Reaction of Methylenecyclopropanes with Palladium Chloride

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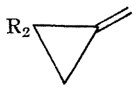
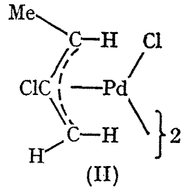
Summary The preparation of π-allylpalladium complexes from methylenecyclopropanes and palladium chloride is described.

MUCH attention has been focused on the reaction of cyclopropane derivatives with transition-metal complexes.[1] We have examined the reaction with palladium chloride.

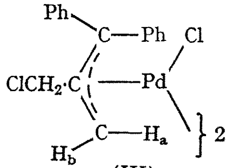
Methylenecyclopropane (Ia) in benzene was added with stirring (room temp.) to dichloro-bis(benzonitrile)palladium in the same solvent. The resulting yellow crystals were recrystallised from benzene–n-hexane (1 : 4) to give di-μ-chloro-bis(2-chloro-1-methyl-π-allyl)dipalladium(II) (II) in nearly quantitative yields, m.p. 179—183° (decomp.) (lit.,[2] 182—186°). The spectral properties were in agreement with those of an authentic sample. Under the same conditions, 2,2-diphenylmethylenecyclopropane (Ib) afforded di-μ-chloro-bis(2-chloromethyl-1,1-diphenyl-π-allyl)dipalladium(II) (III) [80%, m.p. 208—210° (decomp.)]. The i.r. spectrum (tetrachloroethylene suspension) indicated the absence of methyl and terminal methylene groups. The n.m.r. spectrum ($CDCl_3$, δ from Me_4Si): 3·52 (br s, H_a, $w_{\frac{1}{2}}$ 3·3 Hz), 4·16 (d, H_b, J 1·5 Hz), 4·07 and 4·31 (AB qu, J_{AB} 11·4 Hz, CH_2Cl), and 7·1—7·7 p.p.m. (m, C_6H_5). The assigned structure confirmed by reduction (H_2, 60°) to give 1,1-dimethyl-2,2-diphenylethylene (65%). On treatment with thallous acetylacetonate, (III) was converted to mononuclear acetylacetonato(2-chloromethyl-1,1-diphenyl-π-allyl)palladium(II) (IV), [85%, m.p. 55—58°; n.m.r. ($CDCl_3$): δ 1·99 and 2·05 (2 s, CH_3), 3·39 (br s, H_a, 3·3 Hz), 4·00 (d, H_b, J 1·2 Hz), 4·03 and 4·20 (AB qu, J_{AB} 10·8 Hz, CH_2Cl), 5·37 (s, H_c), and 7·1—7·7 p.p.m.(m, C_6H_5)].



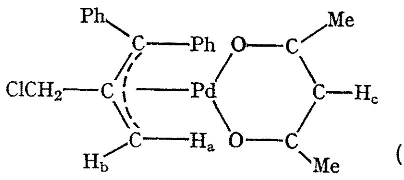
(Ia) R=H
(Ib) R=Ph



(II)



(III)



(IV)

Hence the reaction leads to the formation of π-allylic palladium complexes. The direction of ring fission is markedly influenced by substitution. The reaction of methylenecyclopropane itself (Ia) involves the fission of the C-1–C-2 bond, (*cf.* the reaction of vinylcyclopropane derivatives with palladium chloride$_3$). The diphenyl derivative (Ib), however, gives the C-2–C-3 cleavage product. These findings are reminiscent of the behaviour of methylenecyclopropanes towards di-iron enneacarbonyl.[4]

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