Cleavage of Cyclopropane Rings with Rhodium(I) Octaethylporphyrin Anion

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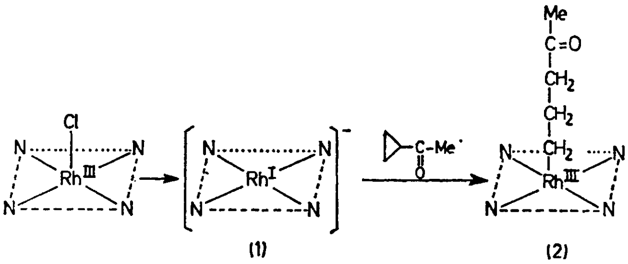
Summary Reactions of rhodium(I) octaethylporphyrin ion with cyclopropanes substituted with an electron-withdrawing group and with highly strained cyclopropane derivatives such as quadricyclane gave alkylrhodium(III) octaethylporphyrin complexes resulting from C–C bond cleavage of the cyclopropane ring.

ALTHOUGH cyclopropane rings are usually cleaved by an acid-catalysed process or oxidative addition to transition-metal complexes, we have found that nucleophilic attack of Rh$^{\rm I}$ octaethylporphyrin anion on some cyclopropyl derivatives leads to the cleavage of the cyclopropyl ring under mild conditions. The Rh$^{\rm I}$ octaethylporphyrin ion (**1**) was easily prepared by treatment of a solution of chlororhodium(III) octaethylporphyrin in EtOH with $NaBH_4$ in 0·5N-NaOH solution under argon. The reaction mixture shows the characteristic visible spectrum of rhodium(I) porphyrin ion[1] at 384, 420, and 521 nm. Reaction of (**1**) with cyclopropyl methyl ketone at room temperature afforded 4-oxopentylrhodium(III) octaethylporphyrin (**2**)† in 77% yield. Formation of an axial alkyl–Rh$^{\rm III}$ bond was shown by the ^{1}H n.m.r. spectrum in $CDCl_3$: τ 15·66 [2H, d of t, RhCH_2, J (^{103}Rh–H) 3 Hz], 14·67 (2H, m, $RhCH_2CH_2$), 11·06 (2H, t, CH_2CO), and 9·47 (3H, s, COMe). The proton signals of the axial ligand show upfield shifts due to the porphyrin ring current.[2]



The Rh–C bond was formed at the γ-position with respect to the COMe substituent. In contrast, cyclopropane cleavage was not observed for cyclopropane and phenylcyclopropane under the same conditions. This observation suggests that the transformation through the π-complex to the σ-complex intermediate requires the presence of an electron-withdrawing group to stabilize the negatively charged site.

The reaction of (**1**) with quadricyclane is of particular interest in comparison with that of other low-valent rhodium complexes such as $[Rh(CO)_2Cl]_2$.[3] The resulting complex (**3**) is a nortricyclylrhodium(III) complex produced by cleavage of one cyclopropane ring in quadricyclane. In the n.m.r. spectrum of compound (**3**) (Figure) the axial organo-group appeared at a higher field than Me_4Si. A tentative assignment has been made on the basis of the splitting pattern and the shifts arising from the anisotropic effect due to the diamagnetic ring current of the porphyrin ring. The presence of the nortricyclyl group was established by comparison with the organorhodium(III) complex (**4**) obtained by reaction of nortricyclyl bromide with (**1**). Complexes (**3**) and (**4**) have identical n.m.r. spectra. The present results indicate that one cyclopropane ring of quadricyclane is cleaved effectively without fission of the other cyclopropyl ring. Earlier investigations have shown that, in contrast to (**1**), Rh$^{\rm I}$ complexes catalyse the valence isomerization of quadricyclane to norbornadiene. The present unusual reactions might be due to the rigidity of the planar porphyrin ligand.

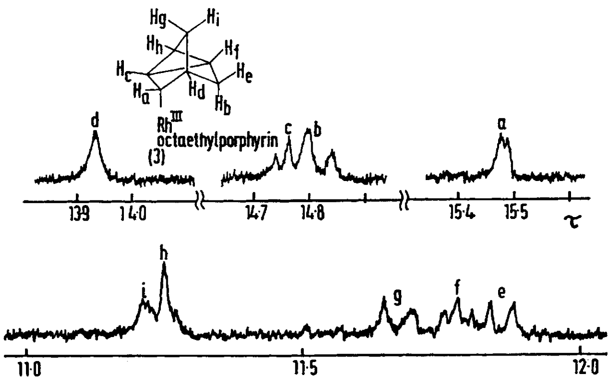


FIGURE. N.m.r. spectrum (220 MHz; $CDCl_3$) of the axial organo ligand of compound (**3**), upfield of Me_4Si.

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† Satisfactory elemental analyses have been obtained for these compounds.

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