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Preliminary communication

# THE REACTION OF ALLENE WITH DICARBONYLCHLORORHODIUM: FORMATION OF NEW π-ALLYLIC COMPLEXES OF RHODIUM(III)

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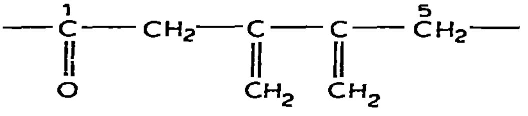
## Summary

The reaction of allene with $[Rh(CO)_2Cl]_2$ to give a new π-allylic complex of rhodium(III) containing an allene dimer is described; the reactions of this complex with $PPh_3$ and $AsPh_3$ are reported.

In studies of the reactions of allene with rhodium(I) complexes we observed the intermediacy of rhodacyclopentane complexes in some stoichiometric and catalytic reactions of allene with β-diketonatorhodium(I) compounds [1, 2]. We have now extended this work to the reaction of allene with $[Rh(CO)_2Cl]_2$, and have isolated new π-allylic derivatives of rhodium(III) whose formation is readily explained by assuming that a metallocyclic intermediate is again involved.

When allene is bubbled through a suspension of $[Rh(CO)_2Cl]_2$ in benzene at room temperature the precipitate dissolves in a few minutes to give a yellow solution. Addition of pentane precipitates a microcrystalline pale-yellow solid of formula $[C_8H_8O_2ClRh]_{2.5}$ (yield 80%) (I).

I remains unchanged in air for prolonged periods. Its IR spectrum (KBr) exhibits a strong band at 2070 $cm^{-1}$ attributable to a terminal carbonyl group bound to rhodium(III) [3] and a band at 1735 $cm^{-1}$ in the kero-region. The NMR spectrum is complicated, and has not been fully interpreted. Information on the structure of I was obtained from its chemical behaviour. Reduction with a large



$$-\overset{1}{C}(=O)-CH_2-C(=CH_2)-C(=CH_2)-\overset{5}{C}H_2-$$

(II)

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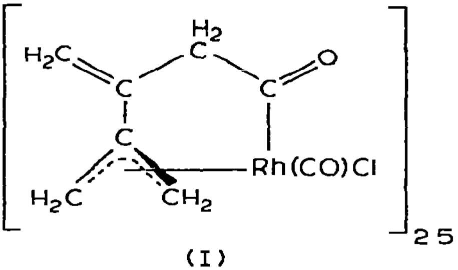
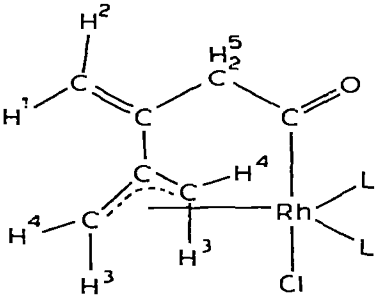
excess of $LiAlH_4$ leads to metallic rhodium and to a mixture of products in which 3,4-dimethyl-1-pentanol predominates. Treatment of I with an excess of $PPh_3$ in benzene for about 2 h gives *trans*-$(PPh_3)_2RhCl(CO)$ and 3,4-dimethylenecyclopentanone in high yields. These results suggest that I contains the grouping II bonded to rhodium by carbon atoms 1 and 5, and we suggest for I the following structure:



(I)

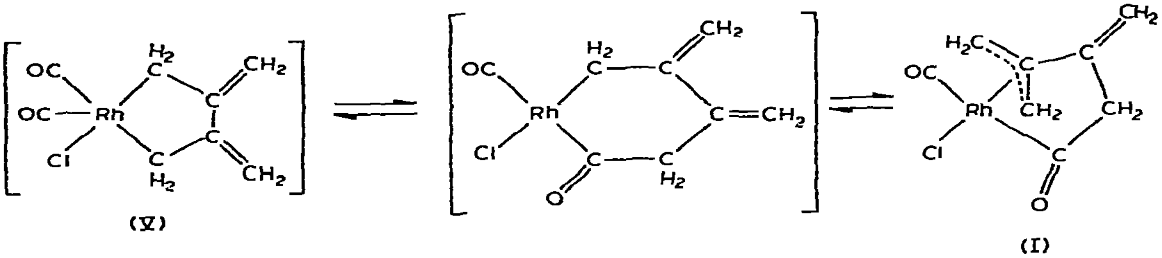
If the reaction of I with $PPh_3$ or $AsPh_3$ is carried out in benzene at room temperature for about 10 min and pentane is then added, two compounds are obtained as microcrystalline pale-yellow solids of formulae $(C_7H_8O)Rh(PPh_3)_2Cl$ (III) and $(C_7H_8O)Rh(AsPh_3)_2Cl$ (IV), respectively. The IR spectra of III and IV reveal a strong band in the keto-region (1680 and 1660 $cm^{-1}$ respectively) but no terminal carbonyl absorption. III and IV also contain the grouping II, since reduction with $LiAlH_4$ gives 3,4-dimethyl-1-pentanol in both cases. Conclusive information on the structure of III and IV was obtained from the NMR spectra, which are consistent with the following structure:



(III) L = $PPh_3$
(IV) L = $AsPh_3$

Since the NMR spectra (measured in $CDCl_3$ at 37°; TMS as internal standard) of both compounds are very similar we report only the data for complex III. Protons 1 (or 2) and 2 (or 1) give two singlets at δ 4.5 and 4.8 ppm; protons 5 appear at δ 2.8 ppm; protons 3 and 4 give rise to one broad signal centred at δ 4.05 ppm and the phenyl protons appear at δ 7.4 ppm.

The formation of I can be rationalized by assuming that an intermediate V, formed by "oxidative coupling" of allene to rhodium(I), is trapped by carbonyl insertion to give I. Such coupling reactions may well be important in transition



metal catalyzed reactions of allene such as oligomerization and polymerization. Oxidative coupling reactions of alkynes to some low valent transition metal compounds similar to those reported above have been previously described [4, 5].

## Acknowledgement

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