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Reaction Intermediate in the Dimerization of Ethylene Catalyzed by a Palladium(II) Complex. NMR Spectral Evidence for the Formation of the π-Bonded Chloro-acetylacetonato-(1-butene)palladium(II) Complex

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In a previous paper,[1] it has been shown that bidentate ligands, such as β-diketones, have marked effects on the dimerization of ethylene to butene catalyzed by di-μ-chlorobis(ethylene)dipalladium (I), $(Pd(C_2H_4)Cl_2)_2$; that is, when bidentate ligands, especially β-diketones, are added to the ethylene-

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[1] K. Kawamoto, T. Imanaka and S. Teranishi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 639 (1968).

palladium(II) chloride-acetic acid system, the additive increases the rate of the dimerization besides accelerating the reduction of palladium(II) to metallic palladium. The order of the acceleration effect was as follows: acetylacetone>ethyl acetoacetate>diethyl malonate.

Though various π-allyl-acetylacetonato-palladium complexes have been isolated by Robinson and Shaw,2) no olefin-acetylacetone-palladium complex in which the olefin is coordinated with palladium by the π-bond has ever been reported. The present paper will report the NMR spectral evidence for the formation of the π-bonded chloro-acetylacetonato(1-butene)palladium (IV), $(Pd(C_5H_7O_2)(C_2H_5CH{=}CH_2)Cl)$, which is assumed to be an intermediate in the dimerization of ethylene in the presence of an acetylacetone additive. Moreover, a possible mechanism for the dimerization with an acetylacetone additive is also discussed on the basis of the present results.

The procedure of synthesizing complex IV was similar to that described for the synthesis of di-μ-chloro-bisacetylacetonatodipalladium (II), $(Pd(C_5H_7O_2)Cl)_2$, in the previous paper.1) Into a reaction vessel there were charged complex I and acetylacetone (an equivalent mole to palladium), plus dichloromethane as a solvent, and then ethylene was bubbled into the solution under reflux for half an hour. The resulting solution was filtered and cooled at −40°C, and the solvent was removed. After the residue had been dried under 10^{-3}—10^{-4} mmHg at −40°C, a reddish-brown complex IV was obtained. This material was very unstable, and when warmed to room temperature, changed into a brown complex which was identified as complex II,1) with a partial precipitation of metallic palladium.

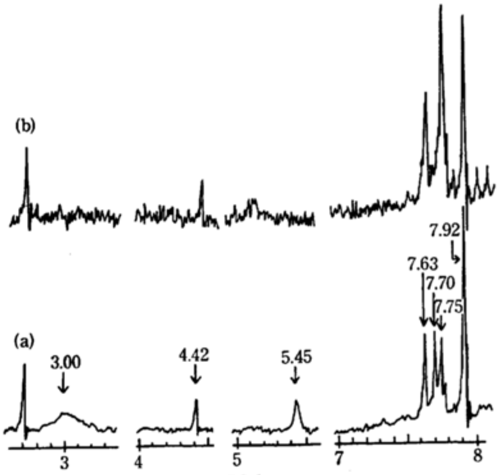

Fig. 1. NMR spectrum of complex IV.
(a) measured at −45°C in $CDCl_3$.
(b) After standing at room temperature for half an hour.

The NMR spectra[*1] of the unstable reddish-brown complex IV are shown in Fig. 1, where (a) is measured at −45°C and where (b) is examined after the complex has stood at room temperature for half an hour, during which the complex IV decomposed, evolving butene gas[*2] with the precipitation of metallic palladium. The assignment of the NMR spectrum is shown in Table 1. As is apparent from Table 1, the signals at τ 7.70, 7.75, and 4.42 (relative intensities 1.5 : 1.5 : 0.5) can be attributed to two methyl groups and one central methyne group respectively in the coordinated acetylacetonate group. In fact, the stable acetylacetonato-palladium complex II synthesized from acetylacetone and the ethylene-palladium complex I has NMR signals at τ 7.75 and 4.42 for the methyl and methyne groups respectively. In (b), the signal at τ 7.70 disappears with an increase in the intensity of the signal at τ 7.75; therefore, it can arise from a different methyl group besides that of complex II.

Table 1. Assignment of NMR spectrum

τ Value	Relative intensity −45°C	Relative intensity Room temp.	Assignment	Ref.
3.00	2	disappear	$=CH_2$ in 1-butene	2, 3
4.42	0.5		>C–H of acac* in complexes II and IV	2, 4, 5
5.54	1	disappear	–CH= in 1-butene	2, 3
7.63	2		$-CH_2-$ in 1-butene	2, 3
7.70	1.5	disappear	$-CH_3$ of acac* in complex IV	2, 4, 5
7.75	1.5	increase	$-CH_3$ of acac* in complex II	2, 4, 5
7.92	3	decrease	$-CH_3$ in 1-butene	2, 3

* acac=acetylacetonate group

When warmed to room temperature, this complex IV evolves butene gas.[*2] Therefore, the signals at τ 7.63, 3.00, 5.45, and 7.92 (relative intensities 2 : 2 : 1 : 3), which disappear or decrease at elevated temperatures were assigned to saturated methylene, olefinic methylene, olefinic methyne,

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2) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, **1963**, 4806.

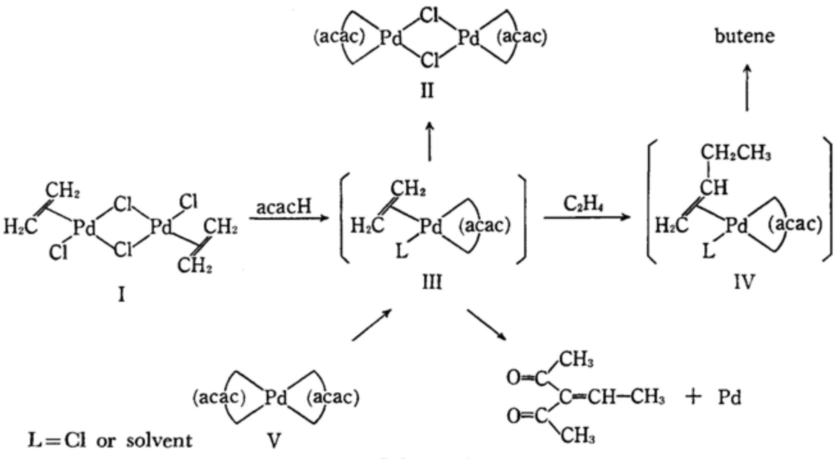
[*1] NMR spectra were obtained with a JNM-4H-100 spectrometer, using tetramethylsilane as an internal standard.

[*2] The composition of the gas was: *trans*-2-butene, 68 mol%; *cis*-2-butene, 27 mol%; 1-butene, 5 mol%.

3) A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967).

4) I. P. Collman, *Angew. Chem.*, **77**, 154 (1965).

5) G. Allen, J. Lewis, R. F. Long and C. Oldham, *Nature*, **202**, 589 (1964).



Scheme 1

and methyl groups respectively in 1-butene. However, the signals at τ 3.00 and 5.45 could also be assigned to olefinic methyne and methylene on account of these τ values. It is not clear at this time which assignment is best. The signals at τ 7.63 and 7.92 which remain in (b) might be due to a methyl group of the free acetylacetone or of the other products derived from the complex IV by decomposition, since the free acetylacetone has the signal at *ca.* τ 7.92. On the basis of these results, it could be concluded that the unstable complex obtained in the case of adding an acetylacetone was the chloro-acetylacetonato-(1-butene)palladium(IV).

Furthermore, in order to investigate the by-products of dimerization with an acetylacetone additive, acetylacetone (10 mol equivalents to palladium) was added to a solution of complex I dissolved in acetic acid, and then ethylene was bubbled into the solution for three hours. After work-up as usual, ethylideneacetylacetone was obtained in a 30% yield; it was identified through comparison with an authentic sample prepared from acetaldehyde and acetylacetone.[6] From the present results, it can be assumed that the dimerization with an acetylacetone additive proceeds *via* the two acetylacetonato-olefin-palladium complexes III and IV as is shown in Scheme 1.

Moreover, as the isomer of butene is in a nearly equilibrium composition, in which 2-butene is a main product,*2 there might be a process of isomerization from coordinated 1-butene to free 2-butene. The intermediate complexes III and IV in the dimerization with an acetylacetone additive could not be successfully isolated, but the existence of an intermediate III could be verified from the following facts: (i) the dimerization of ethylene catalyzed by the bisacetylacetonato-palladium (V), $(Pd(C_5H_7O_2))_2$, gave butene, and also palladium metal was formed; (ii) the acetylacetonato-palladium complex II was isolated from the reaction mixture;[1] (iii) the NMR spectrum supported the idea of the formation of the intermediate complex IV, and (iv) ethylideneacetylacetone, which was the adduct of ethylene and acetylacetone, was obtained as the by-product.

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[6] E. Knoevenagel and W. Ruschhaupt, *Ber.*, **31**, 1028 (1898).