EVIDENCE FOR THE ACYL NATURE OF $[(PPh_3)_2Pd(COCH_2CH_3)]^+$ COMPLEX IN SOLUTION FROM HETERONUCLEAR $^{13}C-\{^1H\}$ NOE STUDIES.

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According to $^{31}P, ^{13}C$ and ^1H NMR data the molecular intermediate, observed in $Pd(OAc)_2/PPh_3/CF_3COOH/H_2O$-catalytic system for the synthesis of diethylketone from CO, H_2 and C_2H_4, may be attributed to either propionyl trans-$[(PPh_3)_2Pd(COCH_2CH_3)]^+$ (A) or carbonylethyl $(PPh_3)_2Pd(CO)(C_2H_5)$ (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 ^1H-^{13}C approximation, using the equation

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

where N is the number of protons, interacting with the carbon nucleus; γ_C and γ_H are magnetogyric 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

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

where τ_C is the correlation time for the vector between C and H nuclei; r(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(CH) = 1.09 Å in CH_2 and taking into account equation (2), $r(COCH_2)$ can be calculated from equation (3):

$$r^6(COCH_2)= r^6(CH_2)T_{1d}^{-1}(CH_2)/T_{1d}^{-1}(CO). \quad (3)$$

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 carbonylethyl complex. Thus, we conclude that the observed molecular intermediate is propionyl complex of palladium - trans - $[(PPh_3)_2Pd(COCH_2CH_3)]^+$.