Tetrahedron Letters No.22, pp. 1913-1916, 1970. Pergamon Press. Printed in Great Britain.

THE ANCHIMERIC ASSISTANCE IN THE LIGAND-COUPLING REACTIONS OF Π-ALLYLIC PALLADIUM ACETATE COMPLEXES

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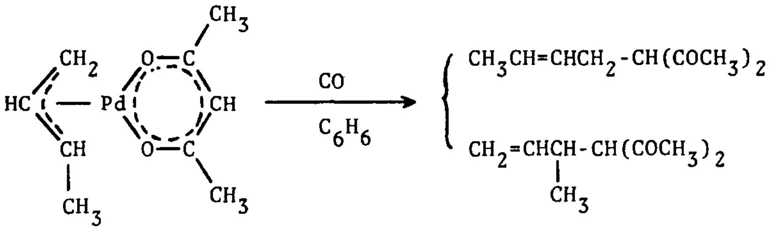
(Received in Japan 10 March 1970; received in UK for publication 14 April 1970)

π-Allylic acetylacetonatopalladium complexes were found to react in the atmosphere of carbon monoxide to give allylic acetylacetones(1). This type of ligand coupling reactions could be applied generally for some allylic palladium complexes, in which a ligand other than halogen was included, that is acetato(2), amines(2) and allylic groups(3).

The analogous reactions of asymmetrically substituted π-allylic complexes would give two kinds of the products. In fact, starting from π-crotylacetylacetonatopalladium complex, crotyl- and 3-bute-1-nylacetylacetone were obtained;



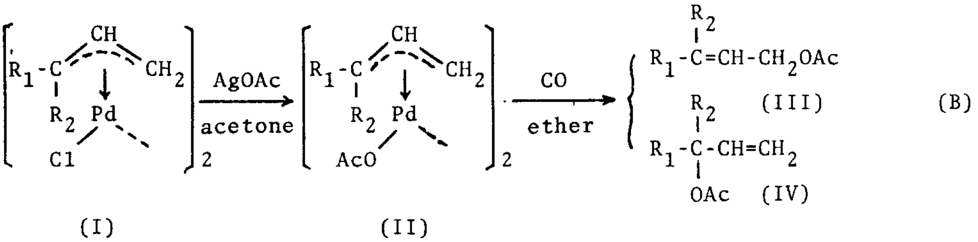
(A)

The total yield of acetylacetones was 48 % and the isomer ratio, former/latter, about 6, when the reaction was carried out in benzene at room temperature(2).

In the case of acetoxy complexes II, derived from halogen-bridged dimers I, two isomers of acetates III and IV could be obtained according to Equation B. But, bis{π-(4-butenyl)allylpalladium acetate} IIa(R_1, $CH_2{=}CHCH_2CH_2$;R_2, H) gave the sole product, 3-acetoxyheptadiene-1,6 IVa, assigned by nmr spectrum.

As this selective formation of IV would suggest that a functional group in the substituents of the complex II would interact specifically with palladium atom and affect the product ratio, analogous reactions were performed with ten complexes.

All π-allylic complexes Ia-j were prepared by authentic routes(4, 5, 6 and 7) and their structures were identified by ir and nmr spectra and elemental analysis. Complexes II were prepared by the reactions of I with silver acetate in acetone, and decomposed without their isolation under the atmosphere of carbon monoxide in ether at room temperature.

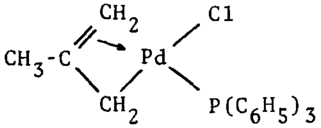


After metallic palladium was filtered off, the filtrates were analyzed by gas chromatography, ir and nmr spectra. The products were acetate esters III and IV, and the isomer ratio III/IV was determined by nmr spectrum. All the results were summarized in the table.

The side chain length of allyl group had no significant effect, while the C=C bond in it caused serious change in product ratios, and gave secondary acetates predominantly. On the other hand, in the case of methoxy or acetoxy group in substituents of π-allyl group, primary acetates III were major products. The product IIIj was identified by ir and nmr spectra, being consistent in its structure with authentic sample prepared from butenediol-1,4 and acetic anhydride.

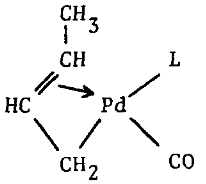
Dent and co-workers(8) carried out the reaction of carbon monoxide with bis-{π-crotylpalladium chloride} at high pressure and temperature, and obtained mainly propenylacetyl chloride, CH_3-CH=CH-CH_2COCl, which could be formed by the insertion reaction of carbon monoxide to primary carbon-palladium bond. Our results (preponderant formation of primary derivatives) in coupling reactions of π-crotyl complexes are quite similar with the insertion reaction of carbon monoxide. The primary carbon atom bonded to palladium atom in an intermediate (2) complex of the coupling reaction, therefore, would be attacked by the other ligand; in our case, acetato-ligand.

Chloro-π-methallyltriphenylphosphinepalladium complex has the σ-π structure, suggested by X-ray analysis(9), as follows,

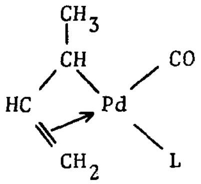


(V)

Either carbon monoxide or triphenylphosphine belongs to a strong π-acid. Therefore, its co-ordination to palladium atom of π-crotyl-palladium complex would change the π-structure to the σ-π bonded complex, as shown in VI, but not VII.



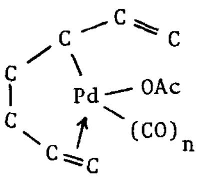
(VI)



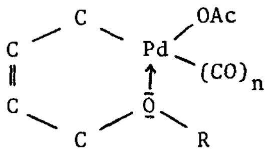
(VII)

But, in our case, which the co-ordinative functional groups are included in substituents of the π-allyl group, the co-ordination of these groups to metal atom should be considered as a factor to distinguish which structure (type VI or VII) is major one.

From the results shown in the table, the following two tentative intermediates were assumed. The selective formation of secondary or primary acetate from intermediate VIII or IX, respectively, might be explained, if the carbon atom, linked to palladium atom, was assumed to be attacked by acetate group. The stability of ring structure, formed by anchimeric assistance of $C{=}C$ bond or oxygen atom, would facilitate the existence of intermediate VIII or IX.



(VIII)



(IX)

The co-ordination of carbon monoxide molecules to metal atom would be presumed, as a small amount of insertion by-products, acid anhydrides, were formed. (3)

Table. The Decomposition Products of π-Allylic Palladium Complexes under carbon monoxide

	Complex (I)				Product (III,IV)	
run	R_1	R_2	Yield(%)	M.p.(°C)	Total yield(%)	III/IV
a	$CH_2=CHCH_2CH_2$	H	quant.	---	30.6	0/ 100
b	$CH_2=C(CH_3)CH_2CH_2$	H	quant.	---	42.4	0/ 100
c	$CH_3CH_2CH_2CH_2$	H	90.6	66	48.6	39/61
d	$CH_2=CHCH_2CH_2$	CH_3	92.0	---	47.3	0/100
e	$CH_2=C(CH_3)CH_2CH_2$	CH_3	97.1	---	45.1	0/100
f	$CH_3CH_2CH_2$	H	79.4	98-99	31.6	33/67
g	CH_3CH_2	H	92.0	80-81	52.8	45/55
h	CH_3	H	84.5	116-118	43.9	43/57
i	CH_3OCH_2	H	87.1	102-103	24.3*	100/0
j	CH_3COOCH_2	H	68.4	133-134	45.2*	100/0

* In ether solution, the acetate yield was very low. Therefore, benzene was used as a solvent instead of ether. The isomer ratio has little dependency on solvent used(2).

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