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THE REACTION OF ALLENE WITH COMPOUNDS OF THE TYPE (β-DIKETONATO)Rh(CO)$_2$: PREPARATION AND PROPERTIES OF DINUCLEAR RHODIUM(I)-ALLENE COMPLEXES AND OF η^3-ALLYLIC DERIVATIVES OF RHODIUM(III)

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Summary

The reaction of allene with (acac)Rh(CO)$_2$, at 30°C, and with (hfacac)Rh(CO)$_2$, at —78°C, leads to the rhodium(I) derivatives of formula (β-diketonato)$_2$Rh$_2$(CO)$_2$(C$_3$H$_4$) in which both allene double bonds are engaged with coordination to two rhodium atoms. In solution, two diastereoisomers of these compounds are in equilibrium, one being largely predominant. The reaction of allene with (hfacac)Rh(CO)$_2$, at —30°C, gives a rhodium(III) compound of formula (hfacac)Rh(C$_7$H$_8$O) in which the 2,3-dimethylenepentan-5-one-1,5-diyl group is present. The mechanism of formation of this complex is briefly discussed. On reaction of (hfacac)Rh(CO)$_2$ with allene, at temperatures between —20 and +20°C, the complex (hfacac)Rh(C$_3$H$_4$)$_4$ is obtained which contains an allene tetramer, i.e. the 2,3,5,6-tetramethyleneoctane-1,8-diyl, bonded to rhodium in a bis(η^3-allylic) fashion.

Introduction

Several rhodium(I) compounds have been reported to be suitable catalysts for the polymerization of allene [1—5]. Under given conditions the activity varies markedly when the ligands attached to rhodium are changed. With a view to obtaining information about the active intermediate species in these polymerizations and, thus to throw light on the way in which the ligands in the initiators exert their influence on the activity, a systematic study of the reactions of allene with transition metal complexes (basically Rh^I and Ir^I derivatives) was undertaken [6—11]. As a part of this study we examined the reaction of allene with the dicarbonyl derivatives of rhodium(I) (I), and this has led to isolation of new

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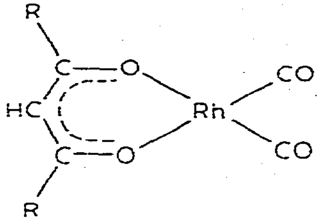
rhodium(I)— and rhodium(III)—allene compounds, the preparation and properties of which we report in this paper.



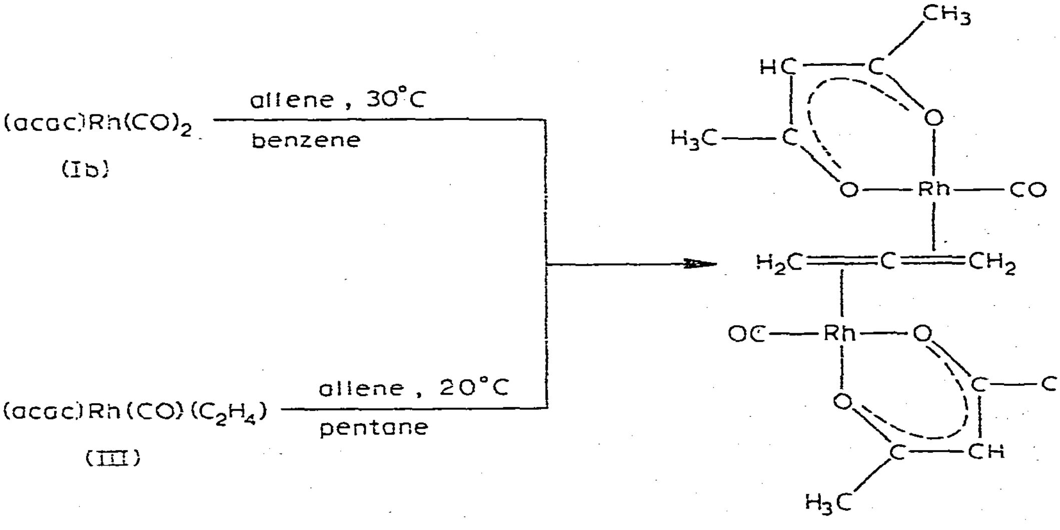
(Ia) R = CF_3
(Ib) R = CH_3
(Ic) R = C_6H_5

Results and discussion

Preparation and properties of dinuclear rhodium(I)—allene complexes

At temperatures between —78 and +30°C, Ic does not react with allene at atmospheric pressure in hydrocarbon solution. In contrast, when allene is bubbled through a benzene solution of Ib, at 30°C, a fast reaction takes place with the formation of a compound of formula $(acac)_2Rh_2(CO)_2(C_3H_4)$ (IIb) (Scheme 1). The depicted structure was assigned to IIb by comparing its properties with those of an authentic sample prepared [12] by reaction of $(acac)Rh(CO)(C_2H_4)$ (III) with allene. The structure of IIb has been determined by X-ray diffraction studies [12].

SCHEME 1

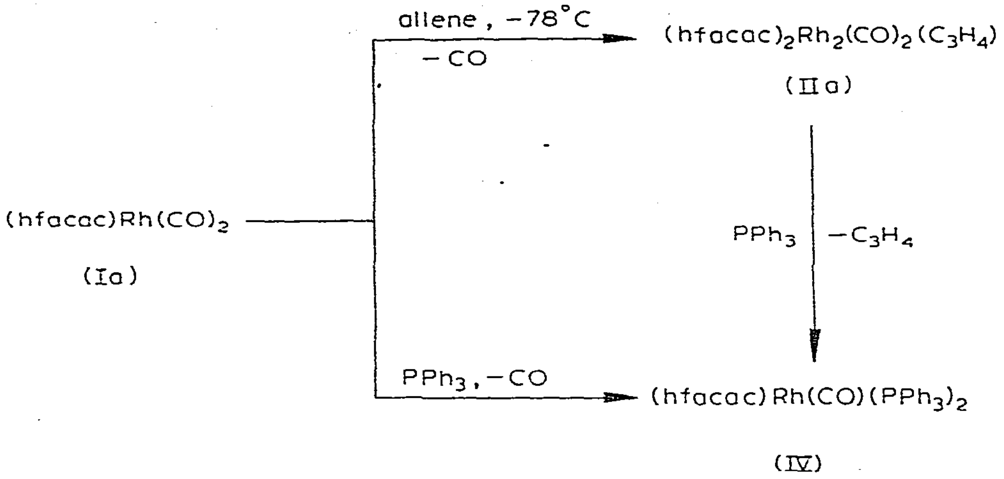


(IIb)

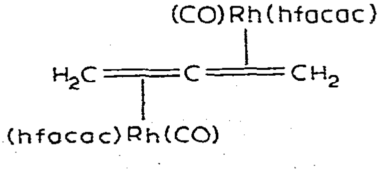
A crystalline diamagnetic compound of formula $(hfacac)_2Rh_2(CO)_2(C_3H_4)$ (IIa), analogous to IIb, is obtained from the reaction of Ia with liquid allene at

−78°C. At room temperature IIa is very stable for many weeks in an inert atmosphere. When pentane solutions of IIa are treated with a large excess of triphenylphosphine at room temperature, a rapid reaction occurs with evolution of allene (identified by GLC) and precipitation of golden-yellow needles of a product identified as (hfacac)Rh(CO)$(PPh_3)_2$ (IV). IV is also obtained on treatment of (hfacac)Rh$(CO)_2$ (Ia) with PPh_3 (Scheme 2).

SCHEME 2

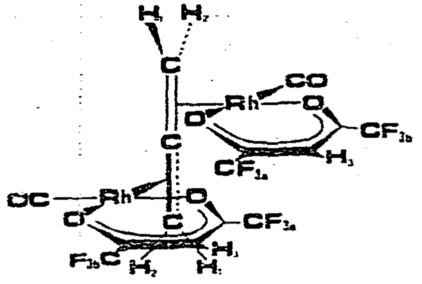


The IR spectrum of IIa reveals that both hexafluororacetylacetonato groups are bonded to rhodium by the two oxygen atoms (ν(C⩦O) 1640 cm^{-1}; ν(C⩦C) 1610 cm^{-1}); moreover, two bands at 2054 and 2040 cm^{-1} indicate the presence of terminal CO. The bands [13] associated with an allene molecule bonded to rhodium by one of its double bonds are absent. On the basis of these findings we assign to IIa the schematic structure shown in which both of the double bonds of the allene are engaged in coordination to two rhodium atoms. Three

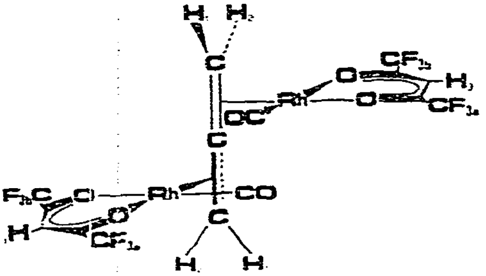


(IIa)

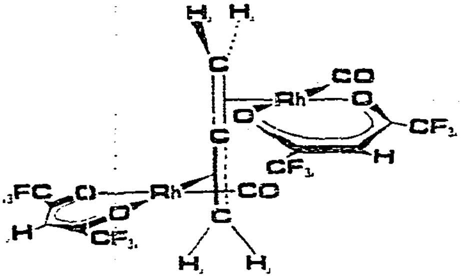
diastereoisomeric structures, IIa_1, IIa_2, and IIa_3 are to be expected for IIa (Fig. 1). Each of these isomers exists in two enantiomeric forms, since IIa_1 and IIa_2 have C_2 symmetry, and IIa_3 has C_1 symmetry. In order to establish the configuration of IIa, its ^{1}H NMR and ^{19}F NMR spectra were examined. Since diastereoisomers IIa_1 and IIa_2 have C_2 symmetry, they should exhibit similar NMR spectra. For each of them the ^{1}H NMR spectrum should consist of three signals of relative intensities 1/1/1, i.e. one singlet due to the two equivalent methine protons of hexafluoroacetylacetonato group, and two multiplets due to the four, two by two equivalent, allenic protons. On the other hand, the ^{19}F NMR



(IIa$_1$) C_2



(IIa$_2$) C_2



(IIa$_3$) C_1

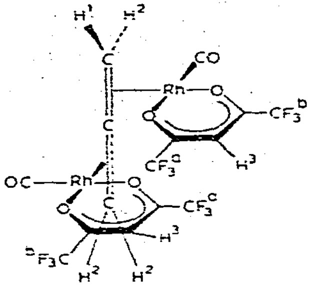
Fig. 1. Diastereoisomers of $(hfacac)_2Rh_2(CO)_2(C_3H_4)$ (IIa).

spectrum should show only two signals for the four trifluoromethyl groups which, in their turn are two by two equivalent. The ^1H NMR of IIa$_3$ should exhibit two singlets for the two methine protons and four multiplets for allenic protons; similarly four CF_3 resonances should be observed in the ^{19}F NMR spectrum.

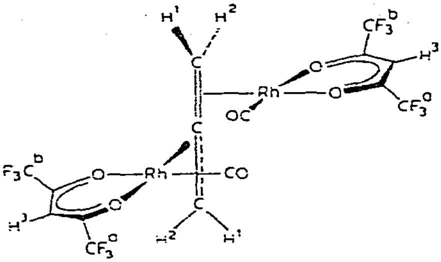
Table 1 lists the proton and fluorine resonances and assignments. The ^1H NMR spectrum reveals two sets of signals. The first set includes a singlet at δ 6.17 ppm and two multiplets at δ 4.40 and 3.62 ppm (relative intensities, 1/1/1); the second set is formed by six less intense signals, two singlets at δ 6.38 and 6.35 ppm, and four multiplets at δ 4.30, 4.12, 3.78, and 3.45 ppm (relative intensities, 1/1/1/1/1/1). The ^{19}F NMR spectrum shows two signals of the same intensity at δ 2.42 and 2.36 ppm, and four less intense signals at δ 1.96, 2.56, 2.67, and 2.83 ppm (relative intensities, 1/1/1/1). These results indicate the presence

TABLE 1

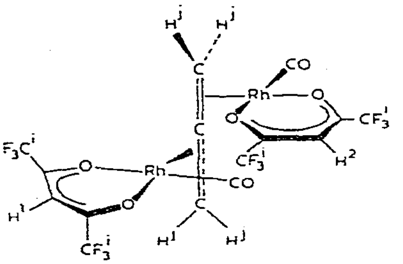
^1H NMR AND ^{19}F NMR FOR THE DIASTEREOISOMERS OF IIa [a]



(IIa₁)



(IIa₂)



(IIa₃)

IIa_1 or IIa_2			IIa_3	
Protons	Chemical shifts [b]		Protons	Chemical shifts [b]
H^1 or H^2	4.40m	2H	H^1 or H^2	6.38s 1H
			H^2 or H^1	6.35s 1H
H^2 or H^1	3.62m	2H	H^j	4.30m 1H
				4.12m 1H
H^3	6.17s	2H		3.78m 1H
				3.47m 1H
Fluorines	Chemical shifts [c]		Fluorines	Chemical shifts [c]
			CF^{3i}	2.83 3F
CF^{3a} or CF^{3b}	2.43	6F		2.67 3F
CF^{3b} or CF^{3a}	2.36	6F		2.56 3F
				1.96 3F

[a] Measured in $CDCl_3$, at 37°C. [b] δ values (ppm), TMS as internal standard; m = multiplet, s = singlet. [c] δ values (ppm), CF_3CH_2OH as internal standard.

in solution of two diastereoisomers, viz. IIa_1 (or IIa_2) and IIa_3, in the molar ratio of 2.6/1 (by NMR).

In contrast, the IR spectrum of IIa (KBr pellet) (see Experimental) shows only two carbonyl bands rather than the four which would be observed if two diastereoisomers were present in the solid state (two CO stretching bands for each isomer are predicted by group-theory). In order to test the hypothesis that in solution equilibrium between the two diastereoisomers is established, a number of IR spectra of heptane solution of IIa were recorded in the region 1900—2200 cm^{-1} at various times. Two of these spectra are shown in Fig. 2. Spectrum a was recorded immediately after the preparation of the solution and shows two bands at 2053 and 2044 cm^{-1}; spectrum b was recorded with the same solution after 4 h, and shows two additional bands at 2012 and 2039 cm^{-1}, indicating the appearance of another compound. This spectrum remained unchanged for 48 h, when the solution was rapidly evaporated to dryness under vacuum. The residue was dissolved in heptane, and yet another IR spectrum was immediately recorded, and found to be identical with spectrum a (Fig. 2). These findings clearly demonstrate that a very fast interconversion between two

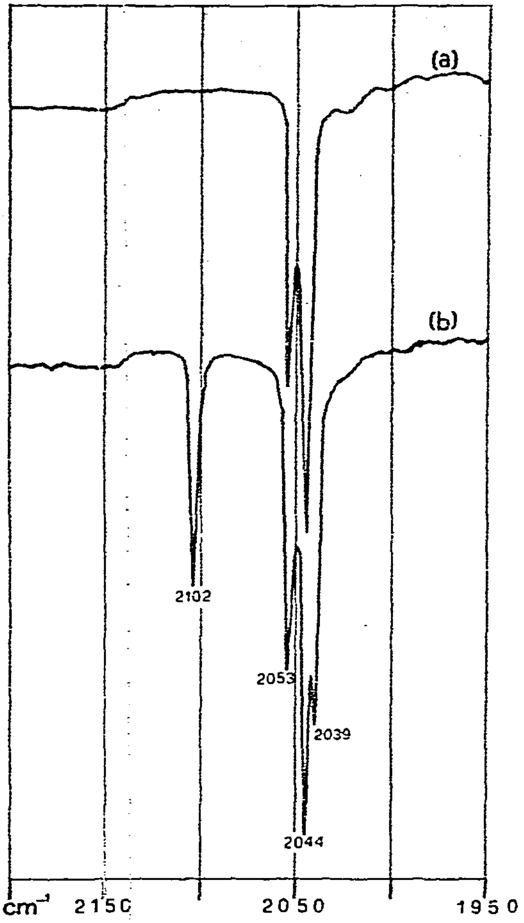


Fig. 2. IR spectra (carbonyl region) of IIa in heptane: (a) measured immediately after preparation of the solution; (b) measured after 4 h.

diastereoisomers of IIa occurs in solution. However, on the basis of available data it is not possible to decide which of the two C_2 symmetry isomers, i.e. IIa$_1$ or IIa$_2$, is present in addition to IIa$_3$, or to assign the configuration of IIa in the crystalline state. By analogy with IIb, we favour the view that in the solid state IIa has the configuration IIa$_1$, which probably also predominates in solution.

Similar behaviour was shown by $(acac)_2Rh_2(CO)_2(C_3H_4)$ (IIb).

The question which remains to be answered concerns the mechanism of interconversion of the diastereoisomers of IIa and IIb. A possibility is that the isomer IIa$_3$ (or IIb$_3$) is formed from IIa$_1$ (or IIb$_1$) and vice versa through unimolecular processes, viz.: (a) an odd number of ligand exchanges on the same rhodium atom (Fig. 3, top); and (b) an odd number of 180° rotations of a rhodium coordination plane around the rhodium-double bond bond-axis (Fig. 3, bottom). The available experimental data do not enable conclusions to be reached concerning this equilibrium. Rate measurements and other studies are in progress.

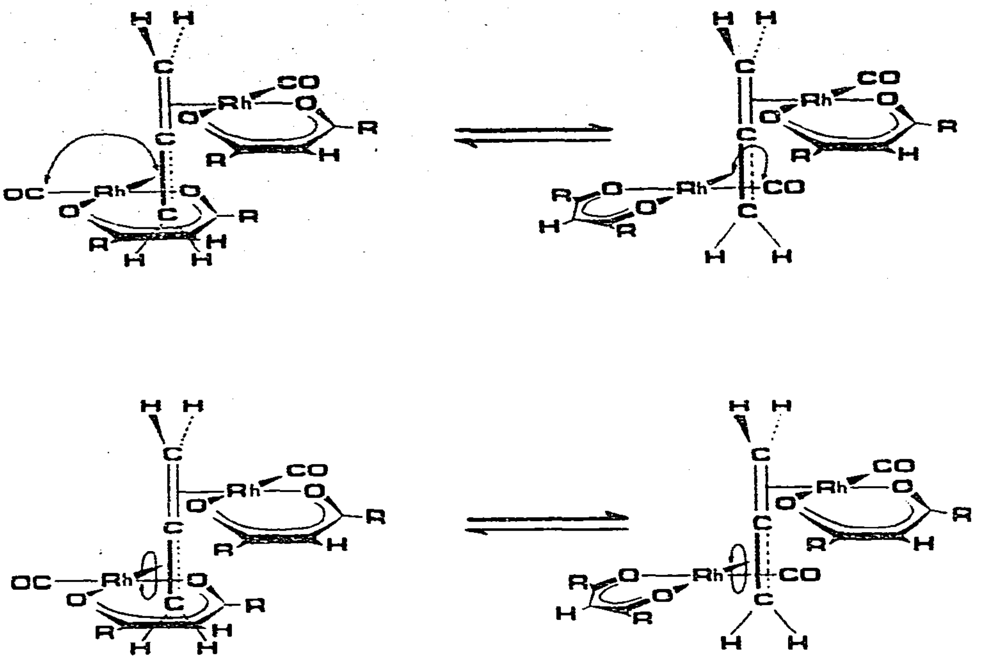


Fig. 3. Suggested mechanisms for the transformation of IIa_1 (or IIb_1) into IIa_3 (or IIb_3), and vice versa.

Preparation and properties of η^3-allylic derivatives of rhodium(III)

(hfacac)$Rh(CO)_2$ (Ia) reacts with allene at −30°C to give a pale-yellow microcrystalline product to which the formula (hfacac)$Rh(C_7H_8O)$ (V) was assigned on the basis of elemental analysis and osmometric molecular weight. V is thermally very stable and can be manipulated in air in the solid state. It is almost insoluble in aliphatic solvents, sparingly soluble in chloroform and benzene, and very soluble in acetone.

V can also be obtained by reaction of allene with $(hfacac)_2Rh_2(CO)_2(C_3H_4)$ (IIa) (Scheme 3).

SCHEME 3

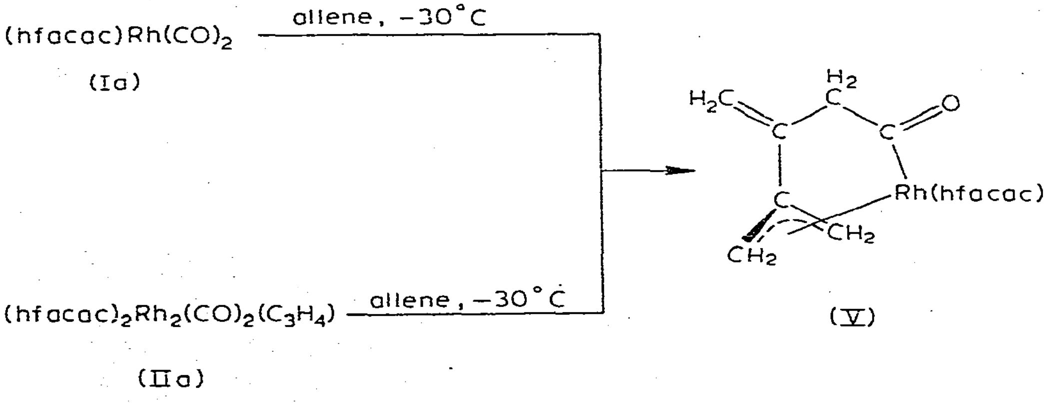
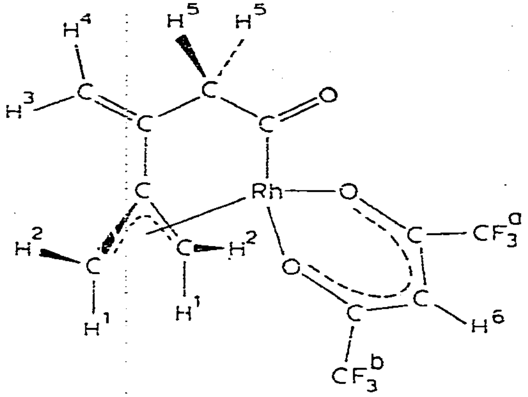


TABLE 2

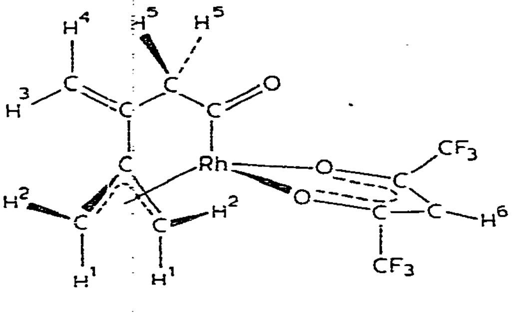
^{1}H NMR AND ^{19}F NMR DATA FOR COMPOUND V [a]



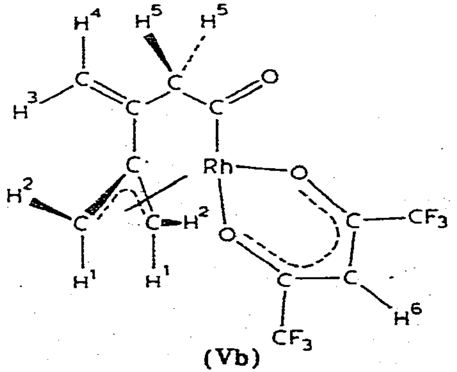
Protons	Chemical shifts [b]		Fluorines	Chemical shifts [c]
H^1	2.85 ud	2H		
H^2	4.16 ud	2H	CF^{3a} or CF^{3b}	2.25 3F
H^3 or H^4	5.44 m	1H		
H^4 or H^3	5.21 m	1H	CF^{3b} or CF^{3a}	2.14 3F
H^5	3.68 m	2H		
H^6	6.20 s	1H		

[a] Measured in CD_3COCD_3, at 37°C. [b] δ values (ppm), TMS as internal standard; ud = unresolved doublet, m = multiplet, s = singlet. [c] δ values (ppm), CF_3CH_2OH as internal standard.

The assignment of structure V is based upon the ^{1}H NMR, ^{19}F NMR, and IR spectra, and also upon its chemical behaviour. In Table 2 are listed the chemical shifts together with the multiplicities of proton and fluorine resonances. The ^{1}H NMR spectrum exhibits six signals (relative intensities, 1/1/1/2/2/2). The singlet at δ 6.20 ppm was attributed to the methine proton of the hexafluoroacetylacetonato group. The resonances at δ 5.44 and 5.21 ppm were assigned to protons 3 (or 4) and 4 (or 3); the signals at δ 4.16 and 2.85 ppm were attributed to the two by two equivalent *syn* protons 2 and to the *anti* protons 1, respectively. The multiplet at δ 3.68 ppm was assigned to protons 5 which, by double irradiation experiments was shown to be coupled to protons 3 and 4. However, the ^{1}H NMR data do not suffice to fix the geometry of V, since they are consistent either with the square pyramid Va or with the trigonal bipyramid Vb.



(Va)

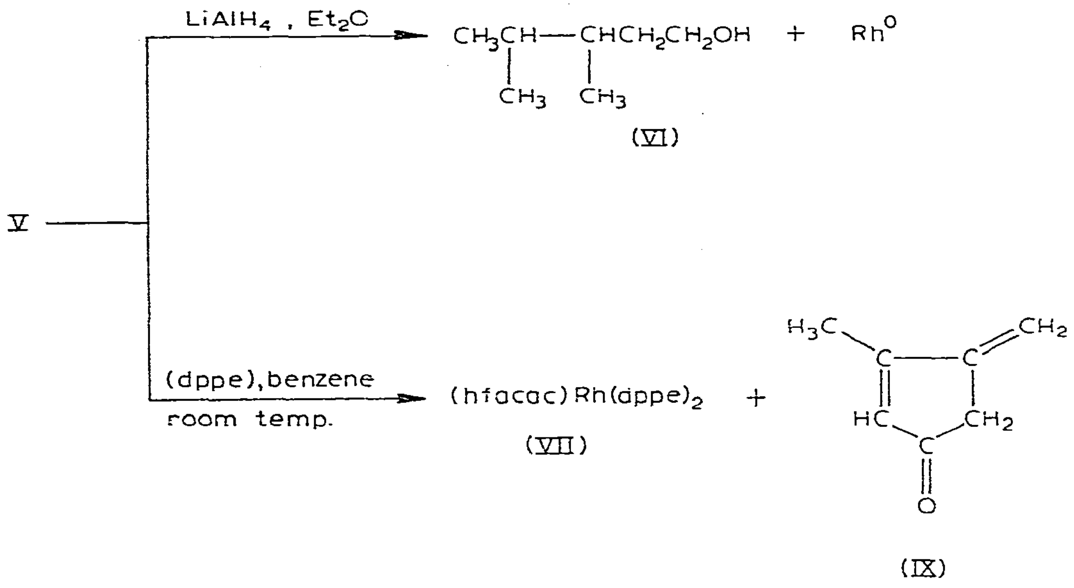


(Vb)

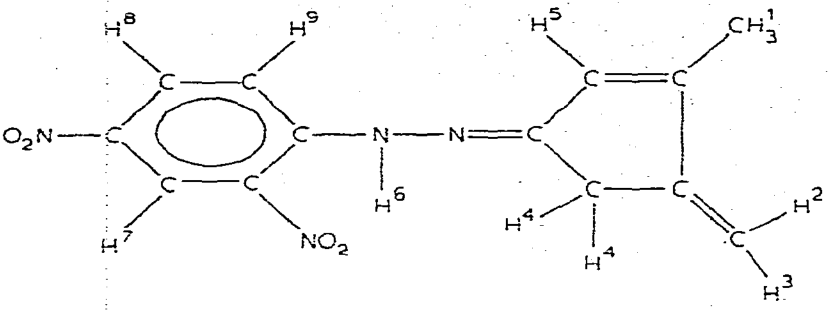
The ^{19}F NMR spectrum of V shows two signals of equal intensity at δ 2.25 and δ 2.14 ppm (relative to CF_3CH_2OH as internal standard). This rules out the structure Va, whose symmetry makes the two trifluoromethyl groups equivalent. The IR spectrum of V shows a band at 1680 cm^{-1} due to the acylic carbonyl [8], and four bands at 1640, 1610, 1550 and 1520 cm^{-1} in the region in which C⋯O and C⋯C stretchings occur for the hexafluoroacetylacetonato group bonded to metal by two oxygen atoms [14].

Reduction of V with a large excess of $LiAlH_4$ leads to metallic rhodium and a mixture of products in which 3,4-dimethyl-1-pentanol (VI) predominates (85%, by GLC) (Scheme 4). VI was identified by comparison with an authentic sample. When benzene solutions of V are allowed to react at room temperature with an excess of 1,2-bis(diphenylphosphino)ethane (dppe), a greenish-yellow crystalline compound of formula (hfacac)Rh(dppe)$_2$ (VII) is obtained, in almost quantitative yields, on addition of pentane to the mixture. (dppe) evidently displaces the 2,3-dimethylenepentan-5-one-1,5-diyl group with subsequent reduction of rhodium(III) to rhodium(I).

SCHEME 4



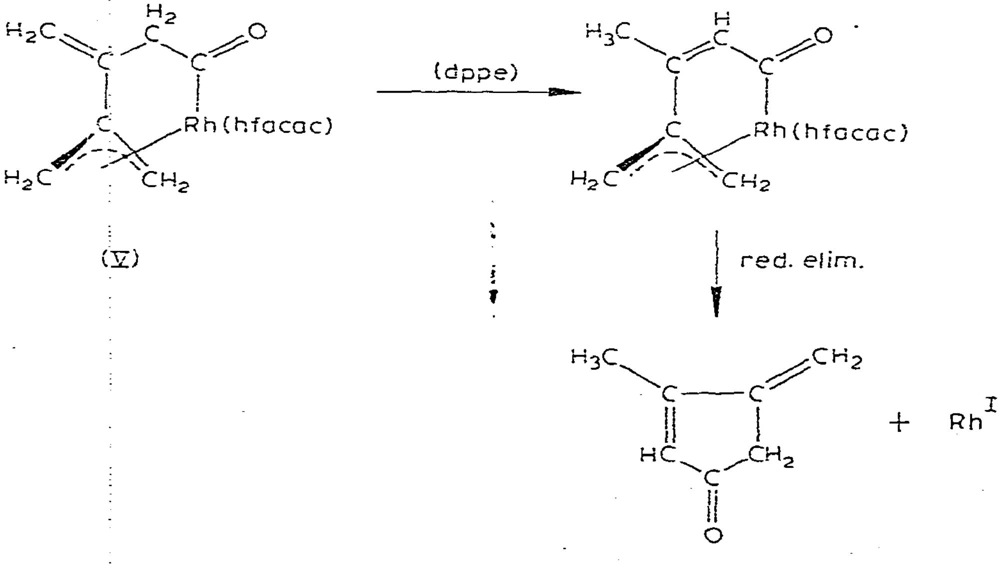
From what is known of the reaction of a rhodium(III) derivative similar to V, viz. chloro(2,3-dimethylenepentan-5-one-1,5-diyl)carbonylrhodium, with π-acids [8], we expected the formation of a cyclic ketone, i.e. 3,4-dimethylenecyclopentanone, by coupling of one of the two terminal chemically equivalent carbon atoms of the η^3-allylic group with the acylic carbon atom. To confirm the presence of this ketone after precipitation of VII and concentration to a small volume the mixture was treated with a large excess of an aqueous alcoholic solution of 2,4-dinitrophenylhydrazine. A red crystalline precipitate, VIII, was obtained, to which the following structure was assigned on the basis of its mass and ¹H NMR spectra:



(VIII)

The mass spectrum of VIII showed in addition to the strong parent peak at *m/e* 288 ($C_{13}H_{12}N_4O_4^+$), a prominent peak at *m/e* 91 (tropylium ion). The ¹H NMR spectrum of VIII ($CDCl_3$, TMS as internal standard) exhibits nine resonances: two double doublets centered at δ 7.90 and 8.31 ppm due to protons 9 (J_8 10 Hz; J_7 2 Hz) and 8 (J_9 10 Hz; J_6 3 Hz), respectively; one doublet at δ 9.13 ppm and one multiplet at δ 11.10 ppm attributed to protons 7 (J_9 2 Hz) and 6, respectively; three multiplets at δ 6.46, 5.26, and 3.40 assigned to protons 5, 2 plus 3, and 4, respectively; one unresolved doublet at δ 2.13 ppm due to protons 1. These assignments are in agreement with NMR data for model compounds [15—17]. The formation of the hydrazone VIII indicates the formation of 3-methyl-4-methylenecylopent-2-ene-1-one (IX) (Scheme 4) instead of the expected 3,4-dimethylenecyclopentanone. The latter is known to isomerise readily and quantitatively to IX even in presence of water at room temperature [19]. We first assumed that isomerization had occurred during the preparation

SCHEME 5

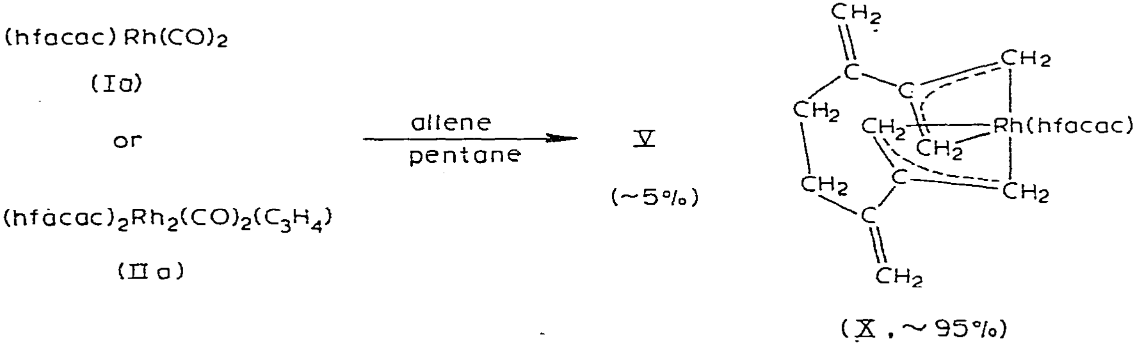


(IX)

of the hydrazone, but this interpretation was rejected by ^{1}H NMR analysis of the crude residue obtained after careful concentration of the mother liquors from the reaction of V with (dppe), after precipitation of (hfacac)Rh(dppe)$_2$. The ^{1}H NMR spectrum ($CDCl_3$) showed all the signals reported by Dowd [19] for 3-methyl-4-methylenecyclopent-2-ene-1-one (IX), in addition to resonances due to a small amount of (hfacac)Rh(dppe)$_2$. It thus seems reasonable to consider the rhodium(I) complex or (dppe) as being responsible for isomerisation of 3,4-dimethylenecyclopentanone to IX, unless the isomerisation of V by dppe occurs before the reductive elimination of the acylallylic group takes place, as outlined in Scheme 5.

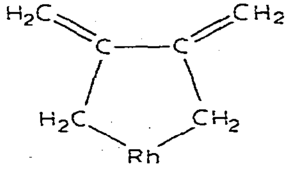
When the reaction between (hfacac)Rh(CO)$_2$ (Ia) and allene is carried out between —20 and +20°C in pentane, in addition to variable amounts of V, the known [7] bis(η^3-allyl)rhodium(III) derivative X is obtained in high yields (Scheme 6). Under the same conditions (hfacac)$_2$Rh$_2$(CO)$_2$(C_3H_4) (IIa) reacts with allene exactly as does Ia (Scheme 6). In contrast, no reaction occurred between allene and V, which was recovered unchanged after 24 h at 30° C.

SCHEME 6



How do η^3-allylic complexes form?

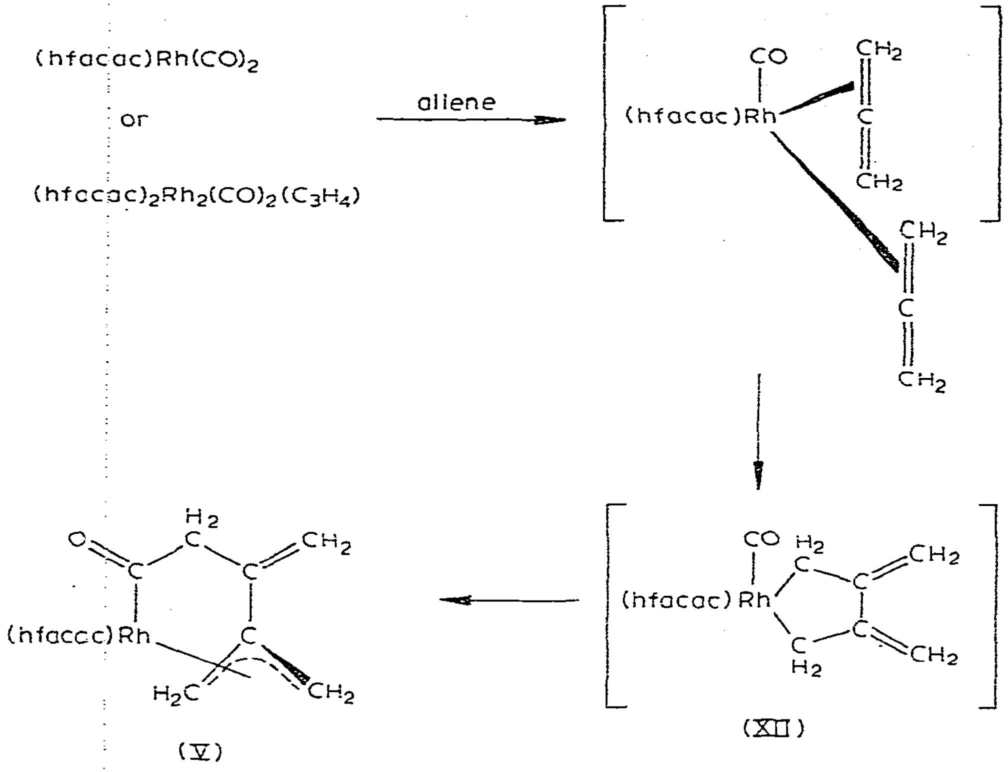
The finding that no reaction occurs between V and allene clearly indicates that V is not a precursor of the bis(η^3-allylic) complex X. On the other hand the intermediacy of rhodium(III) derivatives containing the 3,4-dimethylenerhodacyclopentane moiety XI in the formation of bis(η^3-allylic) complexes such as X from compounds of the type (β-diketonato)Rh(C_2H_4)$_2$, has been demonstrated [7], and the reaction mechanism discussed [11].



(XI)

Assuming that in this case also a compound containing the moiety XI forms as an intermediate, we conclude that the bis(η^3-allylic) complex X forms under conditions in which allene easily removes all the CO molecules of starting compounds. Under milder conditions (—30°C), when at least one CO per rhodium atom is still present, V is formed. In such a case the metallocyclic intermediate XII can be trapped by carbonyl insertion to give V, as outlined in Scheme 7.

SCHEME 7



Experimental

Allene (Matheson, purity ca. 98.7%), hexafluoroacetylacetone and dibenzoylmethane (Fluka), and acetylacetone (Carlo Erba) were used without further purification. (hfacac)Rh(CO)$_2$, and (acac)Rh(CO)$_2$ were prepared as described [18]. 3,4-Dimethylpentan-1-oic acid was kindly supplied by Dr. S. Pucci, C.N.R. Pisa. Solvents were dried and distilled before use. ^{1}H NMR spectra were obtained with a Varian T60 or Jeol PS-100 spectrometer, ^{19}F NMR spectra with the Jeol instrument, and IR spectra with a 225 Perkin—Elmer instrument. Melting or decomposition ~~points~~ were determined with a Kofler hot-stage apparatus and are uncorrected. GLC analyses were carried out with a Carlo Erba Fractovap Mod. GT with a 2 m, 20% SE-30 on 60—80 Chromosorb W column. Mass spectra were obtained with a Varian MAT Mod. CH7 spectrometer. Molecular weights were determined at 37°C by a Mechrolab vapor-pressure Osmometer Mod. 3019. Microanalyses were performed by the Laboratorio di Microanalisi of Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. Manipulations of organometallic compounds were carried out under dinitrogen.

Preparation of (hfacac)$_2$Rh$_2$(CO)$_2$(C$_3$H$_4$) (IIa)

(hfacac)Rh(CO)$_2$ (150 mg) was suspended in liquid allene (4 ml) at —78°C. At 2—3 minute intervals the mixture was heated to —40° C and again cooled to —78°C, until, after ca. 0.5 h, a clear orange solution was obtained. This solution was kept at —78°C for an additional 0.5 h, then evaporated under vacuum. The residue was dissolved in pentane (5 ml). From this solution IIa crystallised as orange needles (97 mg, 60% yield), at —25°C. M.p. 104°C (dec.). (Found: C, 25.54; H, 0.87. Mol. wt. 710 (benzene). $C_{15}H_6F_{12}O_6Rh_2$ calcd.: C, 25.16; H, 0.84%. Mol. wt. 716.01). IR (KBr): 3140vw, 3060vw, 2054s, 2040s, 1805w, 1640s, 1610s, 1560w, 1530w, 1455s, 1345w, 1265s, 1220m, 1255s, 1200m, 1175m, 1150s, 1140s, 1110m, 985m, 950w, 810m, 745w, 685w, 590w, 570w, 530w, 485w, 420w, 400w cm^{-1}.

Reaction of (hfacac)$_2$Rh$_2$(CO)$_2$(C$_3$H$_4$) (IIa) with PPh$_3$: formation of (hfacac)Rh-(CO)(PPh$_3$)$_2$ (IV)

(hfacac)$_2$Rh$_2$(CO)$_2$(C$_3$H$_4$) (50 mg) was dissolved in pentane (5 ml) at room temperature and PPh$_3$ (73 mg) dissolved in pentane (5 ml) was added. Allene was immediately evolved and in a few minutes golden-yellow needles of (hfacac)-Rh(CO)(PPh$_3$)$_2$ (IV) formed, these were filtered off, washed with pentane, and dried. Yield 108 mg (90%), m.p. 122—123°C. (Found: C, 58.35; H, 3.58. Mol. wt., 628 (methyl ethyl ketone). $C_{42}H_{31}F_6O_2P_2Rh$ calcd.: C, 58.48; H, 3.62%. Mol. wt., 862.56.) IR (KBr): 3075m, 3060m, 1980s, 1660s, 1635m, 1570w, 1550w, 1530s, 1510s, 1470s, 1430s, 1320w, 1300w, 1250s, 1140s, 1095s, 1075m, 1030m, 1000m, 938w, 850w, 840w, 800w, 785m, 755m, 745s, 740s, 715w, 705m, 690m, 660m, 610w, 580m, 560m, 540w, 520m, 505m cm^{-1}.

IV was also prepared in good yield (95%) as follows. PPh$_3$ (215 mg) was added to a solution of (hfacac)Rh(CO)$_2$ (Ia) (150 mg) in pentane (10 ml) at room temperature. Evolution of CO and precipitation of IV occurred immediately. The product was worked up as described above.

Preparation of (hfacac)Rh(C$_7$H$_8$O) (V)

Allene was bubbled through a solution of (hfacac)Rh(CO)$_2$ (130 mg) in pentane (6 ml) at —30°C for 15 min. The mixture was kept at this temperature for 4 h, then unchanged allene and pentane were evaporated off under vacuum, and the yellow oily residue which remained was treated with pentane (5 ml). This caused the crystallization of a pale-yellow solid, which was separated, washed with pentane, and dried to give 50 mg of (hfacac)Rh(C$_7$H$_8$O) (yield 30%), m.p. 165—170°C (dec.). (Found: C, 34.46; H, 2.27. Mol. wt. 450 (methyl ethyl ketone). $C_{12}H_9F_6O_3Rh$ calcd.: C, 34.47; H, 2.16%. Mol. wt. 418.09). IR (KBr): 3000w, 2920w, 1680m, 1640s, 1610s, 1550s, 1520m, 1480s, 1460s, 1420w, 1390m, 1330m, 1260s, 1210s, 1140s, 1087s, 1052s, 973m, 946m, 912m, 893w, 810w, 793s, 752m, 740m, 676s, 615m, 587m, 555m cm^{-1}.

V can also be prepared from (hfacac)$_2$Rh$_2$(CO)$_2$(C$_3$H$_4$) (IIa) by this procedure.

Reaction of (hfacac)Rh(C$_7$H$_8$O) (V) with LiAlH$_4$

To a well-stirred suspension of (hfacac)Rh(C$_7$H$_8$O) (80 mg) in Et$_2$O (20 ml) a suspension of LiAlH$_4$ (600 mg) in Et$_2$O (20 ml) was added dropwise at room temperature. The mixture was refluxed for 2 h, and kept overnight at room temperature. It was then treated with moist Et_2O and acidified with diluted H_2SO_4. The ethereal layer was separated, washed with water, and dried over Na_2SO_4. On careful distillation of diethyl ether a liquid residue was obtained. Analytical GLC of this residue indicated the presence of a predominant component (80%), which was identified as 3,4-dimethylpentan-1-ol (VI) by comparison of its retention time with that of an authentic specimen prepared from 3,4-dimethylpentan-1-oic acid.

Reaction of (hfacac)Rh(C_7H_8O) (V) with 1,2-bis(diphenylphosphino)ethane (dppe)

To a solution of V (83.6 mg) in benzene (6 ml) at room temperature was added (dppe) (159.4 mg). The mixture was kept for 2 h at room temperature. Pentane was added, and the greenish-yellow microcrystalline product which separated was filtered off, washed with pentane, and dried, to give 177 mg of (hfacac)Rh(dppe)$_2$ (yield, 80%), m.p. 92°C. (Found: C, 62.76; H, 4.57. Mol. wt., 734.(methyl ethyl ketone). $C_{57}H_{49}F_6O_2P_4Rh$ calcd.: C, 61.85; H, 4.46%. Mol. wt., 1106.96). ^1H NMR ($CDCl_3$): 7.30 (m, 40 H); 5.57 (s, 1 H); 2.10 ((br)m, 8 H) ppm (δ(ppm) from TMS). The mother liquors were concentrated to 1 ml by evaporation of solvent under reduced pressure, and the residue was treated with a large excess of an aqueous alcoholic solution of 2,4-dinitrophenylhydrazine. During 24 h, a red crystalline precipitate formed, and this was washed several times with a 1/1 water/ethanol mixture then dried. M.p. 160°C. This compound was identified as the 2,4-dinitrophenylhydrazone of 3-methyl-4-methylenecyclopent-2-ene-1-one (IX). The mass spectrum and the ^1H NMR spectrum of this compound are described in the text. IR (KBr): 3400m, 3090w, 2965m, 2920s, 2865m, 2850m, 1720w, 1650w, 1640w, 1610s, 1580s, 1530w, 1510m, 1460w, 1420w, 1360w, 1330s, 1300s, 1250s, 910s, 895m, 855m, 830s, 800m, 740s, 690w, 635w, 550w, 510w, 460m, 450w cm^{-1}.

Preparation of (hfacac)Rh(C_3H_4)$_4$ (X)

Allene was bubbled for 10 min through a pentane (10 ml) solution of (hfacac)-Rh(CO)$_2$ (200 mg) at room temperature. After 30 min at this temperature, the mixture was concentrated to 5 ml by evaporation of solvent under reduced pressure and then cooled to −25°C. In about 8 h 244 mg of X were obtained (yield, 95%) as orange-red needles. This was identical with an authentic sample [7].

Preparation of (acac)$_2$Rh$_2$(CO)$_2$(C_3H_4) (IIb)

Allene was bubbled for 30 min through a benzene (10 ml) solution of (acac)-Rh(CO)$_2$ (300 mg) at 30°C. Evaporation of the solvent left an oily residue, which was dissolved in pentane (15 ml). The solution was cooled to −25°C, and in ca. 12 h gave (acac)$_2$Rh$_2$(CO)$_2$(C_3H_4) (yield, 30%), which was identical with an authentic specimen [12].

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