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BIS(η-ARENE)DI-PALLADIUM(I) CHEMISTRY: CATALYTIC DIMERIZATION OF ETHYLENE UNDER MILD CONDITIONS. THE POSSIBLE ROLE OF Pd-Pd BONDS IN THE REACTION.

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Abstract - Pd(I) complexes of formula |(η-arene)PdX|$_2$ (X = $AlCl_4$, Al_2Cl_7; arene = benzene, toluene, p-xylene) are active catalysts for the ethylene dimerization under mild conditions; a mechanism for the reaction is suggested.

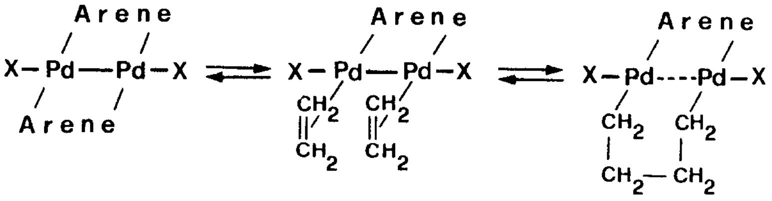
Although palladium(I) complexes have been proposed as intermediates in a number of palladium catalyzed organic reactions$^{(1)}$, studies on the chemistry of Pd(I) oxidation state are not very extensive. In order to get a deeper knowledge of Pd(I) chemistry, with regard to understanding of catalytic processes, we have examined the reaction of olefins with some bis (η-arene)di-palladium(I) complexes of formula|(η-arene)PdX|$_2$ (X=$AlCl_4$, Al_2Cl_7; arene=benzene, toluene, p-xylene), |I|, precedently prepared $^{(2)}$.

We found that ethylene dimerization with these catalyst systems takes place almost quantitatively (95%) without any induction period at room temperature, under atmospheric pressure. Only a trace amount of hexenes was detected in the products. The results are summarized in Table 1.

In a typical experiment 40 mg of catalyst were added under nitrogen to 10 ml of dry benzene in a 250 ml flask; the nitrogen gas in the flask had been evacuated and ethylene (280 ml at STP) introduced at low temperature. The flask was warmed up to room temperature giving a yellow-orange solution and kept with vigorous magnetic stirring.Subsequently all volatile materials (ethylene, butenes and solvent) were transferred into a 50 ml flask by means of a liquid nitrogen trap. Their amounts were determined by gas chromatographic analysis.

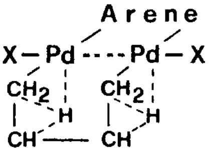
The dimerization of ethylene by means of palladium compounds using palladium (II) complexes as catalyst has been extensively studied; nevertheless details of mechanism of these reactions have not been well understood and the effective catalyst itself has been poorly characterized$^{(3)}$. This work is the first report showing catalytic activity of Pd(I) complexes in the ethylene dimerization. These complexes have been found to be much more active than Pd(II) compounds under the same reaction conditions$^{(4)}$.

In order to suggest insight on the catalytically active species, it must be taken into accounts that the Pd(I) systems,I, were found to be stable and effective catalyst only at room temperature and in aromatic solvents. This suggests that aromatic molecules promote the stabilization of the Pd-Pd unit, which is supposed to remain intact during the reaction. Therefore the dimerization of ethylene could involve, in a first step, the substitution of only one aromatic unit by the ethylene, which is followed by the coupling of two ethylene molecules, occurring in a second step.



[I] [II] [III]

The evolution of III can be supposed to proceed through a hydride transfer process, IV, which is often suggested in palladium chemistry(5), producing butenes and, in the presence of ethylene, again II.



[IV]

Propene is dimerized less readily than ethylene under these mild conditions to give with low convertions (15-20%) a complex mixture of compounds(6). It was also found that these palladium(I) complexes catalyze the isomerization at room temperature of butenes, pentenes and hexenes: the isomerization takes place very radiply without any induction period(6).

It is of interest to observe that a palladium binuclear catalysis, involving as active intermediates Pd(I) species containing Pd-Pd bonds, has also been suggested in some olefin isomerization using palladium(II) compounds as catalysts(7). Our finding supports this hypothesis and seems to point out the relevance of palladium(I) species in some olefin reactions catalyzed by palladium(II) compounds.

Table 1. Dimerization of ethylene catalyzed by bis (π-arene)di-palladium(I) complexes. Ethylene, 12.5 mmol.; T°C, room temperature; solvent, benzene (10 ml).

Catalyst (mmol)	Reaction time (hr)	Conversion %	C_4 distribution (%)		
			1-butene	cis-2-butene	trans-2-butene
(benzene)$PdAlCl_4$ 0.11	0.5	21	traces	14	86
	1	46	1	20	79
	3	80	traces	23	77
	5	95	2	21	77
(benzene)$PdAl_2Cl_7$ 0.10	5	96	1	19	80
(toluene)$PdAlCl_4$ 0.12	3	85	traces	20	80
(p-xylene)$PdAlCl_4$ 0.10	3	90	1	16	83
(benzene)$PdAlCl_4$(*) 0.09	3	92	traces	16	84
(benzene)$PdAlCl_4$(**) 0.10	5	very low	-	-	-

(*) toluene as solvent.

(**) n-heptane as solvent: the catalyst disproportionated to give palladium metal and $PdCl_2$.

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