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COORDINATIVE ADDITION REACTIONS OF TERTIARY PHOSPHINES TO BISPHOSPHINE- AND BISPHOSPHITEPALLADIUM(0) COMPLEXES. FORMATION OF FOURCOORDINATE PALLADIUM(0) SPECIES WITH C_{3v}-SYMMETRY

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Low-temperature ^{31}P-NMR studies of the coordinative additions of tertiary phosphines, Ph_2MeP and Et_3P, to twocoordinate palladium(0) complexes, $(Ph_3P)_2Pd(0)$ and $[(PhO)_3P]_2Pd(0)$, in toluene-d_8 show the formation of fourcoordinate complexes with C_{3v}-symmetry, $(Ph_2MeP)_3(Ph_3P)Pd$ and $(Et_3P)[(PhO)_3P]_3Pd$, respectively.

Despite the T_d-symmetry is expected as the optimum geometry for ML_4 complexes with d^{10} configuration according to EHMO calculations,$^{1)}$ only one example has been known for the fourcoordinate palladium(0) complex. Svatos and Flagg synthesized the tetrahedral palladium(0) complex, $(PF_3)_4Pd$, by the reaction of $Pd(CO)_2Cl_2$ with PF_3,$^{2)}$ and the geometry was concluded to be tetrahedral on the basis of an analysis of vibrational frequencies in IR and Raman spectra by Kruck and Baur.$^{3)}$ In this letter, we describe the formation of fourcoordinate palladium(0) complexes with C_{3v}-symmetry by coordinative addition of tertiary phosphines to bis(triphenylphosphine)palladium(0) ($\underline{1}$)$^{4)}$ or bis(triphenylphosphite)palladium(0) ($\underline{2}$)$^{4)}$ in toluene-d_8 at low temperature.

Coordinative addition reactions of diphenylmethylphosphine to bis(triphenylphosphine)palladium(0) ($\underline{1}$) and of triethylphosphine to bis(triphenylphosphite)-palladium(0) ($\underline{2}$) were followed at low temperature (-80 °C-rt) by ^{31}P-NMR spectroscopy$^{5)}$ in toluene-d_8 solution. The use of toluene-d_8, in which both starting and resulting complexes wewe quite soluble even at low temperature, allowed us to observe all the species formed in the reaction.

Reactions were carried out in the sealed Pyrex NMR sample tubes. After the addition of phosphine ligand to the toluene-d_8 solution of the twocoordinate palladium complex, 1 or 2, under dry argon atmosphere at room temperature, NMR sample tube was immediately sealed and cooled to -78 °C.

Representative spectra of the reacting system of 2.6 equiv. of diphenylmethylphosphine with the complex 1 are shown in Fig. 1.

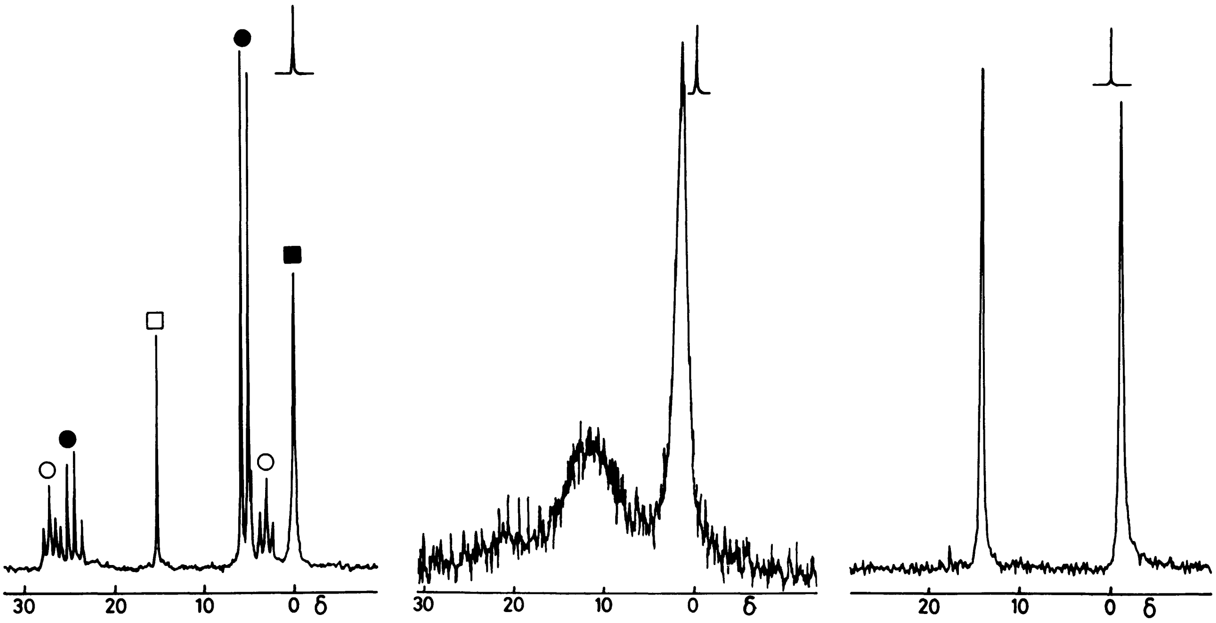

Fig. 1. Variable temperature $^{31}P\{^1H\}$-NMR spectra of the reacting system of 2.6 equiv. of Ph_2MeP with 1 in toluene-d_8: (A) at -60 °C; (B) at -20 °C; (C) at room temperature.
●: $(Ph_3P)(Ph_2MeP)_3Pd$, ○: $(Ph_3P)_2(Ph_2MeP)_2Pd$, □: $(Ph_2MeP)_3Pd$, ■: free Ph_3P.

Formation of $(Ph_3P)_2(Ph_2MeP)_2Pd$ (3),$^{6)}$ $(Ph_3P)(Ph_2MeP)_3Pd$ (4),$^{7)}$ and $(Ph_2MeP)_3$-Pd (5)$^{8)}$ in the molar ratio of 27:62:11 was observed at -60 °C. Broadening and coalescence of these peaks were observed with an increase of the temperature. Appearance of two sharp singlet peaks at room temperature would show a rapid exchange of phosphine ligands of $(Ph_3P)_2(Ph_2Me)_2Pd$ (3). Reversible feature of this process on the temperature was confirmed by taking NMR spectra again at -20 °C and -60 °C. During the measurement of ^{31}P-NMR spectra, decomposition of small amounts (< ∿10%) of the complex 1 was observed. The splitting pattern of the phosphorus signals of $(Ph_3P)(Ph_2MeP)_3Pd$ at -60 °C, doublet peak (δ 5.52, J = 31.3 Hz) for the coordinated Ph_2MeP and quartet peak (δ 24.7, J = 31.3 Hz) for the

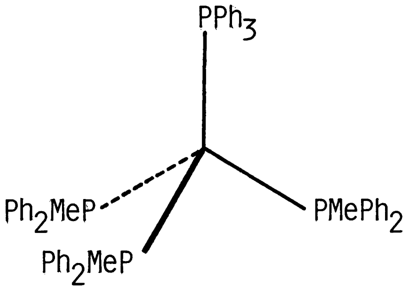

Fig. 2. Possible molecular geometry of 4.

coordinated Ph_3P, shows that three Ph_2MeP ligands are magnetically equivalent. As a possible geometry for the complex 4, which has three magnetically equivalent Ph_2MeP ligands, C_{3v}-symmetry is proposed (Fig. 2). Alternatively, a rapid ligand-exchange reaction within a NMR time scale would give rise to the magnetical equivalency of three Ph_2MeP ligands. In relation to this possibility, dissociation of the ligands in tetrakisphosphine complexes of palladium(0) in toluene-d_8 solution was studied by means of ^{31}P-NMR spectroscopy.

Although the equilibrium was observed at -60 °C in the case of $(Ph_3P)_4Pd$, it was slow process to give the broad signals for $(Ph_3P)_3Pd$, $(Ph_3P)_2Pd$, and Ph_3P in ^{31}P-NMR spectrum. ^{31}P-NMR spectrum of $(Ph_2MeP)_4Pd$ exhibited sharp singlet of coordinated Ph_2MeP at -60 °C. Broadening of the signals was observed over -40 °C. Therefore, the presence of the rapid ligand-exchange reaction at -60 °C would be excluded. Moreover, rapid random process should give rise to the collapse of the coupling between coordinated phosphines to give two singlet peaks in the ratio of 1:3. From these results, it would be concluded that the geometry of the complex 4 in toluene-d_8 at -60 °C was C_{3v}-symmetry as shown in Fig. 2.

In the coordinative addition of triethylphosphine to bis(triphenylphosphite)palladium(0) (2) in toluene-d_8 at -80 °C, fourcoordinate palladium(0) complex with C_{3v}-symmetry, $[(PhO)_3P]_3(Et_3P)Pd$ (6),[9] was formed together with $[(PhO)_3P]_2(Et_3P)_2Pd$ (7)[10] (Fig. 3). It is still ambiguous whether the geometry of the complex 3 and 7 is C_{2v} or D_{2h}.

Additional experimental tests of some of suggestion put force in this letter are now in progress.

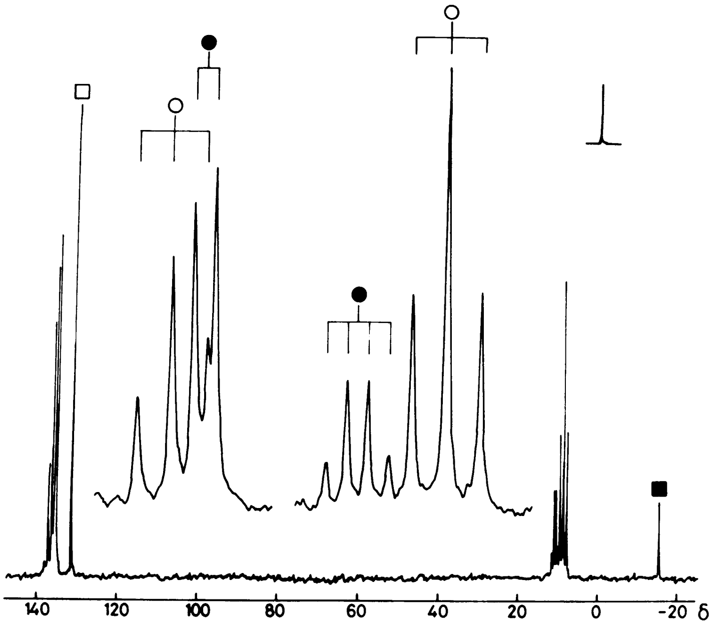

Fig. 3. $^{31}P\{^1H\}$-NMR spectrum of the reacting system of 1.4 equiv. of Et_3P with 2 in toluene-d_8 at -80 °C.
●: $[(PhO)_3P]_3(Et_3P)Pd$, ○: $[(PhO)_3P]_2(Et_3P)_2Pd$,
■: free Et_3P, □: unidentified.

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References

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2) G. F. Svatos and E. E. Flagg, *Inorg. Chem.*, 4, 422 (1965).

3) V. T. Kruck and K. Baur, *Z. Anorg. Allg. Chem.*, 364, 192 (1969).

4) Novel preparative method; H. Urata, H. Suzuki, Y. Moro-oka, and T. Ikawa, submitted for publication.

4) ^{31}P-NMR spectra were obtained on a JNM FX-100 at 40.26 MHz in the proton-decoupled mode. Chemical shifts are expressed in ppm downfield from the external triphenylphosphine.

6) 3: ^{31}P-NMR (toluene-d_8, -60 °C, under Ar) δ 27.08 (t, J = 27.3 Hz, PPh_3), 3.17 (t, J = 27.3 Hz, $PMePh_2$).

7) 4: ^{31}P-NMR (toluene-d_8, -60 °C, under Ar) δ 24.70 (q, J = 31.3 Hz, PPh_3), 5.52 (d, J = 31.3 Hz, $PMePh_2$).

8) 5: ^{31}P-NMR (toluene-d_8, -60 °C, under Ar) δ 15.21 (s, $PMePh_2$).

9) 6: ^{31}P-NMR (toluene-d_8, -80 °C, under Ar) δ 136.1 (d, J = 21.5 Hz, $P(OPh)_3$), 10.97 (q, J = 21.5 Hz, PEt_3).

10) 7: ^{31}P-NMR (toluene-d_8, -80 °C, under Ar) δ 136.9 (t, J = 35.2 Hz, $P(OPh)_3$), 8.77 (t, J = 35.2 Hz, PEt_3).

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