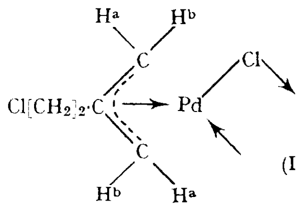
The Reaction of Spiropentane with Di-μ-Chloro-dichlorobis(ethylene)dipalladium: an Unusual Ring-opening Reaction

By A. D. KETLEY* and J. A. BRAATZ

(*W. G. Grace & Co., Washington Research Center, Clarksville, Maryland* 21029)

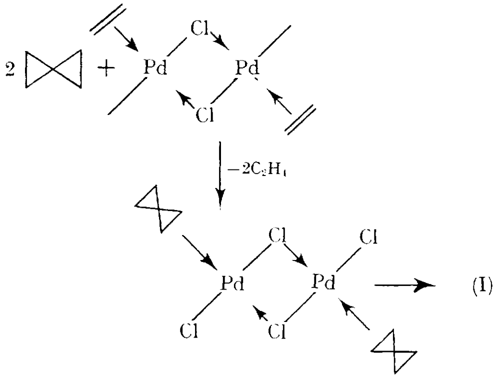
WHEN spiropentane is added to a suspension of di-μ-chloro-dichlorobis(ethylene)dipalladium in methylene chloride at 25°, ethylene is rapidly evolved and a yellow solution is formed, from which yellow crystals begin to separate after 5—10 min.; and ultimately a quantitative yield of a complex which analyses as $C_5H_8PdCl_2$ can be isolated.

The n.m.r. spectrum of this complex indicates that it is 2-(2-chloroethyl)-π-allylpalladium chloride (I) [s, τ 7·03, area 1·1 (H^a); s, τ 6·08, area 1·0 (H^b); t, τ 6·28, area 1·0 (H^c); τ 7·24, area 1·2 (H^d)]. On reduction with hydrogen at 60°, palladium is precipitated and 4-chloro-2-methylbut-1-ene was formed [n.m.r.: s, τ 8·52, area 1·6 (allylic CH_3); t, 7·83, area 1·1 [$C(3)H_2$]; t, τ 6·78, area 1·1 [$C(4)H_2$]; m, τ 5·28 (vinyl)]. Presumably reduction converts the π-allyl to a π-complex which is unstable at 60° and decomposes before reduction to the completely saturated compound can occur.



(I)

In this reaction, one bond of the spiro-linkage apparently acts as a particularly effective leaving group. We believe that the initial reaction [that in which di-μ-chloro-dichlorobis(ethylene) dipalladium loses ethylene and goes into solution] involves formation of an "edge" complex as has been postulated for various platinum cyclopropane adducts.[2]



One possible route from the intermediate to the final product would be the ionization of the Pd–Cl bond followed by rearrangement of the spiropentane ligand to a π-allyl carbonium ion. However, no product is isolated which would be derived from a rearrangement of the primary to a secondary carbonium ion. Since such a rearrangement is observed in the isomerization of the vinyl cyclopropane–$PdCl_2$ complex[3] it is possible that in the present reaction, opening of the spiropentane rings and migration of the chlorine atoms are synchronous. An attempt to isolate and characterize the initially formed complex to check these hypotheses is planned.

Bromine can also act as a leaving group since π-allylpalladium chloride is formed when cyclopropyl bromide is refluxed with $PdCl_2$. In this case the yield is low and there are many uncharacterized side-products. When di-μ-chloro-dichlorobis(ethyl)dipalladium is substituted for $PdCl_2$, pure π-allylpalladium chloride is formed. However, the reaction is much slower than with spiropentane, and requires 30 min. in refluxing benzene for completion. Attempts to prepare π-allylpalladium chloride by the decarboxylation of the sodium salt of cyclopropane carboxylic acid in the presence of $PdCl_2$ were unsuccessful.

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[1] For n.m.r. assignments see K. Vrieze, C. MacLean, P. Cossee, and C. W. Hilbers, *Rec. Trav. chim.*, 1966, **85**, 1077, and references therein.

[2] W. J. Irwin and F. J. McQuillin, *Tetrahedron Letters*, 1968, 1937.

[3] A. D. Ketley and J. A. Braatz, *J. Organometallic Chem.*, 1967, **9**, 5.