

Preliminary communication

π -Allylic complexes of palladium(II) and rhodium(III) from the ring-opening reaction of methylenecyclobutane with PdCl_2 and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$

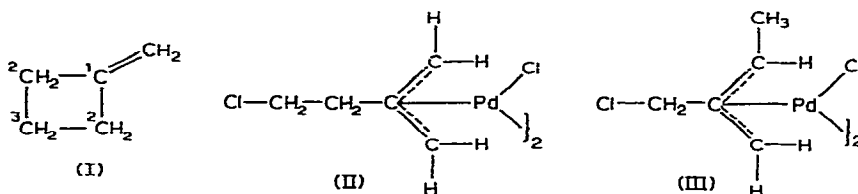
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Current interest in the ring-opening of strained cyclobutane and cyclobutene derivatives¹ prompts us to report the isolation and characterization of some π -allylic complexes obtained by treating methylenecyclobutane (I) with PdCl_2 and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. These appear to be the first examples of metal-promoted ring-opening reactions for methylenecyclobutane.

A mixture of (I) and PdCl_2 (molar ratio 20/1) was kept at 65° for 2 days in a sealed thick-walled glass tube. Pale yellow crystals were formed (60% yield) having the stoichiometry $\text{C}_5\text{H}_8\text{Cl}_2\text{Pd}$. The NMR spectrum indicated the presence of two isomeric complexes, (II) and (III), in the ratio of about 1/1, whose spectral data are reported in Table 1. Repeated recrystallisation from CHCl_3 gave complex (II) in the pure state, but purification of complex (III) was more difficult. The structure of (II) was confirmed by comparison of its properties with those of an authentic specimen of di- μ -chlorobis-[2-(2-chloroethyl)- π -allyl] dipalladium⁴. Treatment of (II) and (III) with H_2 gave products consistent with the structures assigned.



$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was dissolved in (I) at 25° to give a red-yellow solution from which the starting materials could be recovered. However, when the solution was kept in a sealed tube at 60° for 3 days a slow reaction produced pale yellow crystals of a dimeric complex (IV) (95% yield; m.p. 146° decomp.) sparingly soluble in benzene and chloroform of stoichiometry $[\text{C}_7\text{H}_8\text{ClO}_2\text{Rh}]_2$. The IR spectrum (KBr) exhibited a strong band at 2060 cm^{-1} attributable to a terminal carbonyl group bound to

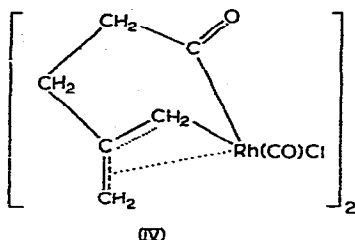
★Satisfactory elemental analyses were obtained for this and the other compounds reported.

TABLE I
NMR DATA FOR COMPLEXES (II), (III) AND (IV)^a

Complex	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7
[Pd ₂ Cl ₂ (C ₅ H ₈ Cl) ₂] (II)	6.09s	7.04s	7.04s	6.09s	7.26t $J_6 \sim 7$	6.30t $J_5 \sim 7$	
[Pd ₂ Cl ₂ (C ₅ H ₈ Cl) ₂] (III) ^b	6.09s	7.04s	6.29q $J_7 \sim 7$		5.64; 6.03ABq $J_{AB} \sim 12$		8.70d $J_8 \sim 7$
[Rh ₂ Cl ₂ (CO) ₂ (C ₆ H ₈ O) ₂] (IV)	5.87bs	6.85bs	5.84bs	5.10bs	7.07m	7.74m	

^a Measured in CDCl₃, at 31°. Chemical shifts (τ values) refer to TMS as internal standard; s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet because of weak and unresolved coupling with the Rh nucleus, m = partly resolved multiplet resonance; J_X = spin-spin coupling of proton with proton X, measured in cps. Protons numbered as shown. ^b For this complex the *syn* structure seems more probable on the basis of the chemical shift of the H³ proton 2,3. This structure is consistent with the proposed mode of opening of (I) to give (III).

rhodium(III)⁵ and two bands at 1720 and 1700 cm^{-1} in the keto-region. The NMR spectrum of (IV) in CDCl_3 (60 MHz) although complex (Table 1), was consistent with an asymmetrically bonded⁶ allylic compound. Conclusive information on the structure of the organic ligand was achieved by reduction of (IV) with a large excess of NaBH_4 to 4-methyl-1-pentanol. The evidence indicates that (IV) has the structure shown below, derived by the opening of the ring of (I):



From the nature of the products it appears that it is the C_2-C_3 bond which is involved in the ring-fission of (I) and the formation of the above complexes, with a hydrogen shift in the case of complex (III).

ACKNOWLEDGEMENT

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