Journal of Organometallic Chemistry, 60 (1973) C35–C38

Preliminary communication

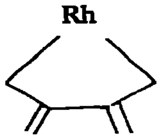
The reaction of allene with β-diketonatorhodium(I) complexes: formation and structure of new rhodacyclopentane derivatives

G. INGROSSO, A. IMMIRZI and L. PORRI

Istituto di Chimica Organica Industriale, Università di Pisa, Pisa (Italy) and Istituto di Chimica delle Macromolecole del C.N.R., Milano (Italy)

(Received August 3rd, 1973)

In a previous communication[1] we reported that (DBM)Rh$(C_2H_4)_2$ and (Acac)Rh$(C_2H_4)_2$[*] react with allene to form derivatives of rhodium(III) in which an allene tetramer is bonded to a rhodium atom by two π-allylic groups. We have now isolated, from the reaction between (Acac)Rh$(C_2H_4)_2$ and allene at −78°, a new rhodium(III) compound in which the 3,4-dimethylenerhodacyclopentane moiety, I, is present:



(I)

This compound is a precursor of the bis-π-allylic complex already described[1], since it gives the latter on further reaction with allene.

When (Acac)Rh$(C_2H_4)_2$ is added to liquid allene at −78°, a fast reaction takes place with formation, within a few minutes, of a microcrystalline yellow precipitate, II, of stoichiometry (Acac)Rh$(C_3H_4)_3$ (yield 85%). In the solid state II is very unstable and decomposes violently, at temperatures above 0°, giving metallic rhodium and unidentified tarry compounds. The IR spectrum of II (nujol mull, −20°) reveals that the acetylacetonate group is bonded to rhodium by the two oxygen atoms [ν(C$\overset{\text{...}}{-}$O) 1585 cm^{-1}; ν(C$\overset{\text{...}}{-}$C) 1515 cm^{-1}]. Moreover the presence of two bands at 1670 and 860 cm^{-1} indicates[2-4] that at least one of the three allene molecules is coordinated to rhodium by one of its double bonds.

On treating II with pyridine, a very stable yellow-green compound of formula (Acac)Rh$(C_3H_4)_2(C_5H_5N)_2$, III, (yield 84%) is formed with evolution of allene. II and III

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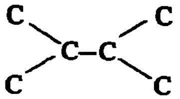
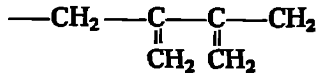
[*] DBM = 1,3-diphenyl-1,3-propanedionato; Acac = acetylacetonato.

react with bromine in carbon tetrachloride to give inorganic compounds and tetrabromomethylethylene in a high yield. Assuming that no coupling occurs during the reaction, this suggests[5] that complexes II and III contain an allene dimer with the following skeletal structure:



This is confirmed by X-ray examination of single crystals of III, whose structure has been determined.

The main crystal data of III (racemic form) are: $a = 13.17$, $b = 9.11$, $c = 9.18$ Å, α 107.9°, β 81.1°, γ 93.1°, D_m 1.4 $g \cdot cm^{-3}$), D_c 1.41 $g \cdot cm^{-3}$, $Z = 2$, $F(000) = 452$, space group $P\bar{1}$, Mo-K_α radiation λ 0.7107 Å. Diffracted intensities were measured with a Philips PW 1100 single-crystal diffractometer. The structure was elucidated by the heavy atom method and refined by the least squares method using, at present, isotropic thermal parameters. The actual disagreement factor is 0.068.

The resulting molecular structure is shown in Fig. 1. The allene dimer C_6H_8 has the structure:  $—CH_2—\underset{\underset{CH_2}{\|}}{C}—\underset{\underset{CH_2}{\|}}{C}—CH_2—$, IV, and is bonded by two σ bonds to the rhodium atom as a chelate ligand. The compound is best described as a d_6 octahedral complex of Rh^{III}. The group IV exerts a considerable *trans* influence: the Rh—O and Rh—N bonds *trans* to Rh—C bonds are both longer than the corresponding *cis* ones by 0.14 Å.

When a solution of II in n-pentane is kept at room temperature for 120 h, a microcrystalline orange-red product of stoichiometry $(Acac)Rh(C_3H_4)_2$, V, precipitates in low yield. The low solubility of V, which is probably polymeric, did not permit the elucidation of its structure by solution methods.

On treating V with PPh_3 a compound, whose elemental analysis and osmometric molecular weight are in accord with the formula $(Acac)_2Rh_2(C_3H_4)_2(PPh_3)_2$, VI, is obtained in rather low yield. The molecular structure of VI was determined by the single-crystal X-ray diffraction method. The main crystal data are: $a = 17.88$, $b = 15.01$, $c = 10.31$ Å, α 100.1°, β 91.4°, γ 108.3°, D_m 1.3 $g \cdot cm^{-3}$, D_c 1.29 $g \cdot cm^{-3}$, $Z = 2$, $F(000) = 1032$, space group $P\bar{1}$, Mo-K_α radiation λ 0.7107 Å.

Diffracted intensity measurements and crystal structure analysis were carried out as for III. The actual disagreement factor is 0.066.

The resulting molecular structure is shown in Fig. 1. VI also contains the allene dimer IV. This is bonded by two σ bonds to a rhodium atom, and is coordinated to a second rhodium atom by the two conjugated methylene double bonds. Compounds VI can be regarded as a two-centre coordination compound of Rh^{III} and Rh^{I}. The molecule exhibits C_s symmetry, the mirror plane containing the two rhodium atoms and the two phosphorus atoms. The coordination around Rh^{I} is best described as a tetragonal pyramid with Rh^{I} hybridized dsp^3. The geometry is very similar to that observed[6] in the complex $RhCl(C_4H_6)_2$, the geometry of the *cis* diene group also being similar.

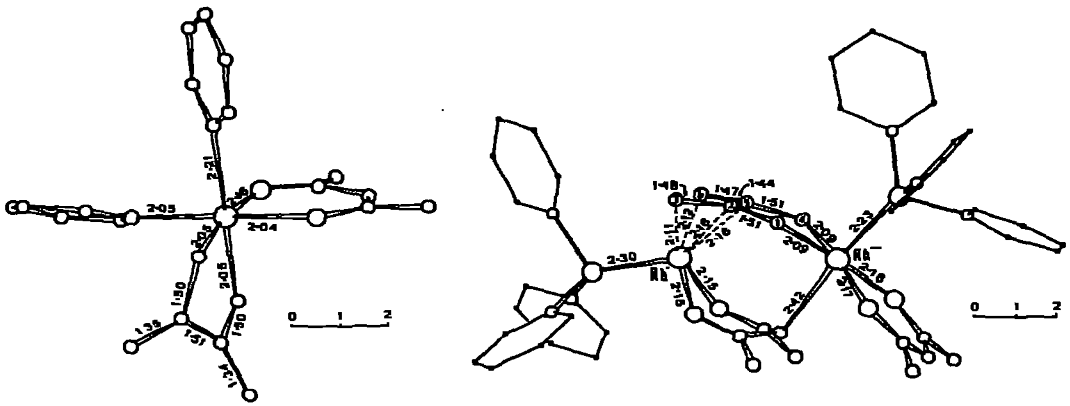


Fig. 1. Projection of the molecules of complex III (left) and VI (right). In complex VI, the Rh^{III}–C_2 and Rh^{III}–C_5 distances are 2.96 Å.

The coordination around Rh^{III} is octahedral. The Acac group bonded to Rh^{I} via the two oxygen atoms is also bonded to Rh^{III} via the central carbon atom, the Rh^{III} distance being 2.42 Å. This can be interpreted as an interaction of Rh^{III} with the electron pair on the central carbon atom of the Acac group, similar to that observed in other β-diketonato derivatives of transition metals[7,8].

Finally it should be noted that complexes containing the structural arrangement I have been postulated[9,10] as intermediate species in some catalytic reactions of allene with transition metal compounds but have not previously been isolated. The finding that allene can enter into an "oxidative coupling" reaction illustrates the analogy between allenes and alkynes[11], conjugated dienes[12,13], and olefins[14] as regards the primary step of some reactions of these compounds with transition metals.

ACKNOWLEDGEMENT

This work was supported by the "Consiglio Nazionale delle Ricerche".

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