

Preliminary communication

The reaction of allene with β -diketonatorhodium(I) complexes: formation of π -allylic derivatives of rhodium(III)

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Considerable interest has been focused recently on the reactions between allene and rhodium complexes¹⁻⁸. Various types of reactions have been observed, such as formation of complexes of rhodium(I) with allene¹⁻⁵ or oligomers of allene⁵⁻⁷, catalytic cyclo-oligomerization⁶⁻⁸, and linear polymerization¹. Most of the studies were concerned with rhodium monohalide complexes.

We have investigated the reaction of allene with $(\text{acac})\text{Rh}(\text{C}_2\text{H}_4)_2$ and $(\text{DBM})\text{Rh}(\text{C}_2\text{H}_4)_2$ ^{*} and have observed the formation of unusual complexes of rhodium(III) in which a linear allene tetramer is bonded to the metal by two π -allylic bonds. We report here the preparation and structure of these complexes.

When allene is bubbled through a suspension of $(\text{DBM})\text{Rh}(\text{C}_2\text{H}_4)_2$ in pentane (260 mg in 8 ml) at room temperature the precipitate readily dissolves to give a clear solution, from which yellow crystals, I, are obtained upon cooling to 0° (yield about 60%). The crystals of I are stable in the air for several days; the elemental analysis is in accord with the formula $(\text{DBM})\text{Rh}(\text{C}_3\text{H}_4)_4$.

Complex I does not react at room temperature either with CO (atmospheric pressure) or with cyclo-1,5-octadiene. Passing H₂ at room temperature through a suspension of I in ethanol gives a saturated hydrocarbon, M⁺ at *m/e* 170, which has been found to be identical with 2,3,6,7-tetramethyloctane⁹.

The NMR spectrum of I is complicated, and has not been fully interpreted. The structure of the complex has been completely determined by X-ray examination of single crystals. Complex I crystallizes in the monoclinic space group $P2_1/n$ with eight molecules in the unit cell. The main crystal data are: $a = 14.50 \text{ \AA}$, $b = 23.86 \text{ \AA}$, $c = 12.93 \text{ \AA}$, $\beta = 94.65^\circ$. The intensities of 4650 independent reflections were evaluated using a Picker automated diffractometer (Mo-K α radiation). The structure was solved by Patterson-Fourier methods and refined by the least squares method. In the asymmetric unit two distinct molecules are present; the same molecular geometry has been found for both with each individual molecule having C_2 symmetry. The final molecular model is represented in Fig. 1.

^{*}acac = acetylacetonato; DBM = 1,3-diphenylpropan-1,3-dionato.

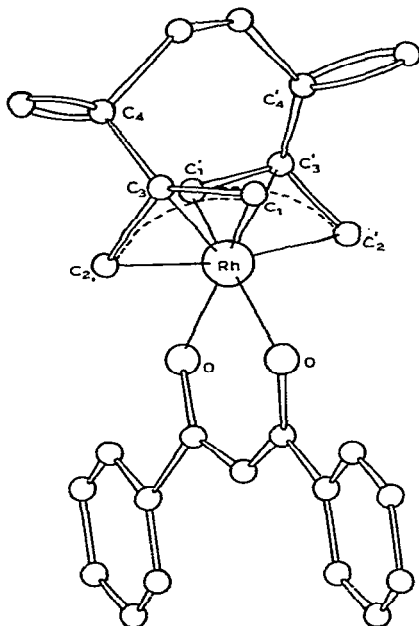
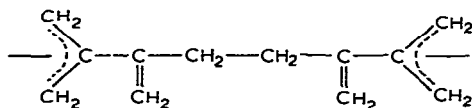


Fig. 1. Molecular model of complex I.

Only the carbon atoms C_1 C_2 C_3 and C'_1 C'_2 C'_3 are coordinated to rhodium, the $Rh-C_i$ and $Rh-C'_i$ distances being 2.18, 2.21 and 2.11 Å ($i = 1, 2, 3$); the bond lengths C_1-C_2 , C_2-C_3 , and $C'_1-C'_2$, $C'_2-C'_3$ are identical (1.44 Å) and the two groups $C_1-C_2-C_3-C_4$, $C'_1-C'_2-C'_3-C'_4$ are planar. This geometry indicates that the $(C_3H_4)_4$ group is bonded to Rh by two allylic bonds and that it is to be formulated as:



From the reaction of allene with $(\text{acac})\text{Rh}(\text{C}_2\text{H}_4)_2$ a yellow compound, II, of formula $(\text{acac})\text{Rh}(\text{C}_3\text{H}_4)_4$ has been obtained as a microcrystalline powder. II gives 2,3,6,7-tetramethyloctane on treatment with H_2 , which suggests that its structure is analogous to that of I.

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