EVIDENCE FOR THE ACYL NATURE OF \([(\text{PPh}_3)_2\text{Pd(COCH}_2\text{CH}_3)]^+\)

COMPLEX IN SOLUTION FROM HETERONUCLEAR $^{13}\text{C}-\{^{1}\text{H}\}$ NOE STUDIES.

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According to $^{31}\text{P},^{13}\text{C}$ and $^{1}\text{H}$ NMR data the molecular intermediate, observed in Pd(OAc)$_2$/PPh$_3$/CF$_3$COOH/H$_2$O-catalytic system for the synthesis of diethylketone from CO, H$_2$ and C$_2$H$_4$, may be attributed to either propionyl trans-\([(\text{PPh}_3)_2\text{Pd(COCH}_2\text{CH}_3)]^+\) (A) or carbonyl-ethyl (PPh$_3$)$_2$Pd(CO)(C$_2$H$_5$) (B) palladium complex. To make a final choice between the two possible complexes (A) or (B) we have estimated the distance between hydrogen nucleus of CH$_2$ group and carbon nucleus of CO group. This distance is expected to be 2.11 Å for complex (A) and more than 4 Å for complex (B).

Values of the Heteronuclear Overhauser Effect with selective irradiation of CH$_2$ protons (NOE=1+η) and spin-lattice relaxation time $T_1$ have been measured for CO and CH$_2$ carbon nuclei [NOE(CO)=1.31±0.08, NOE(CH$_2$)=1.46±0.05; $T_1$(CO)=2.33±0.05s, $T_1$(CH$_2$)=0.20±0.02s].

Dipolar contributions ($T_{1d}^{-1}$) to the total relaxation rates ($T_{1}^{-1}$) have been obtained in $^1\text{H}-^{13}\text{C}$ approximation, using the equation

$$T_{1d}^{-1} = \eta (1/N)(2 \gamma_C/\gamma_H) T_1^{-1},$$  

where $N$ is the number of protons, interacting with the carbon nucleus; $\gamma_C$ and $\gamma_H$ are magnetogyrar ratios for carbon and hydrogen nuclei. Dipolar contributions for the carbon nuclei of CH$_2$ and CO groups were found to be 0.58±0.04 s$^{-1}$ and 0.033±0.003 s$^{-1}$, respectively. At the same time dipolar contribution to $T_1$ depends on the distance between C and H nuclei according to the formula

$$T_{1d}^{-1} = \gamma_C^2 \gamma_H^2 \tau_C^2 / r^6(\text{CH}),$$  

where $\tau_C$ is the correlation time for the vector between C and H nuclei; $r(\text{CH})$ is the internuclear C-H distance.

We have assumed that the molecule as a whole reorients isotropically in solution and free internal rotation of the CH$_2$ group around C-C bond is essentially restricted because of the spatial hindrances caused by bulky PPh$_3$-ligands. In this case, correlation time for the CH$_2$ group is equal to the one for vector between carbon of CO and proton of CH$_2$ and, assuming $r(\text{CH}) = 1.09$ Å in CH$_2$ and taking into account equation (2), $r(\text{COCH}_2)$ can be calculated from equation (3):

$$r^6(\text{COCH}_2) = r^6(\text{CH}_2)T_{1d}(\text{CH}_2)/T_{1d}(\text{CO}).$$  

This distance was estimated to be 1.75 Å. It is evident that the internuclear distance obtained is close to that, typical for propionyl complex and strongly differs from the distance for carbonyl-ethyl complex. Thus, we conclude that the observed molecular intermediate is propionyl complex of palladium - trans - \([(\text{PPh}_3)_2\text{Pd(COCH}_2\text{CH}_3)]^+\).