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THE REACTION OF ALLENE WITH β-DIKETONATORHODIUM(I) COMPLEXES: FORMATION OF BIS(π-ALLYLIC) COMPLEXES OF RHODIUM(III) AND OF RHODACYCLOPENTANE DERIVATIVES

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Summary

The reaction of allene with complexes of the type (β-diketonato)Rh(C_2H_4)$_2$ at temperatures between —30 and +20°, gives Rh^{III} derivatives of formula (β-diketonato)Rh(C_3H_4)$_4$, in which an allene tetramer is bonded to rhodium by two π-allylic groups. The molecular structures of these complexes were determined on the basis of the chemical behaviour, IR and NMR spectra, and, for one of them, also by X-ray examination. The reaction of (Acac)Rh(C_2H_4)$_2$ with allene at —78° yields new rhodium(III) derivatives containing the 3,4-dimethylenerhodacyclopentane moiety. These are precursors of the bis(π-allylic) complexes. The mechanism of formation of the rhodium(III) complexes is briefly discussed.

Introduction

During recent years research in allene chemistry has expanded considerably and increasing attention has been payed to reactions between allene and transition metal compounds. Various types of reactions have been observed, such as formation of complexes in which allene [1-3] or oligomers [4-16] are bonded to the transition metal, catalytic oligomerization [17-24] and linear polymerization [25-36]. Most of these studies were concerned with rhodium(I) monohalide compounds.

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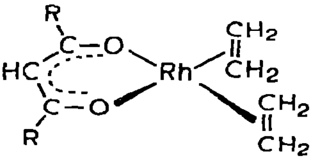
We have examined the reaction of allene with (β-diketonato)$Rh(C_2H_4)_2$ (I), and have observed the formation of unusual compounds of rhodium(III) derived from oxidative addition of allene to the metal atom. The reaction at low temperatures (—78°) gives compounds containing a rhodacyclopentane ring, whereas at higher temperatures (—30 to +20°) bis(π-allylic) derivatives of rhodium(III) are obtained.

This paper reports the preparation and the properties of these complexes*, whose formation is of some interest for an interpretation of the mechanism of polymerization and cyclo-oligomerization of allene catalyzed by rhodium(I) complexes.

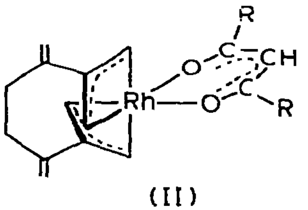
Results and discussion

Preparation and properties of bis(π-allylic) derivatives of rhodium(III)

When (Acac)$Rh(C_2H_4)_2$ (Ia) is allowed to react at about —35° with liquid allene, a compound is obtained whose elemental analysis and osmometric molecular weight are in accord with the formula (Acac)$Rh(C_3H_4)_4$ (IIa). Analogous reaction of (Hfacac)$Rh(C_2H_4)_2$ (Ib) gives a compound of composition (Hfacac)$Rh(C_3H_4)_4$ (IIb). (DBM)$Rh(C_2H_4)_2$ (Ic) (DBM = 1,3-diphenylpropan-1,3-dionato), reacts very slowly with allene at —35°, but it reacts rapidly at room temperature, in hydrocarbon solution or suspension, to give an analogous compound of formula (DBM)$Rh(C_3H_4)_4$ (IIc). All these complexes are very stable at room temperature and, in the solid state, they can be stored in the air for a long time. Their solubility in all the common organic solvents is high and purification is easily achieved by low temperature crystallization from pentane.



(I)



(II)

a, $R = CH_3$; b, $R = CF_3$; c, $R = C_6H_5$

Complexes II were identified on the basis of their chemical behaviour and their IR and NMR spectra, and complex IIc also by X-ray examination.

Catalytic hydrogenation of complexes II at room temperature and atmospheric pressure gave metallic rhodium and a mixture of products, from which a compound of formula $C_{12}H_{26}$ was isolated. This hydrocarbon was identified as 2,3,6,7-tetramethyloctane (III) by comparison with an authentic sample (Scheme 1).

This suggests that in complexes II the four allene molecules are bonded to form a linear tetramer. On reaction of IIa and IIc with CO, at room temperature and atmospheric pressure, the corresponding β-diketonatodicarbonyl-

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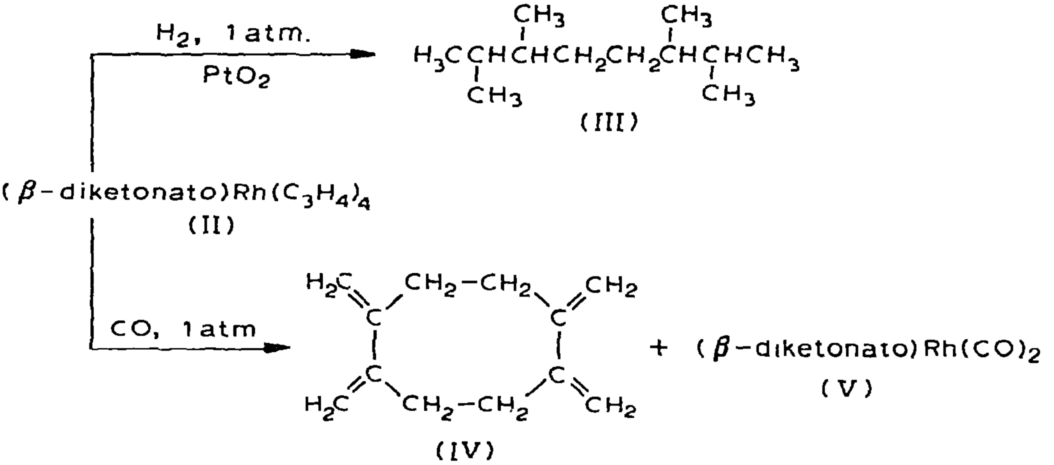
* Preliminary accounts on these complexes have been published [6, 41].

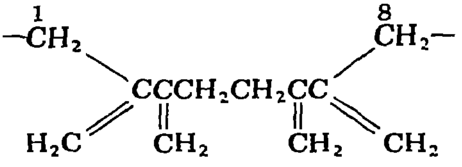
rhodium (V) and 1,2,5,6-tetramethylenecyclooctane (IV) were obtained (Scheme 1).

Scheme 1



IIa reacts more rapidly than does IIc with CO, reaction being complete in 5 and 72 h respectively; IIb seems to be unreactive under the same conditions.

These results suggest that compounds II contain the 2,3,6,7-tetramethyleneoctane-1,8-diyl group (VI) bonded to rhodium by the carbon atoms 1 and 8.



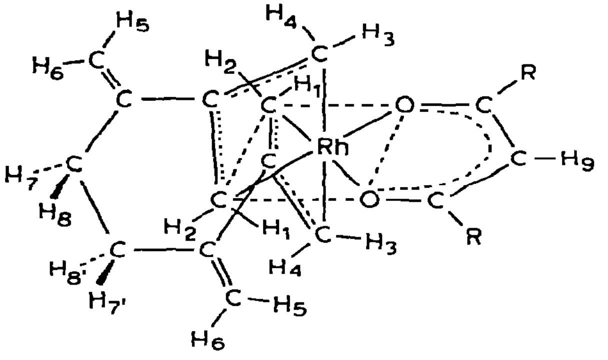
(VI)

All the previous findings in fact agree with what is known of the reactivity of transition metal compounds containing two σ- or two π-allylic metal—carbon bonds [37]. IR spectra reveal that in complexes II the β-diketonato group is bonded by the two oxygen atoms to rhodium (IR spectra are reported in the Experimental section).

These conclusions were confirmed by X-ray examination of IIc [6], which revealed that VI is bonded to rhodium by two π-allylic bonds, and are also in agreement with the NMR spectra of the complexes (Table 1). Due to the analogy of the NMR spectra of the three complexes only the spectrum of IIb will be examined in detail. Since the complexes have C_2 symmetry the two π-allylic groups are equivalent but since the four terminal allylic hydrogens of each group are in significantly different environments, it is to be expected that these protons will give rise to four signals, as already observed for bis(π-allylic) complexes of analogous geometry [38]. Thus, the NMR spectrum of IIb consists of eight signals (Table 1).

TABLE 1

NMR DATA FOR BIS(π-ALLYLIC) COMPLEXES OF RHODIUM(III) (II) [a]



(II)

Protons	IIa (R = CH_3)	IIb (R = CF_3)	IIc (R = C_6H_5)
Methyl(Acac)	1.91	—	—
1	1.91	2.13 s	2.12 s
2	1.91	2.17	2.25
7,7',8,8'	2.33	2.45 m	2.25
3	2.75 d (J_4 2.9)	2.96 m (J_4 1.7)	2.87 d (J_4 2.2)
4	4.45 d	4.72 d	4.50 d
5 or 6	5.00 ud	5.18 ud	4.92 ud
6 or 5	5.47 ud	5.60 ud	5.39 ud
9	5.26 s	6.03 s	6.69 s

[a] Measured in $CDCl_3$, at 37°. Chemical shifts (δ values) refer to TMS as internal standard; s = singlet, d = doublet, m = multiplet, ud = unresolved doublet; J_x = spin—spin coupling of proton with proton x measured in Hz.

The singlet at δ 6.03 ppm and the two unresolved doublets at δ 5.18 and 5.60 ppm we assigned to the methine proton of the 1,1,1,5,5,5-hexafluoropentane-2,4-dionato group and to vinylidene protons 5 (or 6) and 6 (or 5), respectively (Table 1). The protons 7, 7', 8, 8' give an AA'BB' spectrum centred at δ 2.45 ppm since 7 (and 8) and 7' (and 8') are chemically equivalent (due to the C_2 axis) but they are magnetically non-equivalent.

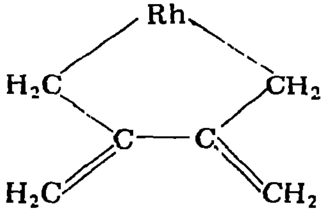
The signals at δ 4.72 and 2.96 ppm, by analogy with the bis(π-allylic) complexes of rhodium(III) [38], were assigned respectively to *syn* protons 4 and to *anti* protons 3. The proton 3 signal appears as a double doublet since 3 is coupled to 4 (J_4 1.7) and to the ^{103}Rh nucleus (J 1.1). The remaining signals at δ 2.13 and 2.17 ppm were assigned to protons 1 and 2, respectively.

The large difference between the chemical shifts of protons 3 and 4, the value of their coupling constant and the small difference between the chemical shifts of protons 1 and 2 all permit one to conclude that the allylic ligands are asymmetrically bonded to the rhodium atom. This means that two carbon atoms of each allylic group are bonded by a bond of a higher order (these two carbon atoms are joined by a dashed line in the structure reported in Table 1) than the two other (joined by a dotted line). The same phenomenon was observed for complexes of the type $Rh_2X_2(all)_4$ by Powell and Shaw [39], whose representation of an allylic group asymmetrically bonded to metal atom we have adopted. The X-ray structure of IIa [6] accounts for this asymmetry. An interesting phenomenon was observed on studying the variation of NMR spectra with temperature: while the NMR spectra of complexes of type $Rh_2X_2(all)_4$ consist of an AX_4 pattern [39] at about 140°, the spectra of compounds II remain almost unaltered up to 120°, at which temperature the protons 1 and 2 give rise to one signal. This is well explained if we assume that a process involving rotation around the carbon—carbon bond of the allylic group takes place as already proposed [40] for other π-allylic complexes.

Complexes II react at 60-70° with allene in hydrocarbon solutions, to give highly crystalline polymers of regular constitution $-[CH_2-C(=CH_2)]_n-$ along with a mixture of oligomers. The polymers appear to be identical with those obtained by other transition metal based catalysts [25-36].

Reaction of allene with (Acac)Rh(C₂H₄)₂ at —78°; formation of rhodacyclopentane derivatives

If the reaction between $(Acac)Rh(C_2H_4)_2$ and allene is carried out at —78°, a new rhodium(III) compound containing the 3,4-dimethylenerhodacyclopentane moiety (VII) can be isolated.



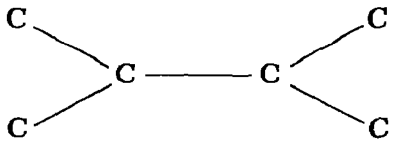
(VII)

This compound is of some interest for an interpretation of the mechanism of formation of the bis(π-allylic) complex IIa since it gives the latter on further reaction with allene at —35°.

When $(Acac)Rh(C_2H_4)_2$ is added to liquid allene at —78°, a very fast reaction takes place with formation of a microcrystalline yellow precipitate of stoichiometry $(Acac)Rh(C_3H_4)_3$ (VIII) which can easily be crystallized from liquid allene. In the solid state VIII is highly unstable and decomposes violently at temperatures above 0° giving metallic rhodium and unidentified tarry compounds. Hydrocarbon solutions of VIII are also unstable, but in these conditions VIII does not decompose to metallic rhodium but transforms to another complex, already reported briefly [41].

The IR spectrum of VIII (measured at —20°) reveals that the acetylacetonate group is bonded to rhodium by the two oxygen atoms [ν(C$\overset{...}{-}$O) 1585 cm^{-1}; ν(C$\overset{...}{-}$C) 1514 cm^{-1}]; moreover, the presence of two bands at 1670 and 860 cm^{-1} indicates [1,2] that at least one of the three allene molecules is coordinated to rhodium by one of its double bonds. Due to the high instability of VIII it was not possible to carry out further spectroscopic analysis or molecular weight measurement.

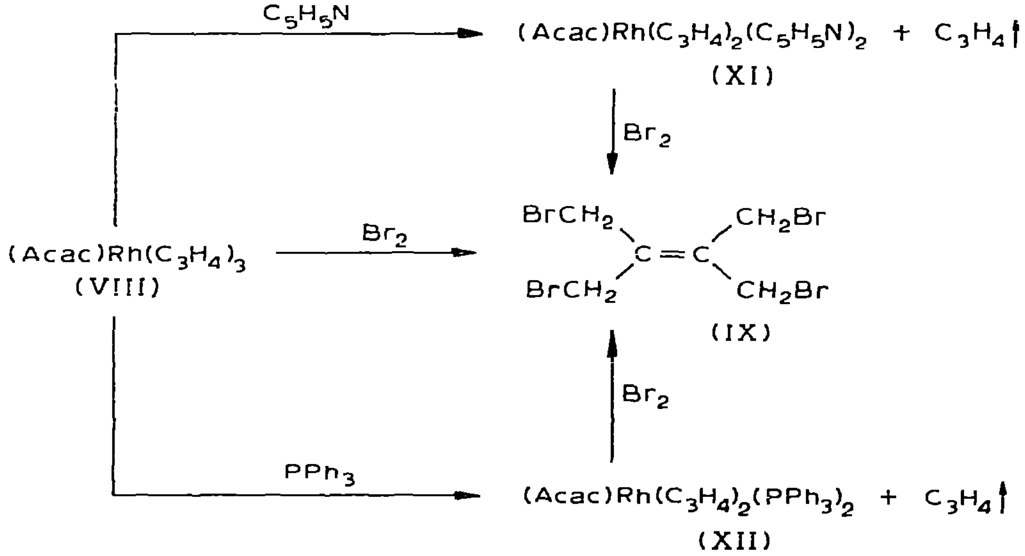
VIII reacts with bromine in carbon tetrachloride to give inorganic compounds and tetrabromomethylethylene (IX) in high yields (Scheme 2). If we assume that no coupling occurs during the reaction this result suggests that complex VIII contains an allene dimer having the skeletal structure X.



(X)

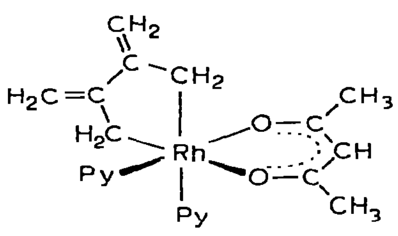
Further information on the structure of VIII was obtained from its chemical behaviour. Thus, on treating VIII with pyridine or triphenylphosphine, stable compounds of formulae $(Acac)Rh(C_3H_4)_2(C_5H_5N)_2$ (XI) and $(Acac)Rh(C_3H_4)_2$-$(PPh_3)_2$ (XII) are formed with evolution of allene (Scheme 2).

Scheme 2

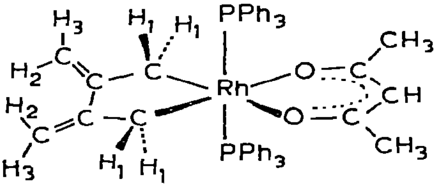


IR spectra of compounds XI and XII reveal that the acetylacetonate group is bonded by the two oxygen atoms to rhodium. XI and XII also contain an allene dimer of skeletal structure X since both these complexes react with bromine to give tetrabromomethylethylene (IX) (Scheme 2).

Since these compounds are mononuclear the dimer must be bonded to rhodium to form the rhodacyclopentane ring (VII): this was confirmed by X-ray examination of single crystals of XI whose structure (schematically represented below) we have already reported [41].

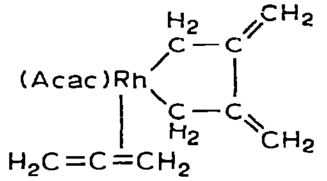


(XI)



(XII)

Compound XII was assigned a *trans* configuration on the basis of the symmetry of its NMR spectrum which reveals one signal at δ 1.75 ppm due to methyl protons, one signal at δ 7.25 ppm due to aromatic protons and one broad signal centred at δ 2.2 ppm attributed to four equivalent protons 1. The signals at δ 5.0, 4.4 and 3.8 ppm were attributed to the methinic proton of the β-diketonato group and to protons 2 (or 3) and 3 (or 2) respectively. On the basis of this evidence we suggest the following formula for compound VIII:



(VIII)

In conclusion, the finding that allene can enter into an "oxidative coupling" reaction accounts for the transformation $Rh^{I} \rightarrow Rh^{III}$, and this reaction is most probably the first step in the formation of bis(π-allylic) complexes II. It is, however, impossible at present to say through which mechanism complexes II are formed from an intermediate species containing the moiety VII. Nevertheless, the finding that allene can enter into such a reaction illustrates the analogy between allenes and alkynes [45, 46], conjugated dienes [42, 43], and olefins [44] as regards the primary step of some reactions of these compounds with transition metals.

Finally, it should be noted that complexes containing the structural arrangement VII have been postulated [18, 19] as intermediate species in some catalytic reactions of allene but had not previously been isolated.

Experimental

Allene (Matheson, purity ca. 98.7 %) and hexafluoracetylacetone (Fluka, purity ca. 90 %) were used without further purification. The following rhodium compounds were prepared essentially as described in the literature reference [47]: $Rh_2Cl_2(C_2H_4)_4$, $(Acac)Rh(C_2H_4)_2$, $(DBM)Rh(C_2H_4)_2$*.

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* This compound was prepared following the procedure of Cramer for the preparation of $(Acac)Rh(C_2H_4)_2$ [47].

Solvents were used after dehydration and distillation. All the operations were carried out in an atmosphere of pure dry nitrogen.

^1H NMR spectra were obtained on a Jeol PS-100 spectrometer. IR spectra on a 225 Perkin—Elmer instrument. Melting or decomposition points were determined on a Kofler hot-stage apparatus and are uncorrected. GLC analysis was carried out on a Carlo Erba Fractovap Mod. GT with a 2 m, 20% SE-30 on 60-80 Chromosorb W column. Molecular weights were determined at 37° by a Mechrolab vapor-pressure Osmometer Model 3019.

Preparation of (Hfacac)Rh(C_2H_4)$_2$ (Ib)

Preparation of thallium hexafluoracetylacetonate. To a solution of $TlOC_2H_5$ (8 g) in EtOH (60 ml) hexafluoracetylacetone (6.7 g) was added at room temperature. After 30 min the solvent was removed under reduced pressure. The residue was washed with pentane and dried. Tl(Hfacac) was so obtained (11.8 g, 95 %) as a microcrystalline solid.

Reaction of Tl(Hfacac) with $Rh_2Cl_2(C_2H_4)_4$. Tl(Hfacac) (2.3 g) was added at room temperature to a suspension of $Rh_2Cl_2(C_2H_4)_4$ (1.1 g) in pentane (50 ml). The suspension was stirred for 4 h then filtered. The resulting orange-red solution was cooled at —20° and the solvent was removed under reduced pressure. By sublimation at 30°/0.1 mmHg the dark-red residue gave (Hfacac)Rh(C_2H_4)$_2$ (1.26 g) as red prisms, m.p. 49-50°. (Found: C, 29.23; H, 2.72. $C_9H_9F_6O_2Rh$ calcd.: C, 29.50; H, 2.47%). NMR *o*-deuterochlorobenzene): 2.9 (s, 8H); 6.1 (s, 1H) ppm (δ from TMS).

Preparation of complexes II

A suspension of Ia or Ib (5 mmol) in liquid allene (8 ml) was kept at —30° for 24 h, during which time allene was allowed to evaporate. The orange crystalline residue was dissolved in pentane (ca. 15 ml), and the resulting solution was cooled to —30° to give, in about 48 h, orange crystals of IIa or IIb (yield ca. 75 %). An additional amount of product (ca. 5 %) was obtained from the mother liquid.

Complex IIc was obtained by bubbling allene, for about 30 min, through a suspension of Ic (4 mmol) in pentane (20 ml), maintained at room temperature. A yellow solution was obtained, which was filtered and cooled to —30° to give orange crystals (yield 80 %) of IIc.

The following analytical data and infrared spectra were obtained for the three complexes:

IIa. M.p. 109-110°(dec.). (Found: C, 56.60; H, 6.38. Mol.wt., 359 (benzene). $C_{17}H_{23}O_2Rh$ calc.: C, 56.36; H, 6.40 %. Mol.wt., 362.3). IR: 3070w, 3000w, 2980w, 2930w, 1810m, 1770w, 1620m, 1585s, 1515s, 1450s, 1390s, 1310m, 1257s, 1204m, 1170m, 1018m, 1002m, 975w, 960m, 955m, 925m, 904s, 888s, 880m, 870m, 850w, 765m, 770m, 757m, 745m, 730m, 695m, 650w, 585m, 535m, 500w, 435w, 420m cm^{-1} (KBr).

IIb. M.p. 105-106° (dec.). (Found: C, 43.07; H, 3.73. Mol.wt., 463 (benzene). $C_{17}H_{17}F_6O_2Rh$ calcd.: C, 43.32; H, 3.64 %. Mol.wt., 470.2). IR: 3080w, 3010w, 2950w, 1840w, 1775w, 1645s, 1622m, 1570w, 1550m, 1515m, 1475s, 1450m, 1415w, 1340m, 1265s, 1220s, 1197s, 1165s, 1120m, 1098s, 1008w, 982w, 943w, 913m, 890m, 850w, 835w, 810w, 780m, 776m, 755m, 740w, 730w, 690w, 680m, 590m, 535w, 500w, 480w, 440w cm^{-1} (KBr).

IIc. M.p. 180°(dec.). (Found: C, 66.55; H, 5.54. Mol.wt., 503 (benzene). $C_{27}H_{27}O_2Rh$ calcd.: C, 66.60; H, 5.55 %. Mol.wt., 486).

Hydrogenolysis of complexes II

A well-stirred solution of (Acac)Rh(C_3H_4)$_4$ (IIa) (0.15 g) in pentane (15 ml), containing PtO_2 (10 mg) as catalyst, was kept under hydrogen atmosphere, at room temperature. After 96 h, the colourless mixture was filtered and distilled on Na. Analytical GLC of the distillate indicated the presence of one predominant compound (95 %). This was separated by preparative GLC and identified as 2,3,6,7-tetramethyloctane (III) by comparison of its properties with those of an authentic sample prepared from 2,3-dimethylbutene-1 following the procedure of Brown and Snyder [48].

The hydrogenolysis of complexes IIb and IIc was carried out as above reported and gave the same result.

Reaction of complexes IIa and IIc with CO

A solution of (Acac)Rh(C_3H_4)$_4$ (IIa) (0.12 g) in pentane (15 ml) was kept under CO atmosphere, at room temperature, for 5 h. During this time a red-green dichroic solid, identified as (Acac)Rh(CO)$_2$, slowly precipitated. The solution was then eluted on silica-gel and the solvent distilled off. Analytical GLC indicated the presence of one component that was identified as 1,2,5,6-tetramethylenecyclooctane (IV) on the basis of its NMR spectrum which was identical with that reported [49] for this compound. The yield was almost quantitative.

The reaction of IIc with CO was carried out under the same conditions, but in this case 72 h were necessary to complete the transformation.

Preparation of (Acac)Rh(C_3H_4)$_3$, (VIII)

(Acac)Rh(C_2H_4)$_2$ (1.77 g) was suspended in liquid allene (20 ml) at −78°. A very fast reaction took place with formation of a microcrystalline pale-yellow solid. This was dissolved by heating the reaction mixture to −40° for a few minutes, then reprecipitated by cooling again to −78°. The crystallization was complete in about 5 h. 1.88 g (85 % yield) of (Acac)Rh(C_3H_4)$_3$ were obtained. (Found: C, 52.29; H, 5.85. $C_{14}H_{19}O_2Rh$ calcd.: C, 52.18; H, 5.92 %). IR: 1950w, 1776w, 1745w, 1670m, 1630m, 1585s, 1515s, 1285m, 1264m, 1190w, 1110m, 1018m, 990m, 933m, 870s, 860s, 803w, 780m, 765m, 700w, 612m, 580m, 540m, 490w cm^{-1} (Nujoll mull, −20°).

Reaction of (Acac)Rh(C_3H_4)$_3$ (VIII) with bromine

To a suspension of (Acac)Rh(C_3H_4)$_3$ (0.39 g) in CCl_4 (50 ml) at −78°, bromine (3 ml) was added. The temperature was then slowly raised to 20° and the mixture was stirred for 90 min at this temperature. The reaction mixture was washed with water, then with a saturated solution of $Na_2S_2O_3$, and finally again with water. The organic layer was dried, then the solvent was distilled off under vacuum to give a residue (0.35 g), which after crystallization from cyclohexane was identified as tetrabromomethylethylene (IX) by comparison of its properties with those of an authentic sample prepared as reported [50].

Reaction of (Acac)Rh(C_3H_4)$_3$ (VIII) with pyridine: formation of (Acac)Rh(C_3H_4)$_2$(C_5H_5N)$_2$ (XI)

To a suspension of (Acac)Rh(C_3H_4)$_3$ (0.43 g) in pentane (20 ml) pyridine (1 ml) was added at −78°. The temperature was then raised to 20°; evolution of gas, identified as allene, was observed. A yellow-green solution was obtained which was concentrated to 4 ml, filtered and cooled to −30°. During 48 h (Acac)Rh(C_3H_4)$_2$(C_5H_5N)$_2$ (XI) (0.44 g, 84 % yield) precipitated as yellow-green needles, m.p. 117° (dec.). (Found: C, 57.20; H, 5.74. Mol.wt., 455 (benzene). $C_{21}H_{25}N_2O_2Rh$ calcd.: C, 57.28; H, 5.72 %. Mol.wt., 440.35). IR: 3050w, 2950w, 2890w, 2860w, 1595s, 1585s, 1510s, 1485m, 1445s, 1405s, 1350m, 1280m, 1210m, 1150m, 1095w, 1060m, 1040w, 1020w, 1016w, 925w, 870m, 850m, 790w, 770w, 760s, 700m, 690m, 630w, 595w, 435w, 425w cm^{-1} (KBr).

Reaction of (Acac)Rh(C_3H_4)$_2$(C_5H_5N)$_2$ (XI) with bromine

This reaction was carried out as reported for the reaction of the compound VIII with bromine. Starting from 0.44 g of XI, 0.24 g of tetrabromomethylethylene (IX) (60 % yield) were obtained.

Reaction of (Acac)Rh(C_3H_4)$_3$ (VIII) with PPh_3: formation of (Acac)Rh(C_3H_4)$_2$(PPh_3)$_2$, (XII)

To a suspension of (Acac)Rh(C_3H_4)$_3$ (0.12 g) in pentane (20 ml) PPh_3 (0.27 g) was added, at −78°. The temperature of the mixture was raised to 20°; evolution of gas, identified as allene, was observed. A microcrystalline pale-yellow solid precipitated during 15 min. The solid was separated from the reaction mixture, washed with pentane and dried. 0.23 g of XII (44 % yield) were so obtained: m.p. 119-120° (dec.). (Found: C, 70.50; H, 5.55. Mol.wt., 439 (benzene). $C_{47}H_{45}O_2P_2Rh$ calcd.: C, 70.09; H, 5.63 %. Mol.wt., 805.3). IR: 3050w, 2920w, 2890w, 1590s, 1550m, 1510s, 1480m, 1435s, 1405s, 1350w, 1285w, 1255m, 1200w, 1185w, 1120m, 1090m, 1025m, 995w, 930w, 870s, 860m, 775m, 740s, 690s, 620w, 580w, 530s, 520s, 495m cm^{-1} (KBr).

Reaction of (Acac)Rh(C_3H_4)$_2$(PPh_3)$_2$ (XII) with bromine

The reaction was carried out as reported for the reaction of compound VIII with bromine. From 0.4 g, of XII, 0.12 g of tetrabromomethylethylene were obtained.

Polymerization of allene

All the polymerization runs were carried out in the following way. Through a heptane solution of the catalyst (compounds I and II), maintained at 70°, allene was bubbled for 24 h. The polymer, insoluble in heptane, was separated and washed with heptane, then with methanol and finally dried.
IR and NMR spectra of polymer samples were identical to those reported for a poly-allene of high regular constitution, $-[CH_2-C(=CH_2)]_n-$ [25–36]. X-ray powder spectrum revealed a degree of crystallinity of ca. 80 %.

Acknowledgement

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