

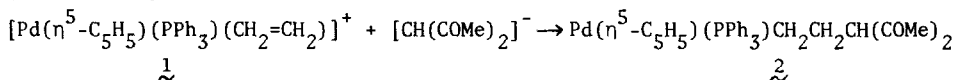
THE FIRST DIRECT EVIDENCE FOR TRANS ADDITION OF β -DIKETO ANIONS AND PALLADIUM
 TO ETHYLENE

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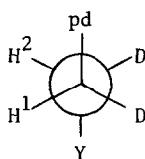
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Palladium assisted alkylation of olefins under mild conditions is of current synthetic interest.¹⁻⁵ The cis mode of the addition of palladium and methyl or aryl anions to both cyclic and acyclic olefins was well documented,^{2,3} while the stereochemical study of the carbopalladation using "stabilized carbanions" has been limited only to a special case, namely the trans addition of the diethyl malonate anion to cyclic olefins bound to the palladium atom through chelate coordination.⁴ We have now found the first unambiguous evidence for the trans addition⁶ of β -diketo anions and palladium to ethylene by isolating the carbopalladation adduct from ethylene and the anion of 2,4-pentanedione.

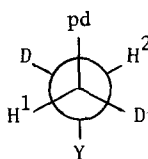
Treatment of the cationic η -ethylene complex,⁷ $[\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{L}]\text{ClO}_4$ ($\underline{1}$ (L= $\text{CH}_2=\text{CH}_2$) with sodium 2,4-pentanedionate in THF at -19°C afforded an orange crystalline complex, $\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{COMe})_2$ ($\underline{2}$, m.p. 102-104 $^\circ\text{C}$ (dec.) (55 % after recrystallization from benzene).



The structure of $\underline{2}$ was deduced from elemental analysis, infrared and ^1H n.m.r. data⁸ and the reactivities described later. Particularly, the two methylene group resonances in the 100 MHz ^1H n.m.r. spectra of $\underline{2}\text{-d}_c$ or $\underline{2}\text{-d}_t$, prepared from $\underline{1}$ (L= cis or trans- $\text{CHD}=\text{CHD}$, respectively), showed simple splitting patterns ($\delta(\text{H}^1) = 1.13(\text{dd})$,⁹ $\delta(\text{H}^2) = 1.73(\text{dd})$; $J_{\text{H}^1\text{-H}^2} = 4.2$ or 12.3 Hz for $\underline{2}\text{-d}_c$ or $\underline{2}\text{-d}_t$, respectively), indicating the dominant conformation of each complex as shown below.



($\underline{2}\text{-d}_c$)



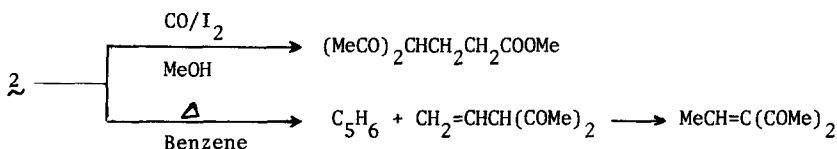
($\underline{2}\text{-d}_t$)

pd: $\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$

Y: $\text{CH}(\text{COMe})_2$

Thus, it is quite obvious that the mode of the addition of the $[\text{CH}(\text{COMe})_2]^-$ nucleophile and the $\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$ moiety across the C=C bond of ethylene is exclusively trans. In further agreement with, but not necessarily indicative of, the attack of the nucleophile directly at the olefinic carbon coordinated with the palladium atom is the fact that the carbon-palladium bonded complex,¹⁰ $\text{Pd}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{CH}(\text{COMe})_2$ ($\underline{3}$) failed to undergo the ethylene insertion reaction under the conditions similar to those employed in the above reaction.

When $\underline{2}$ was treated with iodine in methanol under carbon monoxide, methyl 4,4-diacetylbutanoate¹¹ was obtained in good yield. Heating a benzene solution of $\underline{2}$ at 50 C for 15 min. gave 3-vinyl-2,4-pentanedione,¹² together with cyclopentadiene, in high yields. The former further isomerized to 3-ethylidene-2,4-pentanedione¹³ after a long period (ca. 1 day).



The β -elimination of $\underline{2-d_c}$ or $\underline{2-d_t}$ gave mixtures of the stereoisomeric olefins, e.g. cis and trans-CHD=CDCH(COMe)₂ non-selectively, unlike the β -elimination of the analogous alkylpalladium complex,¹⁴ Pd(η^5 -C₅H₅)(PPh₃)CHDCHD·OMe.

Finally, it should be noted that the β -elimination step was accelerated remarkably by adding maleic anhydride or m-chloroperbenzoic acid to the benzene solution of $\underline{2}$, but retarded considerably by triphenylphosphine (up to 5 fold excess). These results suggest that the β -elimination of $\underline{2}$ proceeds via the pre-dissociation of the triphenylphosphine ligand, generating a coordinatively unsaturated intermediate, Pd(η^5 -C₅H₅)CH₂CH₂CH(COMe)₂. In other words, the fulfillment of coordinative saturation around the palladium atom may be responsible, in part, for the successful isolation of $\underline{2}$.

References and Notes

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2. R. F. Heck, "Organotransition Metal Chemistry," Academic Press, New York, 1974, p.98.
3. S. Murahashi, M. Yamamura, and N. Mita, J. Org. Chem., 42, 2870 (1977).
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5. T. Hayashi and L. S. Hegedus, J. Am. Chem. Soc., 99, 7093 (1977).
6. The mode of the addition of the diethyl malonate anion and palladium to styrene in the presence of palladium 2,4-pentanedionate was postulated as trans only tentatively on the basis of the regiochemical results of the alkylation.³
7. T. Majima and H. Kurosawa, J. Organometal. Chem., 134, C45 (1977).
8. $\nu(\text{C}=\text{O})$ 1695, 1725 cm⁻¹. δ (in CDCl₃) ca.1.0-1.3(m) and 1.6-1.9(m) (CH₂CH₂); 1.91(s) (MeCO); 3.03(t) J_H = 7.0 Hz (-CH<); 5.67(d) J_p = 1.4 Hz (C₅H₅).
9. J_{H-p}¹ = 5.6 Hz.
10. $\underline{2}$ was obtained by treatment of Pd(η^5 -C₅H₅)(PPh₃)Br with thallium 2,4-pentanedionate in THF at -19 C; m.p. 108-113 C. $\nu(\text{C}=\text{O})$ 1620, 1650 cm⁻¹. δ (in CDCl₃) 2.30(s) (MeCO); 3.47(d) J_p = 7.0 Hz (-CH<); 5.33(d) J_p = 3.0 Hz (C₅H₅).
11. R. Chong and P. S. Clezy, Aust. J. Chem., 20, 123 (1967).
12. δ (in C₆D₆) 1.77(s) (MeCO); 4.67(dd) J_{gem} = 1.5, J_{trans} = 17.3 Hz and 4.96(dd) J_{cis} = 10.5 Hz (CH₂=); 5.92(dd) (-CH=); no resonance due to -CH< could be detected.
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(Received in Japan 23 October 1978)