π-Allyl-cycloocta-1, 5-diene-rhodium(I)

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Recently a number of organometallic π-complexes of π-allyl systems have been reported,[1] and the first π-allylic complex of rhodium(III), π-cyclododeca-1, 5, 9-trienyl-rhodium(III)-dichloride, has been isolated.[2] However, no report on an example of the π-allyl complexes of rhodium(I) has yet been published. In this paper we wish to describe the preparation of π-allyl-cycloocta-1, 5-diene-rhodium(I).

The treatment of a solution of bis-(cyclooct-1, 5-diene)-μ, μ'-diiodo - dirhodium[3] in anhydrous tetrahydrofuran with a four-equivalent amount of allyl magnesium bromide in ether at 0°C under nitrogen, followed by hydrolysis with aqueous ammonium chloride and chromatography on alumina, resulted in the formation of pale yellow crystals of π-allyl-cycloocta-1, 5-diene-rhodium(I), (yield, 30%; m. p. 108—112°C (decomp.). Found: C, 51.93; H, 6.97; mol. wt. (in benzene), 248. Calcd. for $C_{11}H_{17}Rh$: C, 52.39; H, 6.79%; mol. wt., 252).

The π-allylic sandwich structure for this compound is supported by its proton magnetic resonance in deuteriochloroform. The spectrum has a peak at 6.04τ of a relative intensity of 4 for the olefin hydrogens of the cyclooctadiene ring; a peak at 6.95τ of a relative intensity of 8 for the methylene hydrogens of the cyclooctadiene ring, and a multiline pattern at 4.83τ of a relative intensity of 1 for the central hydrogen atom of the π-allyl group. The characteristic doublets for the π-allyl group are present at 7.35τ and 8.38τ with $J=6$ c. p. s. and $J=10$ c. p. s. respectively, and with relative intensities of 2 : 2.

π-Allyl-cycloocta-1, 5 - diene - rhodium(I), was found to be diamagnetic, stable enough to be handled in air and soluble in most organic solvents, although it was poorly soluble in cyclohexane and decomposed slowly in hot cyclohexane. The treatment of π-allyl-cycloocta-1, 5-diene-rhodium with hydrochloric acid (in dichloromethane at room temperature) caused a cleavage of the compound at the π-allyl group; bis-(cycloocta-1, 5-diene)-μ, μ'-dichloro-dirhodium[3] was thus isolated. A similar result was obtained when the π-allyl rhodium complex was reacted with anhydrous aluminum chloride in dichloromethane at 0°C.

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