Complexations of 1,4-Dienes to Rhodium(I) Pentane-2,4-dionates; Thermal Rearrangements of the Complexes †

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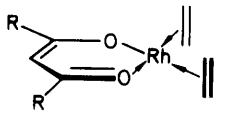
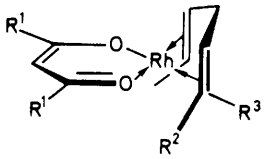
As models for natural products containing a 'skipped' diene fragment (−CH=CHCH$_2$CH=CH−), a series of hepta-2,5-dienes, hepta-2,5-dien-4-ols, and hepta-2,5-dien-4-ol acetates have been prepared. Some of these dienes react with either bis(ethylene)(pentane-2,4-dionato)rhodium(I) or bis(ethylene)(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I) to afford 1 : 1 complexes, *e.g.* [(*E*,*E*)-hepta-2,5-diene](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I). Other dienes, *e.g.* (*Z*,*Z*)-hepta-2,5-diene, form 2 : 1 complexes in which for each molecule of diene, one double bond is co-ordinated to rhodium, whereas the other is not. The (*Z*,*Z*)-dienes do not form 1 : 1 complexes because there would be a severe steric interaction between the terminal substituents of each double bond in such complexes. For the complexes of the dienols and certain allylic alcohols (*e.g.* prop-2-en-1-ol), evidence was obtained for the presence of a stabilising intramolecular hydrogen bond between each OH and its nearest CO of the pentane-2,4-dionate. When heated in benzene with 5 mol % of bis(ethylene)-(pentane-2,4-dionato)rhodium(I) each dienol rearranged to give an enone as the main product [*e.g.* (*E*,*E*)-hepta-2,5-dien-4-ol ⟶ (*E*)-hept-2-en-4-one (85%)]. Their acetates rearranged to isomeric conjugated dienes [*e.g.* (*Z*,*Z*)-4-acetoxyhepta-2,5-diene ⟶ (3*E*,5*Z*)-2-acetoxyhepta-3,5-diene]. The hepta-2,5-dienes were recovered unchanged. The mechanisms of the rearrangements observed are explained in terms of intermediate (π-allyl)rhodium complexes.

In contrast to the many rhodium(I) complexes of simple alkenes [1] and conjugated dienes [2] described, literature reports of Rh^I complexes of 'skipped' dienes (*i.e.* systems of the type −CH=CHCH$_2$CH=CH−) are scarce. For penta-1,4-diene and cyclohexa-1,4-diene, rhodium(I) complexes have been prepared [3] and the products of their thermally induced isomerisations have been identified.[4] Awareness of the increasing importance of fatty acids and their derivatives [the most abundant class of compounds possessing the skipped diene moiety, usually with (*Z*,*Z*)-configuration [5]], particularly the prostaglandins and leukotrienes,[6] has stimulated further research into the reactions of this class of compounds. Complexation of a skipped diene to a metallic centre may offer a means of accomplishing regio- and stereo-selective transformations with the diene (ref. 7 and ch. 20 in ref. 5*a*). With this idea in mind, a series of model compounds, whose salient structural features closely resemble those possessed by unsaturated fatty acids and their derivatives, have been prepared. Their complexations to and rearrangements promoted by bis(ethylene)(pentane-2,4-dionato)rhodium(I), [Rh(C$_2$H$_4$)$_2$(pd)] (1a), and bis(ethylene)(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I), [Rh(C$_2$H$_4$)$_2$(hfpd)] (1b), have been studied. Several of the complexes were obtained as oils which could not be crystallised and fully characterised. However, their structures could be assigned by comparison of their ^{1}H n.m.r. data with data for the crystalline, completely characterised complexes obtained.



(1a) R = Me
(1b) R = CF$_3$



(2a) R^1 = CF$_3$, R^2 = Me, R^3 = H
(2b) R^1 = R^2 = Me, R^3 = H
(2c) R^1 = CF$_3$, R^2 = H, R^3 = Me
(2d) R^1 = R^3 = Me, R^2 = H

Results and Discussion

Complexations of Skipped Dienes.—An excess of (*E*,*E*)-hepta-2,5-diene reacted with either (1a) or (1b) to give ethylene (quantitative evolution) and formation of a 1 : 1 complex. Similar results were obtained for reactions of (*E*,*Z*)-hepta-2,5-diene with complexes (1a) and (1b). The product complexes (2b)—(2d) were isolated as oils, whereas the complex [(*E*,*E*)-hepta-2,5-diene](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I), (2a), could be sublimed to give a red solid (m.p. 55—57 °C). In complex (2a) the co-ordinated double bonds are assumed to be approximately perpendicular to the plane of the pentanedionate ring, by analogy with [Rh(C$_2$H$_4$)$_2$(pd)] [8,9c] and other complexes.[9] The proposed structure for complex (2a) is supported by ^{1}H n.m.r. spectroscopy [3,9] which indicates that upon complexation the two methyl groups (H^1) and (H^7) experience a shielding effect (δ 1.63 free, δ 1.02 co-ordinated). Selective irradiation of the resonance at δ 1.02 caused simplification of the signal at δ 2.89 assigned as H^2, thus allowing the resonance at δ 3.38 to be assigned to H^3. In the complex (2a) the protons at C^4 are non-equivalent and appear at δ 1.72 and 2.70; they have been assigned as H$^4_{exo}$ and H$^4_{endo}$ respectively. The dihedral angle (φ) between H^3 and H$^4_{exo}$ is *ca.* 90° and so coupling between these protons is small. Thus, H$^4_{exo}$ appears as a doublet because of geminal coupling to H$^4_{endo}$ (J_{gem} 12.8 Hz), each component of the doublet showing additional minor coupling to H^3 and ^{103}Rh. The dihedral angle between H^3 and H$^4_{endo}$ is *ca.* 20° because H$^4_{endo}$ appears as a double triplet (J_{gem} 12.8, J_{vic} 7.2 Hz), with negligible coupling to ^{103}Rh. Further spectral evidence for the proposed structure of (2a) is provided by the ^{13}C-{^{1}H} n.m.r. spectrum, which apart from the resonances for the carbons of the pentanedionate unit, shows four other resonances. The carbons of the methyl groups (C^1 and C^7) appear as a singlet at δ 18.7 and the singlet at δ 31.1

† *Non-S.I. unit employed:* 1 mmHg = (101 325/760) Pa.

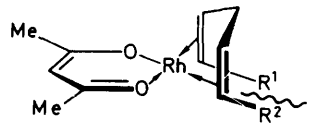


Figure 1. Steric interaction in (*Z*,*Z*)-hepta-2,5-diene complexes of rhodium(I) pentane-2,4-dionates

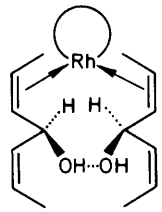


Figure 2. (*R*,*S*)-Diastereoisomer of complex (3a) showing intramolecular hydrogen bonding between hydroxyl groups

is assigned to C^4. The resonances at δ 50.3 and 77.8 show coupling to ^{103}Rh of 8.8 and 14.7 Hz and are assigned as C^2 and C^3, respectively.[10]

With an (*E*,*Z*) skipped diene complex there is a steric interaction between the *cis* C^2 substituent and the *cis* C^6 substituent. For (*E*,*Z*)-hepta-2,5-diene these substituents are a methyl group and a hydrogen atom. We isolated 1 : 1 complexes from the reaction of this ligand with (1a) and (1b), and so this steric interaction can be accommodated.[10,11] However, the increased lability of such complexes is manifested in the ^1H n.m.r. spectrum of complex (2c) which indicates the presence of a temperature-dependent dynamic process, occurring at the *trans* double bond. At room temperature the H^1 methyl protons appear as a broad singlet (δ 1.08), whereas at −20 °C this signal is resolved into a doublet (*J* 6 Hz). The *cis* double bond remains unaffected over this temperature range, as judged by the unperturbed H^7 methyl resonance (δ 1.58). We suggest a dynamic process involving association and dissociation at rhodium of the *trans* double bond to relieve steric compression. It is known that *trans*-alkenes do not co-ordinate as strongly to Rh^I as *cis*-alkenes.[1]

With (*Z*,*Z*)-hepta-2,5-diene the interaction between two *cis* methyl groups is so severe as to preclude formation of a bidentate complex between this ligand and Rh^I (*cf.* Figure 1). A similar situation had previously been observed for (*Z*,*Z*)-hexa-2,4-diene, which does not give a bidentate complex with Rh^I, but is catalytically transformed to (*E*,*E*)- and (*E*,*Z*)-hexa-2,4-diene.[4] However, with (*Z*,*Z*)-hepta-2,5-diene no isomerisation was observed; instead, reaction of two mol equiv. of ligand with one mol equiv. of (1b) caused immediate evolution of ethylene and the ^1H n.m.r. spectrum of the resulting oil indicated the presence of unstable bis(monodentate ligand) complexes in solution (resonances for free and co-ordinated alkene were observed). Nelson and co-workers [2] have previously isolated a bis(monodentate ligand)(1,3-diene) complex and confirmed its structure by *X*-ray crystallography. The results presented show that for the series of (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-1,4-dienes, the order of preference for bidentate co-ordination to Rh^I is (*E*,*E*) > (*E*,*Z*) ≫ (*Z*,*Z*).

Complexations of Skipped Dienols.—The corresponding dienols, *i.e.* (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-hepta-2,5-dien-4-ol, do not strictly conform to the behaviour of their parent dienes, particularly in reactions with complex (1b). However, both (*E*)-hexa-1,4-dien-3-ol and (*E*,*E*)-hepta-2,5-dien-4-ol reacted with (1a) and (1b) in a 1 : 1 ratio to give bidentate complexes,

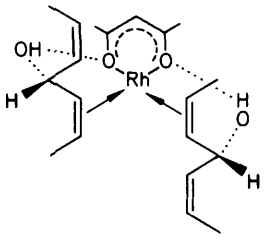
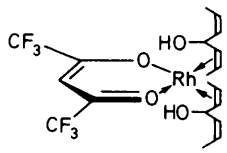
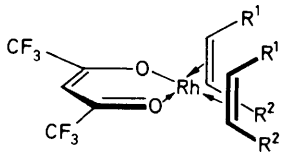


Figure 3. (*R*,*R*)-Diastereoisomer of complex (3a) showing intramolecular hydrogen bonding from each hydroxyl group to the nearest pentane-2,4-dionate oxygen



(3a)

[(3b) as above, but with (*E*,*Z*)−dienol ligands]



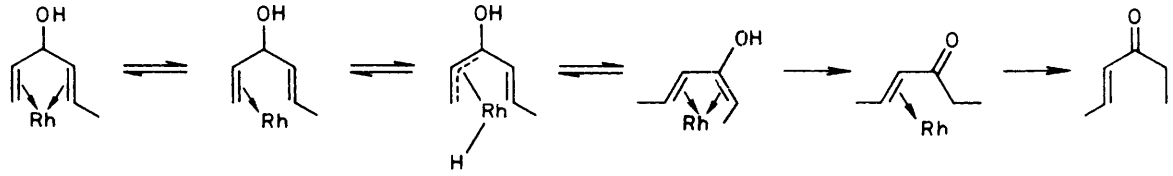
(4a) $R^1 = H$, $R^2 = CH_2OH$
(4b) $R^1 = H$, $R^2 = CH(Me)OH$
(4c) $R^1 = R^2 = CH_2OH$

presumably similar in structure to complexes (2a)—(2d). These complexes were isolated as oils and were characterised by ^1H n.m.r. and i.r. spectroscopy. Two interesting features to note for these complexes are the chemical shift of the O−H protons (*e.g.* δ 1.78 and 1.85), and the O−H stretching frequency (*e.g.* 3 605 and 3 610 cm^{-1}). The chemical shift data, taken with the knowledge that the single proton (−C*H*OH−) attached to the same carbon as the hydroxyl group shows no coupling to ^{103}Rh, indicate that the hydroxyl group is *exo* to the metal. This is confirmed by the i.r. stretching frequency which indicates no intramolecular hydrogen bonding at high dilution.

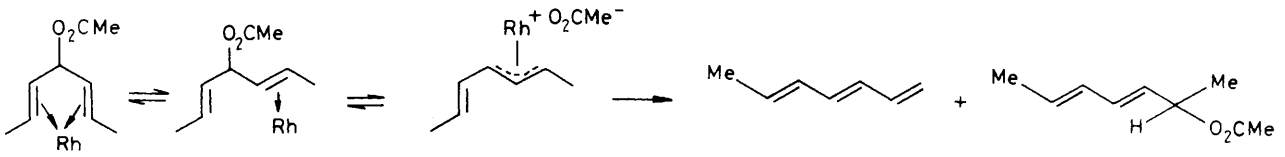
The complexes formed between (*Z*,*Z*)-hepta-2,5-dien-4-ol or (*E*,*Z*)-hepta-2,5-dien-4-ol and (1b) contrast dramatically with this behaviour. (*Z*,*Z*)-Hepta-2,5-dien-4-ol (two mol equiv.) was reacted with one mol equiv. of complex (1b) to give an orange crystalline product. This was fully characterised by ^1H n.m.r., i.r., and mass spectroscopy, and by a combustion analysis, as a bis(monodentate ligand)rhodium(I) complex (3a). Its ^1H n.m.r. spectrum shows the presence of both co-ordinated [δ 2.45 (H^2, m), 2.88 (H^3, t)] and uncoordinated [δ 5.52 (H^5/H^6, m)] double bonds, while the proton of the hydroxyl group is shifted to relatively low field (δ 6.80). I.r. data show this group to be participating in intramolecular hydrogen bonding as indicated by the O−H stretching vibration at 3 270 cm^{-1}, which remains unaltered on dilution in CCl_4 solution. The intramolecular hydrogen bonding adds considerably to the stability of this complex, compared to the situation with (*Z*,*Z*)-hepta-2,5-diene. The exact nature of this hydrogen-bond interaction is not clear, but two possibilities are obvious. One involves interaction between two proximate hydroxyl groups; the other involves an interaction between the hydroxyl groups and the oxygen atoms of the chelating hexafluoropentanedionate ring.

Consider first, hydroxyl group interaction alone (Figure 2). Molecular models show that for this type of interaction to occur the methyl substituents on the co-ordinated double bonds would face each other, causing steric interactions.

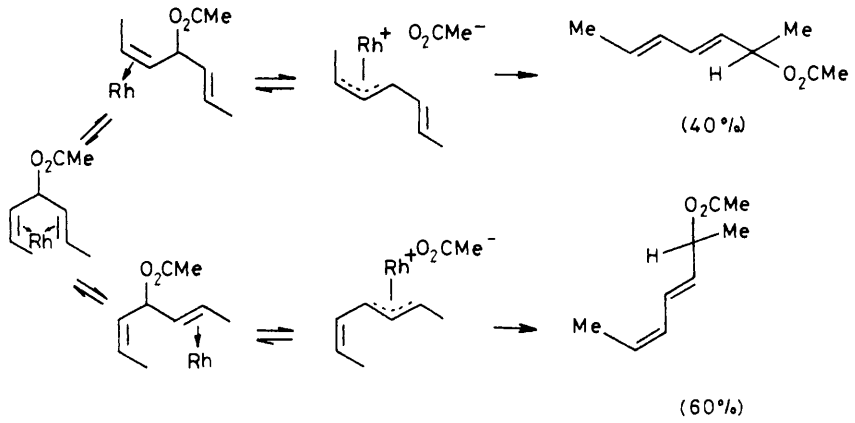
The second possibility, which we favour over the first, is illustrated in Figure 3. Here the substituents on the double bonds are distant from one another. The low-field resonance of the hydroxyl protons in the ^1H n.m.r. spectrum can be explained by the hydroxyl groups being hydrogen-bonded in



Scheme 1. Mechanism for the Rh^{I}-catalysed conversion of (*E*)-hexa-1,4-dien-3-ol into (*E*)-hex-2-en-4-one



Scheme 2. Mechanism for the Rh^{I}-catalysed conversion of (*E,E*)-4-acetoxyhepta-2,5-diene into (*E,E*)-hepta-1,3,5-triene and (*E,E*)-2-acetoxyhepta-3,5-diene



Scheme 3. Mechanism for the Rh^{I}-catalysed conversion of (*E,Z*)-4-acetoxyhepta-2,5-diene into (*E,E*)- and (*E,Z*)-2-acetoxyhepta-3,5-diene

the plane of the hexafluoropentanedionate ring, thus experiencing an anisotropic deshielding effect. Both possibilities have diastereomeric forms (*cf.* Figures 2 and 3), although the ^{1}H n.m.r. spectrum shows the presence of only one species, whichever type of hydrogen bonding is present. Thus, a stereoselective process occurs in the formation of complex (3a). The initial complexation must involve formation of a (monoethylene)(mono-diene)rhodium(I) intermediate, which then reacts with a second molecule of diene to give a single stereoisomeric product. This behaviour is further exemplified by the reaction of (*E,Z*)-hepta-2,5-dien-4-ol with complex (1b).

Whereas (*E,Z*)-hepta-2,5-diene gave a bidentate complex containing one molecule each of diene and [Rh(hfpd)], (*E,Z*)-hepta-2,5-dien-4-ol reacted analogously to the (*Z,Z*)-dienol isomer to give an orange crystalline product, which was fully characterised as a bis(monodentate dienol) complex (3b) containing two molecules of dienol to one of Rh^{I}. ^{1}H N.m.r. spectroscopy indicates that it is the *trans* double bond which is co-ordinated rather than the *cis* double bond.

The importance of hydrogen bonding in these (allylic alcohol)rhodium(I) complexes has been confirmed by the preparation of three well characterised, crystalline complexes (4a)—(4c) by the reaction of prop-2-en-1-ol, but-3-en-2-ol and (*Z*)-but-2-en-1,4-diol respectively, with complex (1b). Prior to this work, no rhodium complexes of unconjugated diene alcohols had been reported, although complexes involving conjugated dienols are known.[12]

The propensity of (*E*) and (*E,E*) skipped dienes to form bidentate complexes is further illustrated by the reactions of (*E*)-3-acetoxyhexa-1,4-diene with complexes (1a) and (1b), and (*E,E*)-4-acetoxyhepta-2,5-diene with complex (1b). In all cases complexes were isolated as oils, and have a similar structure to the parent dienes and dienols, *i.e.* the acetate function is in the *exo* position. This is supported by ^{1}H n.m.r. spectroscopy, which shows H_{endo} as a triplet, and i.r. spectroscopy which shows the carbonyl stretching frequencies (1 732 cm^{-1}) for co-ordinated (*E,E*)-4-acetoxyhepta-2,5-diene virtually unchanged from that in the free acetoxydiene.[12,13]

Thermal Isomerisations.—The mechanisms by which Rh^{I} facilitates the isomerisations of alkenes in aprotic solvents are well documented [4] and we have applied them to rationalise the Rh^{I}-induced thermolytic rearrangements of skipped dienols and dienol acetates (see Schemes 1—3). (*E*)-Hexa-1,4-dien-3-ol was converted smoothly to (*E*)-hex-2-en-4-one by treatment with 5 mol % of complex (1a) in benzene at 80 °C ('standard conditions' referred to below). This transformation must involve an initial isomerisation of the terminal double bond to give the conjugated enol, which then tautomerises to the product (Scheme 1); (*E,Z*)- and (*E,E*)-hepta-2,5-dien-4-ol both gave (*E*)-hept-2-en-4-one as the major product (85%). However, for the (*E,Z*) isomer isolation of products at a shorter reaction time showed the presence of both (*E*)- and (*Z*)-hept-2-en-4-one. For both the (*E,Z*)- and (*E,E*)-hepta-

2,5-dien-4-ol a secondary product (15%) was (*E,E*)-hepta-2,5-dien-4-one, arising from a dehydrogenation reaction facilitated by rhodium.[14] Interestingly, (*Z,Z*)-hepta-2,5-dien-4-ol gave only 20% reaction after 3 d under the standard conditions. However, the product is the synthetically useful (*Z*)-hept-2-en-4-one, easily separated from the reaction mixture.

The corresponding skipped acetoxydienes were also readily isomerised by complex (1a). Treatment of (*E,E*)-4-acetoxyhepta-2,5-diene under the standard conditions resulted in the formation of two products: (*E,E*)-hepta-1,3,5-triene (55%) and (*E,E*)-2-acetoxyhepta-3,5-diene (45%) (Scheme 2). The triene must arise by elimination of acetic acid from the intermediate Rh^{III} species, whereas return of acetate to the 2-position gives the conjugated acetoxydiene. (*E,Z*)-4-Acetoxyhepta-2,5-diene gave (*E,Z*)- and (*E,E*)-2-acetoxyhepta-3,5-diene (60 : 40) as the only products (Scheme 3). The absence of a triene among the products from this thermolysis suggests a different intermediate from that involved in the isomerisation of the (*E,E*) isomer. The product distribution indicates a preference for reaction at the *trans* double bond leading to a predominance of the (*E,Z*)-conjugated diene in the products. Predictably, (*Z,Z*)-4-acetoxyhepta-2,5-diene needed the longest time for complete reaction, but gave a single product, (*E,Z*)-2-acetoxyhepta-3,5-diene.

This study has defined the modes of complexation of a range of skipped dienes to rhodium(I) pentane-2,4-dionates. The advantage of using this metal system is that stoicheiometric complexes can be prepared that are diamagnetic and relatively unreactive. These characteristics have been previously exploited to prepare (1,5-diene)(pentane-2,4-dionato)-rhodium(I) complexes, *e.g.* from *cis*-1,2-divinylcyclopropane.[15] The mechanisms of reactions of skipped dienes catalysed by metals [see, for example, refs. 7 and 16] may be understood by reference to the established properties of the complexes between rhodium(I) pentane-2,4-dionates and skipped dienes.

Experimental

Pentane was purified by stirring overnight with alkaline potassium permanganate, followed by drying and distilling. Other solvents were either AnalaR grade or redistilled laboratory reagents. Solutions in organic solvents were dried with anhydrous magnesium sulphate; solvents were removed at *ca.* 20 °C with a rotary evaporator. [$^2H_6$]Benzene was dried with 3A molecular sieves.

Rhodium trichloride was obtained from Johnson-Matthey. Di-μ-chloro-tetrakis(ethylene)dirhodium(I) was prepared by the method of Cramer; [17] it was converted into bis(ethylene)-(pentane-2,4-dionato)rhodium(I) (1a), by the two-phase (diethyl ether, aqueous KOH) method of ref. 17.

Hexa-1,4-dien-3-ols and hepta-2,5-dien-4-ols were prepared by literature methods [16,18] and were converted into the corresponding acetates by $(MeCO)_2O$–pyridine; the syntheses of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-hepta-2,5-diene (isomeric purity 96, 95, and 96% respectively) will be described elsewhere.[19]

Hydrogen-1 n.m.r. spectra were recorded with a Perkin-Elmer R-34 spectrometer operating at 220 MHz; ^{13}C-{^1H} n.m.r. spectra were recorded with a Bruker WH90 spectrometer at 22.63 MHz. For all n.m.r. spectra the internal reference was $SiMe_4$. I.r. spectra were recorded with a Perkin-Elmer 257 instrument. U.v. spectra were measured with a Cecil (model CE505) instrument. Electron impact (e.i.) mass spectra were obtained with a Kratos MS80 instrument. Field ionisation (f.i.) mass spectra were carried out by Dr. R. T. Aplin (Oxford).

Bis(ethylene)(1,1,1,5,5,5-*hexafluoropentane*-2,4-*dionato*)-*rhodium*(I) (1b).—Ethyl trifluoroacetate (7.2 g, 50 mmol) was dissolved in dry diethyl ether and stirred with sodium methoxide (2.74 g, 50 mmol) under nitrogen. Trifluoroacetone (5.6 g, 50 mmol) was added dropwise and the solution was heated under reflux for 2 h. Removal of solvent under vacuum gave a white powder which was recrystallised from ether–pentane, to give sodium 1,1,1,5,5,5-hexafluoropentane-2,4-dionate (10 g, 86%). This sodium salt (2.5 g, 10.7 mmol) was dissolved in dry ether (25 cm^3) and stirred with di-μ-chloro-tetrakis(ethylene)dirhodium(I) (2.1 g, 5.4 mmol), under N_2, for 4 h. Centrifugation, followed by decantation and evaporation gave a red-brown residue which was sublimed (40—60 °C at 0.05 mmHg) to give bis(ethylene)(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I) as red prisms (2.5 g, 62.5%), m.p. 44—45 °C (lit.[20] 49—50 °C). ^1H N.m.r. ($CDCl_3$): δ 3.15 (2 × 4 H, br s), 6.14 p.p.m. (1 H, s). ^{13}C N.m.r. ([$^2H_3$]-nitromethane): 62.8 (C=C), 91.1 p.p.m. (CH, hfpd) (resonances for *C*=O and *C*F_3 were not observed).

Complexation of Hepta-2,5-dienes to Rh^I.—(*a*) (*E,E*)-Hepta-2,5-diene (26.4 mg, 0.275 mmol) in dry ether (1 cm^3) was added to complex (1b) (100 mg, 0.274 mmol). When evolution of ethylene ceased, the solvent was removed to give red-brown crystals which were sublimed (40—50 °C at 0.1 mmHg) to give [(*E,E*)-hepta-2,5-diene](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I), (2a) (61 mg, 55%), m.p. 55—57 °C. ^1H N.m.r. ([$^2H_6$]benzene): δ 1.02 (2 × 3 H, H^1, d, *J* 6), 1.72 (1 H, H^4_{exo}, m), 2.70 (1 H, H^4_{endo}, dt, $J_{gem.}$ 12.8, $J_{vic.}$ 7.2 Hz), 2.89 (2 H, H^2, m), 3.38 (2 H, H^3, m), 6.00 p.p.m. (1 H, H^3 of hfpd, s). ^{13}C N.m.r. ([$^2H_3$]nitromethane): 18.7 (2 Me), 31.1 (CH_2), 50.3 (2 C^2, J_{Rh-C} 8.8), 77.8 (2 C^3, J_{Rh-C} 14.7 Hz), 91.4 p.p.m. (CH of hfpd) [resonances for *C*=O and *C*F_3 were not observed].

(*b*) (*E,E*)-Hepta-2,5-diene (37.3 mg, 0.388 mmol) was reacted with complex (1a) (100 mg, 0.388 mmol) as described in (*a*) to give complex (2b) as an orange oil which did not crystallise from pentane at −78 °C. ^1H N.m.r. ([$^2H_6$]benzene): δ 1.34 (2 × 3 H, H^1, d), 1.75 (2 × 3 H, H^1 of pd, s), 2.04 (1 H, H^4_{exo}, m), 3.00 (2 H, H^2, m, and H^4_{endo}, m), 3.59 (2 H, H^3, m), 5.11 p.p.m. (1 H, H^3 of pd, s).

(*c*) (*E,Z*)-Hepta-2,5-diene was reacted with complex (1b), as described in procedure (*a*), to give a red oil which could not be crystallised. ^1H N.m.r. ($CDCl_3$): δ 1.08 (3 H, H^1, br s at room temp., d at −20 °C), 1.58 (3 H, H^7, d), 2.50 (1 H, H^4_{exo}, m), 3.21 (1 H, H^4_{endo}, dt), 3.25 (2 H, H^6, m, and H^3, m), 4.12 (1 H, H^2, m), 4.30 (1 H, H^5, m), 6.05 p.p.m. (1 H, H^3 of pd, s).

(*d*) (*E,Z*)-Hepta-2,5-diene was reacted with complex (1a) as described in procedure (*b*) to give an orange oil. ^1H N.m.r. ($CDCl_3$): 1.10 (3 H, H^1, d), 1.53 (3 H, H^7, d), 2.40 (1 H, H^4_{exo}, m), 3.00 (1 H, H^6, m), 3.20 (1 H, H^4_{endo}, dt), 3.45 (1 H, H^2, m), 3.85 (1 H, H^3, m), 4.05 (1 H, H^5, m), 5.30 p.p.m. (1 H, H^3 of pd, s).

(*e*) (*Z,Z*)-Hepta-2,5-diene (2 mol equiv.) was reacted with complexes (1b) and (1a), as described in procedures (*a*) and (*b*), respectively. The products were isolated as oils which did not give well resolved ^1H n.m.r. spectra. However, as with Rh^I complexes of (*Z,Z*)-hepta-2,5-dien-4-ol (see below), a characteristic feature was the appearance of multiplets in the alkene region of absorption [*e.g.* ^1H ($CDCl_3$): δ 5.40 and 5.65 p.p.m.].

Thermal Stability of Hepta-2,5-dienes in the Presence of Rh^I.—Treatment of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-hepta-2,5-diene respectively, with either 5 mol% complex (1a) or (1b) at 80 °C in [$^2H_6$]benzene for 72 h did not cause isomerisation of any of these dienes. Heating [(*E,E*)-hepta-2,5-diene](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I) in [$^2H_6$]benzene at 80 °C for 72 h gave an unchanged complex.

Complexation of Allylic Alcohols and Acetoxydienes to Rh[I].—(*a*) (*E*)-Hexa-1,4-dien-3-ol (25 mg, 0.255 mmol) in dry ether was added to complex (1a) (65.6 mg, 0.255 mmol). Removal of solvent gave [(*E*)-hexa-1,4-dien-3-ol](pentane-2,4-dionato)rhodium(I) as an orange oil which could not be crystallised. ^{1}H N.m.r. ($CDCl_3$): δ 1.28 (3 H, H^6, d, *J* 6.2), 1.68 (O–H), 1.92 (2 × 3 H, pd, s), 2.46 (1 H, H^1, d, J_{trans} 12.3), 2.62 (1 H, H^1, d, J_{cis} 7.9), 3.35 (1 H, H^5, m), 3.96 (1 H, H^4, m), 4.13 (1 H, H^2, m), 5.10 (1 H, H^3_{endo}, t, *J* 6.5 Hz), 5.31 p.p.m. (1 H, H^3 of pd, s).

(*b*) The above procedure was repeated using complex (1b) (37.5 mg, 0.1 mmol) and (*E*)-hexa-1,4-dien-3-ol (10 mg, 0.1 mmol), to give [(*E*)-hexa-1,4-dien-3-ol](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I) as a red oil which could not be crystallised. ^{1}H N.m.r. ($CDCl_3$): δ 1.31 (3 H, H^6, d), 1.78 (1 H, O–H), 2.85 (2 H, H^1, m), 3.70 (1 H, H^5, m), 4.26 (1 H, H^4, m), 4.42 (1 H, H^2, m), 5.25 (1 H, H^3, m), 6.12 p.p.m. (1 H, H^3 of hfpd, s) (all signals except H^3 of hfpd were broad, even at − 30 °C).

(*c*) (*E,E*)-Hepta-2,5-dien-4-ol (13.1 mg, 0.12 mmol) was reacted with complex (1b) (44 mg, 0.12 mmol) as described in procedure (*a*) to give [(*E,E*)-hepta-2,5-dien-4-ol](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I) as a red oil. ^{1}H N.m.r. ($CDCl_3$): δ 1.25 (2 × 3 H, H^1, d, *J* 6.2), 1.85 (1 H, O–H), 3.50 (2 H, H^2, m), 4.15 (2 H, H^3, m), 5.20 (1 H, H^4_{endo}, t, *J* 6.5 Hz), 6.10 p.p.m. (1 H, H^3 of hfpd, s) (addition of a further equivalent of dienol produced no change in this spectrum). I.r., $\nu_{max.}$ (2.5%, in CCl_4): 3 610w sp (sp = sharp), 3 050w, 2 950w, 2 910m, 1 620s, 1 606s, 1 555m, 1 462s, 1 378m, 1 348m, 1 255s, 1 206s, 1 150s, 1 100m, 1 070m, 1 036m and 968w cm^{-1}.

(*d*) (*E,E*)-Hepta-2,5-dien-4-ol (13.1 mg, 0.117 mmol) was reacted with complex (1a) (30 mg, 0.117 mmol), as described above to give [(*E,E*)-hepta-2,5-dien-4-ol](pentane-2,4-dionato)-rhodium(I) as an orange oil. ^{1}H N.m.r. ($CDCl_3$): δ 1.25 (2 × 3 H, H^1, d, *J* 6.2), 1.85 (1 H, O–H), 1.87 (2 × 3 H of pd, s), 3.15 (2 H, H^2, m), 3.87 (2 H, H^3, m), 5.13 (1 H, H^4_{endo}, t, *J* 6.5 Hz), 5.30 p.p.m. (1 H, H^3 of pd, s).

(*e*) (*Z,Z*)-Hepta-2,5-dien-4-ol (57.3 mg, 0.512 mmol) in dry ether (1 cm^3) was added to complex (1b) (93.5 mg, 0.255 mmol). The solvent was removed to leave a solid which was recrystallised from ether–pentane to give orange-yellow crystals of bis[(*Z,Z*)-hepta-2,5-dien-4-ol](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I), (3a) (124 mg, 91%), m.p. 118—120 °C (Found: C, 42.75; H, 4.65. $C_{19}H_{25}F_6O_4Rh$ requires C, 42.7; H, 4.65%). ^{1}H N.m.r. ([$^2H_6$]benzene): δ 1.44 (2 × 3 H, H^1, d, *J* 6.5), 1.62 (2 × 3 H, H^7, d, *J* 6.5 Hz), 2.45 (2 H, H^2, m), 2.88 (2 H, H^3, t), 5.15 (2 H, H^4, t), 5.52 (4 H, 2 H^5 + 2 H^6, m), 6.06 (1 H, H^3 of hfpd, s), 6.80 p.p.m. (2 H, br, OH). I.r., $\nu_{max.}$ (0.5% and 2.5%, in CCl_4): 3 270m br, 3 020m (sp), 2 935w, 1 658s, 1 460s, 1 348m, 1 248s, 1 210s, 1 150s, 1 100w, 1 010w, 950w, and 680w cm^{-1}. Mass spectrum (f.i.): *m/z* 534 (M^+), 532, 516, 500.

(*f*) The reaction of (*Z,Z*)-hepta-2,5-dien-4-ol with complex (1a) according to procedure (*e*) gave an orange oil which could not be crystallised. ^{1}H N.m.r. spectroscopy indicated formation of a complex analogous to (3a), but the spectra were ill defined with broad and indistinct resonances.

(*g*) (*E,Z*)-Hepta-2,5-dien-4-ol (31 mg, 0.277 mmol) in dry ether (1 cm^3) was added to complex (1b) (50 mg, 0.137 mmol). Removal of solvent gave orange crystals which were recrystallised from ether–pentane to give bis[(*E,Z*)hepta-2,5-dien-4-ol](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I), (3b) (63 mg, 86%), m.p. 88—89 °C (Found: C, 42.9; H, 4.2. $C_{19}H_{25}F_6O_4Rh$ requires C, 42.7; H, 4.65%). ^{1}H N.m.r. ([$^2H_6$]benzene): δ 1.51 (4 × 3 H, m), 3.03 (2 H, H^2, m), 3.89 (2 H, H^3, m), 4.73 (2 H, H^4, m), 5.48 (4 H, 2 H^5 + 2 H^6, m), 6.02 p.p.m. (1 H, H^3 of hfpd, s). I.r. $\nu_{max.}$ (0.5%, in CCl_4): 3 260br, 3 010w, 2 970m, 2 910m, 1 643s, 1 605s, 1 454s, 1 335m, 1 196m, and 1 155s cm^{-1}. Mass spectrum (relative intensities in parentheses): *m/z* (e.i.) 422 (10), 212 (13). 196 (10), 97 (85), 69 (100); *m/z* (f.i.) 534 (M^+) 532, 516, 500.

(*h*) Allyl alcohol (16 mg, 0.275 mmol) in dry ether (1 cm^3) was added to complex (1b) (50 mg, 0.137 mmol). Removal of solvent gave yellow crystals which were recrystallised from ether–pentane to give (1,1,1,5,5,5-hexafluoropentane-2,4-dionato)bis(prop-2-en-1-ol)rhodium(I), (4a) (51 mg, 87%), m.p. 93—94 °C (Found: C, 31.2; H, 3.05. $C_{11}H_{13}F_6O_4Rh$ requires C, 31.0; H, 3.1%). ^{1}H N.m.r. ([$^2H_6$]benzene): δ 1.96 (2 H, H^3, d, J_{cis} 7.8), 2.87 (2 H, H^2, m), 3.18 (2 H, H^3, d, J_{trans} 13.3 Hz), 3.48 (4 H, H^1, m), 6.07 (1 H, H^3 of hfpd, s), 6.40 p.p.m. (2 H, O–H). I.r., $\nu_{max.}$ (0.5%, in CCl_4): 3 320m br, 3 010w, 2 920w, 1 622m (sp), 1 445m (sp), 1 258s (sp), 1 220s (sp), 1 160s, 1 100m (sp), 1 018m (sp), 995w (sp), and 685w (sp) cm^{-1}. Mass spectrum: *m/z* (e.i.) 368 (12), 208 (7), 139 (100), 69 (99); *m/z* (f.i.) 426 (M^+).

(*i*) But-3-en-2-ol (20 mg, 0.277 mmol) was reacted with complex (1b) (50 mg, 0.136 mmol) as described for allyl alcohol. The crude product was recrystallised from ether–pentane to give yellow crystals of bis(but-3-en-2-ol)(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I), (4b) (51 mg, 82%), m.p. 117 °C (decomp.) (Found: C, 34.5; H, 3.8. $C_{13}H_{19}F_6O_4Rh$ requires C, 34.4; H, 3.75%). ^{1}H N.m.r. ([$^2H_6$]-benzene): δ 1.18 (2 × 3 H, H^1, d, *J* 6.6), 1.90 (2 H, H^4, J_{cis} 7.8), 2.80 (2 H, H^3, m), 3.18 (2 H, H^4, d, J_{trans} 13.3 Hz), 3.86 (2 H, H^2, m), 6.20 (1 H, H^3 of hfpd, s), 6.80 p.p.m. (2 H, O–H). I.r., $\nu_{max.}$ (0.5%, in CCl_4): 3 320m br, 3 005w, 1 930s, 1 630m, 1 450m (sp), 1 225s, 1 165s, 1 000m, and 996w cm^{-1}. Mass spectrum: *m/z* (e.i.) 382 (3), 208 (8), 139 (100), 69 (62).

(*j*) (*Z*)-But-2-en-1,4-diol (24 mg, 0.273 mmol) in ether–acetone (3 : 1, v/v) was added to complex (1b) (50 mg, 0.137 mmol). An orange precipitate was formed and was collected by filtration. Washing of this solid with ether gave yellow crystals of bis[(*Z*)-but-2-en-1,4-diol](1,1,1,5,5,5-hexafluoropentane-2,4-dionato)rhodium(I), (4c) (56 mg, 84%), m.p. 113—114 °C (Found: C, 32.5; H, 3.6. $C_{13}H_{17}F_6O_6Rh$ requires C, 31.1; H, 3.55%). ^{1}H N.m.r. ([$^2H_6$]acetone): δ 2.87 (3 H, O–H), 3.22 (4 H, 2 H^2 + 2 H^3, m), 3.68 (4 H, H^1, dd, $J_{gem.}$ 12.7, $J_{1,2}$ 5.1 Hz), 4.14 (4 H, $H^{1'}$, m), 4.29 (1 H, O–H), 6.20 p.p.m. (1 H, H^3 of hfpd, s). I.r., $\nu_{max.}$ (0.5%, in CCl_4): 3 360m br, 1 630m, 1 270s, 1 215s, 1 160s, and 765s cm^{-1}. Mass spectrum: *m/z* (e.i.) 398 (7), 381 (14), 209 (17), 139 (75), 69 (100).

(*k*) (*E,E*)-4-Acetoxyhepta-2,5-diene (21 mg, 0.137 mmol) in dry ether (1 cm^3) was added to complex (1b) (50 mg, 0.137 mmol). Removal of the solvent gave a red oil. ^{1}H N.m.r. ($CDCl_3$): δ 1.24 (2 × 3 H, H^1, d, *J* 6.5), 1.93 (3 H, s), 3.44 (2 H, H^2, m), 4.11 (2 H, H^3, m), 5.90 (1 H, H^4, t, *J* 6.5 Hz), 6.12 p.p.m. (1 H, H^3 of hfpd, s). I.r., $\nu_{max.}$ (2%, in CCl_4): 3 020w, 2 970w, 2 920w, 1 855w, 1 742m (C=O stretch, unchanged from free acetoxydiene), 1 625m, 1 550m, 1 420m, 1 268s, 1 222s, 1 155s, 1 095w, 1 028m, and 963w cm^{-1}.

(*l*) (*E*)-3-Acetoxyhexa-1,4-diene (10 mg, 71.4 μmol) was reacted with complex (1b) (26.1 mg, 71.4 μmol) as described in procedure (*k*) to give a red oil. ^{1}H N.m.r. ($CDCl_3$): δ 1.26 (3 H, H^6, d, *J* 6.5), 1.94 (3 H, s), 2.69 (1 H, H^1, d, J_{trans} 12.5), 2.85 (1 H, H^1, d, J_{cis} 8.0 Hz), 3.59 (1 H, H^5, m), 4.19 (1 H, H^4, m), 4.35 (1 H, H^2, m) 5.90 (1 H, H^3, t), 6.14 p.p.m. (1 H, H^3 of hfpd, s).

(*m*) (*E*)-3-Acetoxyhexa-1,4-diene was reacted with complex (1a) as described in procedure (*k*) to give an orange oil. ^{1}H N.m.r. ($CDCl_3$): δ 1.28 (3 H, H^6, d, *J* 6.6), 1.93 (2 × 3 H, pd, s), 2.40 (1 H, H^1, d, J_{trans} 12.5), 2.65 (1 H, H^1, d, J_{cis} 8.0 Hz), 3.30 (1 H, H^5, m), 3.92 (1 H, H^4, m), 4.09 (1 H, H^2, m), 5.32 (1 H, H^3 of pd, s), 5.86 p.p.m. (1 H, H^3, t). Note: reactions between (*E,E*)-4-acetoxyhepta-2,5-diene and com-

plex (1a) caused isomerisation of the diene. This also occurred in the reactions of (*E*,*Z*)- and (*Z*,*Z*)-4-acetoxyhepta-2,5-dienes with both complex (1a) and (1b).

Rh^{I}-*induced Thermal Rearrangements of* 3-*Acetoxy*-1,4-*dienes and* 4-*Acetoxy*-2,5-*dienes, and of Dienols*.—(*a*) (*E*,*E*)-4-Acetoxyhepta-2,5-diene (0.5 g, 3.25 mmol) in dry benzene (5 cm^3) was maintained at 80 °C in the presence of 5 mol % of complex (1a) (41 mg, 0.15 mmol). After 4 h the ^{1}H n.m.r. spectrum indicated complete reaction. Fractional distillation gave the following compounds. (*i*) (*E*,*E*)-1,3,5-Heptatriene, b.p. 111—113 °C (lit.,[21] 114—115 °C) (143 mg, 55%). ^{1}H N.m.r. ([^{2}H$_6$]benzene): δ 1.53 (3 H, H^7, d, *J* 6.5), 4.96 (1 H, H^1, d, J_{cis} 10), 5.10 (1 H, H^1, d, J_{trans} 17 Hz), 5.48 (1 H, H^6, m), 6.10 (3 H, m), 6.30 p.p.m. (1 H, m). U.v., $\lambda_{max.}$ (hexane): 248 (ε 34 000), 260 (ε 46 500), 269 nm (ε 38 000 dm^3 mol^{-1} cm^{-1}) (for comparable published data see ref. 21). (*ii*) (*E*,*E*)-2-Acetoxyhepta-3,5-diene * (200 mg, 45%). ^{1}H N.m.r. ($CDCl_3$): δ 1.31 (3 H, H^1, d, *J* 6), 1.75 (3 H, H^7, d, *J* 6.5), 2.00 (3 H, s), 5.35 (1 H, H^2, m, $J_{2,3}$ 6), 5.50 (1 H, H^3, dd, $J_{3,4}$ 15.5, $J_{2,3}$ 6), 5.73 (1 H, H^6, dq, $J_{5,6}$ 15.5, $J_{6,7}$ 6.5), 6.00 (1 H, H^5, dd, $J_{4,5}$ 10.5, $J_{5,6}$ 15.5), 6.19 p.p.m. (1 H, H^4, dd, $J_{3,4}$ 15.5, $J_{4,5}$ 10.5 Hz). I.r. $\nu_{max.}$ (film): 3 020m (sp), 2 965s, 2 910m, 1 855m, 1 730s, 1 652m, 1 443m, 1 365s, 1 230s, 1 142m, 1 042s, 990s, 945s, and 830w cm^{-1}. U.v., $\lambda_{max.}$ (hexane) 227 nm (ε 27 900 dm^3 mol^{-1} cm^{-1}). Mass spectrum: *m*/*z* (e.i.) 154 (M^+, 6), 112 (14), 95 (84), 79 (49), 42 (100).

(*b*) (*E*,*Z*)-4-Acetoxyhepta-2,5-diene was thermolysed with 5 mol % complex (1a) in [^{2}H$_6$]benzene as described in (*a*). After 24 h, ^{1}H n.m.r. spectroscopy indicated complete reaction to give (*E*,*Z*)- and (*E*,*E*)-2-acetoxyhepta-3,5-diene (3 : 2). ^{1}H N.m.r. ($CDCl_3$): for (*E*,*E*) isomer see (*a*); for (*E*,*Z*) isomer, δ 1.31 (3 H, H^1, d, *J* 6), 1.78 (3 H, H^7, d), 2.00 (3 H, s), 5.32 (1 H, H^2, m), 5.50 (1 H, H^3, dd, $J_{3,4}$ 15.5, $J_{2,3}$ 6), 5.70 (1 H, H^6, dq, $J_{5,6}$ 11, $J_{6,7}$ 7.5), 6.08 (1 H, H^5, dd, $J_{4,5}$ 10.5, $J_{5,6}$ 11), 6.62 p.p.m. (1 H, H^4, dd, *J* 15.5 and 10.5 Hz). See section (*c*) below for i.r., u.v., and mass spectral data.

(*c*) Treatment of (*Z*,*Z*)-4-acetoxyhepta-2,5-diene with 5 mol % complex (1a) and thermolysis in benzene for 50 h gave (*E*,*Z*)-2-acetoxyhepta-3,5-diene, b.p. 85—87 °C at 2 mmHg. ^{1}H N.m.r. ($CDCl_3$): see (*b*). I.r., $\nu_{max.}$ (film): 3 020m, 2 970s, 2 935s, 1 735s, 1 438m, 1 365s, 1 228s, 1 160m (sp), 1 123m (sp), 1 025s (sp), 993s (sp), 940s (sp), 845w (sp), and 720m cm^{-1}. U.v., $\lambda_{max.}$ (hexane) 228 nm (ε 23 300 dm^3 mol^{-1} cm^{-1}). Mass spectrum: *m*/*z* (e.i.) 154 (M^+, 16), 112 (24), 95 (39), 79 (100), 43 (85).

(*d*) (*E*)-Hexa-1,4-dien-3-ol (0.3 g, 3.1 mmol) in dry benzene (5 cm^3) was thermolysed with 5 mol % complex (1b) (56 mg, 0.15 mmol) at 80 °C. After 60 h, ^{1}H n.m.r. spectroscopy indicated that the reaction was complete and had given one product. Distillation gave (*E*)-hex-2-en-4-one (0.27 g, 90%) (spectral properties identical to those of an authentic sample).

(*e*) (*E*,*E*)-Hepta-2,5-dien-4-ol (60 mg, 0.536 mmol) was thermolysed with 5 mol % complex (1b) (7 mg, 26.8 μmol) in [^{2}H$_6$]benzene at 80 °C. After 12 h, distillation gave (*E*)-hept-2-en-4-one (85%) and (*E*,*E*)-hepta-2,5-dien-4-one (15%) (both compounds identified by spectral comparison with authentic samples).

(*f*) Treatment of (*E*,*Z*)-hepta-2,5-dien-4-ol with 5 mol % complex (1b) as in (*e*) gave after 12 h at 80 °C, a mixture containing *ca.* 85% (*E*)- and *ca.* 15% (*Z*)-hept-2-en-4-one. A prolonged reaction (36 h) gave 85% (*E*)-hept-2-en-4-one and 15% (*E*,*E*)-hepta-2,5-dien-4-one (identical to authentically prepared samples).

(*g*) Treatment of (*Z*,*Z*)-hepta-2,5-dien-4-ol with 5 mol % complex (1b) as described in (*e*) gave only 20% reaction after 3 d at 80 °C, the major product being (*Z*)-hept-2-en-4-one (identical to an authentically prepared sample).

* Spectroscopically identical to a sample prepared from hexa-2,4-dienal and MgMeBr, followed by acetylation.

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References

1 R. Cramer, *J. Am. Chem. Soc.*, 1967, **89**, 4621.
2 M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Chem. Soc., Dalton Trans.*, 1973, 1484, 2195.
3 M. Arthurs, S. M. Nelson, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1977, 779.
4 M. Arthurs, M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Chem. Soc., Dalton Trans.*, 1975, 1794; M. Arthurs, C. M. Regan, and S. M. Nelson, *ibid.*, 1980, 2053.
5 (*a*) 'Fatty Acids,' ed. E. H. Pryde, American Oil Chemists Society (A.O.C.S.), Champagne, Illinois, 1979; (*b*) 'Geometrical and Positional Fatty Acid Isomers,' eds. E. A. Emken and H. J. Dutton, A.O.C.S. Monograph, 1979; (*c*) 'Polyunsaturated Fatty Acids,' eds. W. H. Kunau and R. T. Holman, A.O.C.S. Monograph, 1979.
6 J. Ackroyd and F. Scheinmann, *Chem. Soc. Rev.*, 1982, **11**, 321; R. F. Newton and S. M. Roberts, *Ann. Rep. Prog. Chem., Sect. B*, 1981, **78**, 347 and refs. therein.
7 P. Van der Plank and H. J. Van Oosten, *J. Am. Oil Chem. Soc.*, 1979, **56**, 54; P. Van der Plank, A. Van der Ent, A. L. Onderlinden, and H. J. Van Oosten, *ibid.*, 1980, **57**, 343.
8 J. A. Evans and D. R. Russell, *Chem. Commun.*, 1971, 197.
9 (*a*) M. Arthurs, M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Chem. Soc., Dalton Trans.*, 1975, 1794; (*b*) J. M. Brown and D. G. Coles, *J. Organomet. Chem.*, 1973, **60**, C31; (*c*) R. Grigg, B. Kongkathip, and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1978, 333.
10 K. R. Aris, V. Aris, and J. M. Brown, *J. Organomet. Chem.*, 1972, **42**, C67.
11 M. Herberhold, C. G. Kreiter, and G. O. Widersatz, *J. Organomet. Chem.*, 1976, **120**, 103.
12 P. Powell and L. J. Russell, *J. Chem. Res.*, 1978, (*M*) 3652.
13 R. B. King, F. G. A. Stone, and R. A. Manuel, *J. Inorg. Nucl. Chem.*, 1961, **16**, 233.
14 B. R. James, *Adv. Organomet. Chem.*, 1979, **17**, 319; R. Spogliarich, G. Zassinovick, G. Mestroni, and M. Graziani, *J. Organomet. Chem.*, 1980, **198**, 81.
15 J. M. Brown, B. T. Golding, and J. J. Stofko, *J. Chem. Soc., Perkin Trans. 2*, 1978, 436; V. Aris, J. M. Brown, and B. T. Golding, *ibid.*, 1974, 700.
16 B. T. Golding, C. Pierpoint, and R. Aneja, *J. Chem. Soc., Chem. Commun.*, 1981, 1030.
17 R. Cramer, *Inorg. Synth.*, 1974, **15**, 14.
18 E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1951, 2078, 2085; N. Boccara and P. Maitte, *Bull. Soc. Chim. Fr.*, 1972, 1448; K. G. Migliorese, V. Tanaka, and S. I. Miller, *J. Org. Chem.*, 1974, **39**, 739; J. I. Dickstein and S. I. Miller, in 'Chemistry of the Carbon–Carbon Triple Bond,' ed. S. Patai, Wiley, New York, 1978, ch. 19.
19 R. Aneja, B. T. Golding, and C. Pierpoint, unpublished work.
20 G. Ingrosso and L. Porri, *J. Organomet. Chem.*, 1975, **84**, 75.
21 C. W. Spangler and G. F. Woods, *J. Org. Chem.*, 1965, **30**, 2218; C. W. Spangler, T. P. Jondahl, and B. Spangler, *ibid.*, 1973, **38**, 2478.

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