in each case extensive dissociation of either the neutral ligand L or the ionic ligand X occurs in solution. In some cases this dissociation is temperature dependent.<sup>31,34,38</sup> For example, at -50 °C the <sup>1</sup>H NMR spectrum of [(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>3</sub>PtBr<sub>3</sub> possesses a doublet and triplet (both of which have platinum satellites) with 1:2 relative integrated intensities.<sup>38</sup> This is consistent with the pentacoordinate square-pyramidal geometry established by x-ray crystallography for PdL<sub>3</sub>Br<sub>2</sub>, L = 5-ethyl-5*H*-dibenzophosphole<sup>39</sup> and L = 2-phenylisophosphindoline.<sup>40</sup> It is also consistent with a trigonal-bipyramidal geometry with equatorial bromines. Decreasing the temperature to as low as -120 °C failed to slow ligand exchange to the point where any pentacoordinate palladium(II) cyanide species could be observed. On the contrary, we find, for example, that upon heating a solution of [(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>Pd(CN)<sub>2</sub> in nitrobenzene, its triplet <sup>1</sup>H methyl resonance observed at 25 °C begins to broaden at 39 °C, collapses to a singlet at 57 °C, becomes a sharp singlet at 75 °C, and returns to the triplet upon returning to 25 °C. Similar behavior occurs for the other cyanide complexes. For the analogous complexes [(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>PdX<sub>2</sub> (X = Cl, N<sub>3</sub>) exchange could not be initiated even at 140 °C in nitrobenzene.<sup>12,13</sup>

We have found that generally<sup>9,10,12-14</sup> the *cis* isomer of L<sub>2</sub>PdX<sub>2</sub> (X = Cl<sup>-</sup>, N<sub>3</sub><sup>-</sup>) complexes is thermodynamically more stable than the *trans* isomer and in numerous cases both isomers are present in equilibrium in solution. For the 11 complexes investigated herein the *trans* isomer is the thermodynamically more stable isomer and the *cis* isomer could not be detected in solution. The two platinum complexes {CH<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>Pt(CN)<sub>2</sub> and [(CH<sub>3</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>]<sub>2</sub>Pt(CN)<sub>2</sub>, prepared by metathesis from the *cis* chloride complexes, are also *trans* in solution as shown by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR.

The cyanide complexes undergo phosphine exchange much more rapidly than the chloride or azide complexes and conductance titrations indicate that no ionic species are formed

upon addition of excess ligand to solutions of L<sub>2</sub>Pd(CN)<sub>2</sub>. Thus, as anticipated, cyanide does stabilize the pentacoordinate complexes relative to chloride and azide but the pentacoordinate L<sub>3</sub>Pd(CN)<sub>2</sub> species are not detectable in solution.

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**Registry No.** (Me<sub>2</sub>PPh)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-88-2; (MePPh<sub>2</sub>)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-89-3; (BzPPh<sub>2</sub>)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-90-6; (Bz<sub>2</sub>PPh)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-91-7; (Bz<sub>3</sub>P)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-92-8; (MeOPPh<sub>2</sub>)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-93-9; ((MeO)<sub>2</sub>PPh)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-94-0; ((MeO)<sub>3</sub>P)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-95-1; (BzOPPh<sub>2</sub>)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-96-2; ((BzO)<sub>2</sub>PPh)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-97-3; ((BzO)<sub>3</sub>P)<sub>2</sub>Pd(CN)<sub>2</sub>, 60488-98-4; ((MeO)<sub>3</sub>P)(Me<sub>2</sub>PPh)Pd(CN)<sub>2</sub>, 60488-99-5; <sup>13</sup>C, 14762-74-4; <sup>31</sup>P, 7723-14-0.

## References and Notes

- (1) Presented in part at the 30th Annual Northwest Regional Meeting of the American Chemical Society, Honolulu, Hawaii, June 12-13, 1975; see Abstracts, No. 152.
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