

Rhodium(I) Complexes of Diallyl Ethers and Related Compounds

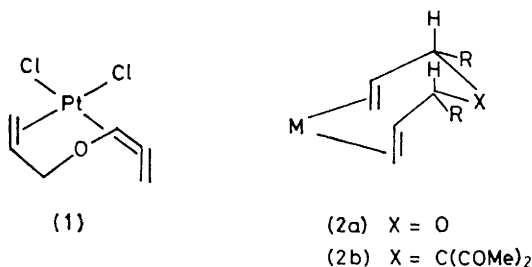
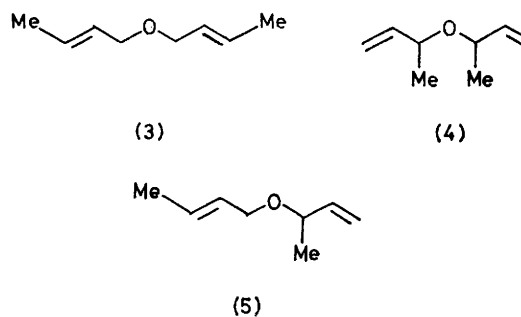
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The preparation of a range of stable diallyl ether complexes of Rh^{I} by displacement of ethylene from $[\text{Rh}(\text{C}_2\text{H}_4)_2(\text{pd})]$ (pd = pentane-2,4-dionate) is described. A number of related rhodium(I) complexes of diallyl amines, allyl acrylate, diallyl sulphone, and 4,4-diacetylhepta-1,6-diene are also reported. The complexes are characterised by spectroscopic methods, and an X-ray crystal structure of (but-2-enyl 1-methylallyl ether)pentane-2,4-dionato-rhodium is reported.

In connection with studies of reactions of diallyl ethers catalysed by transition-metal complexes it became necessary to study the preparation and relative stability of rhodium(I) complexes of diallyl ethers. There are few reports of transition-metal complexes of diallyl ethers apart from a platinum(II) complex of diallyl ether which is obtained from the reaction of either allyl alcohol or diallyl ether with $\text{K}_2[\text{PtCl}_4]$.^{1,2} N.m.r. studies of this complex were interpreted in favour of structure (1) rather than (2a; $\text{M} = \text{PtCl}_2$, $\text{R} = \text{H}$),² but subsequent chemical³ and X-ray structural⁴ studies established (2a; $\text{M} = \text{PtCl}_2$, $\text{R} = \text{H}$ or Me) as the structure of the complexes. Complexes of this type are involved in the hexachloroplatinic(IV) acid-catalysed formation of alkyl allyl and diallyl ethers from the corresponding alcohols.⁵ In contrast, cationic platinum(II) complexes [e.g. $[\text{PtH}(\text{PPh}_3)_2][\text{ClO}_4]$] cause cleavage of diallyl ethers, e.g. diallyl ether gives the η -allyl complex $[\text{Pt}(\text{PPh}_3)_2(\text{C}_3\text{H}_5)]$ -

unsuccessful with cinnamyl alcohol, giving only polymeric material.



$[\text{ClO}_4]$ and propionaldehyde.⁶ The chloro-bridged iridium(I) complex $[\text{Ir}_2(\text{cod})_2\text{Cl}_2](\text{cod} = \text{cyclo-octa-1,5-diene})$ has been reported to form an η -complex with 2 mol of diallyl ether.⁷

RESULTS AND DISCUSSION

Diallyl ethers required for this work were prepared by a modified Williamson synthesis or by the hexachloroplatinic(IV) acid catalytic method. The latter method with but-2-enyl alcohol gave a mixture of all three possible ethers (3)—(5) (4 : 3 : 13) together with a small amount of the platinum(II) complex (2a; $\text{M} = \text{PtCl}_2$, $\text{R} = \text{Me}$). The ethers (3)—(5) were separated by spinning-band distillation. The H_2PtCl_6 method was

Diallyl ethers were found to readily form complexes with $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$, and with $[\text{Rh}(\text{C}_2\text{H}_4)_2(\text{pd})]$ (pd = pentane-2,4-dionate) by displacement of ethylene. The latter complexes, e.g. (diallyl ether)pentane-2,4-dionato-rhodium, were most suitable for our purposes and are conveniently prepared in n-pentane at room temperature. The reaction time (10—24 h) depends on the substitution pattern of the diallyl ether (Table 1). A series of related complexes of diallyl amines, diallyl sulphone, allyl acrylate, and 4,4-diacetylhepta-1,6-diene were also prepared (Table 1). Diallyl sulphide and diallyl sulphoxide also gave complexes but we were unable to purify these sufficiently. In all cases the bidentate organic ligands are 1,6-dienes and we found no evidence of double-bond isomerisation.

The complexes (Table 1) are all monomeric and were characterised by elemental analysis and by n.m.r., i.r., and mass spectroscopy. The co-ordination of diallyl ethers to $[\text{Rh}(\text{C}_2\text{H}_4)_2(\text{pd})]$ with displacement of ethylene is thought to involve initial co-ordination to the coordinatively unsaturated $[\text{Rh}(\text{C}_2\text{H}_4)_2(\text{pd})]$ giving (6), or, less likely, (7) followed by loss of ethylene resulting in (8) or (9). Repetition of this process then leads to (diallyl ether)pentane-2,4-dionato-rhodium. Displacement of ethylene from $[\text{Rh}(\text{C}_2\text{H}_4)_2(\text{pd})]$ by dienes and other olefins is well known and involvement of the ether oxygen atom is therefore not a necessary condition for the reaction. In the case of bis(methylallyl) ether an intermediate complex (10) was isolated on one occasion and

¹ K. A. Jensen, *Acta Chem. Scand.*, 1953, **7**, 866; Y. N. Kukushkin, I. V. Pakhomova, and N. V. Ivannikova, *Zhur. neorg. Khim.*, 1970, **15**, 1590.

² R. Jones, *J. Chem. Soc. (A)*, 1969, 2477.

³ J. Hubert, A. L. Beauchamp, and T. Theophanides, *Canad. J. Chem.*, 1973, **51**, 604.

⁴ E. Benedetti, A. Derenzi, A. Panuzi, and C. Pedone, *J. Organometallic Chem.*, 1972, **39**, 403.

⁵ J. Milgrom and W. H. Urry, U.S.P. 3,173,958/1965.

⁶ H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 1973, **12**, 353, 1566.

⁷ G. Pannetier, R. Bonnaire, and P. Fougereux, *J. Organometallic Chem.*, 1971, **30**, 411.

characterised by n.m.r. and mass spectroscopy. Related rhodium complexes have been isolated by other workers.⁸

There are two possible modes of bidentate co-ordination of diallyl ethers to the rhodium analogous to those of (1) and (2a) considered for platinum. The preferred

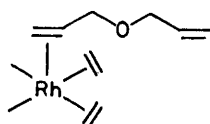
ever, the n.m.r. spectra of the rhodium complexes show no evidence for such equilibria and the X-ray structures of the platinum⁴ and rhodium complexes (see below) show that the oxygen is not bonded to the metal. The problem of the structure of the rhodium(I) diallyl ether

TABLE I
Analytical data for [Rh(diene)(pd)] complexes

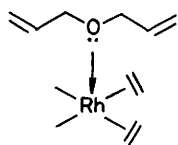
Diene	Reaction time (t/h)	Colour	M.p. (θ _c /°C)	Solvent for recrystallisation	Analysis (%)				Yield (%)
					Found		Calc.		
					C	H	C	H	
Diallyl ether	10	yellow	130	pentane	44.25	5.65	44.0	5.7	56.3
Allyl but-2-enyl ether	24	yellow	81	^a					69.9
Allyl 2-methylallyl ether	10	yellow-orange	132	pentane (sublimation)	46.1	6.1	45.90	6.1	89.0
Bis(but-2-enyl) ether	10	yellow-orange	160	^a					66.5
But-2-enyl 2-methylallyl ether	12	yellow-orange	163	pentane	47.85	6.25	47.6	6.45	78.5
But-2-enyl 1-methylallyl ether	12	yellow	112	pentane	47.75	6.55	47.6	6.45	77.6
Bis(1-methylallyl) ether	12	yellow	139	pentane	47.95	6.2	47.6	6.45	50.0
Allyl cinnamyl ether	12	red	132	pentane	54.55	5.5	54.4	5.35	96.7
But-2-enyl cinnamyl ether	12	red	145	pentane	55.55	5.85	55.4	5.95	49.4
Cinnamyl 2-methylallyl ether	12	red	144	pentane	55.4	6.05	55.4	5.95	89.3
Dicinnamyl ether	10	red	177	hexane	61.2	5.65	61.1	5.55	100
Diallylamine ^b	12	yellow	125 (decomp.)	sublimation	44.15	6.00	44.15	6.05	89.0
Diallyl(2,3-epoxypropyl)amine ^c	12	yellow	120 (decomp.)	pentane	47.35	6.4	47.35	6.25	83.6
Diallyl sulphone ^c	12	red	188 (decomp.)	acetone	37.95	4.9	37.95	4.9	97.8
Allyl acrylate	12	red	158 (decomp.)	acetone	42.05	4.95	42.05	4.8	71.7
Diallyl(methyl)amine ^d	24	yellow	157–158 (decomp.)	pentane	45.9	6.40	46.0	6.45	75.0
4,4-Diacetylhepta-1,6-diene	24	orange	130–131	pentane	50.55	6.0	50.25	6.0	70.0

^a Attempts to crystallise or sublime this complex were unsuccessful. ^b Found: N, 4.7. Calc.: 4.7%. ^c Found: N, 3.95. Calc.: 3.95%. ^d Found: N, 4.5. Calc.: 4.45%. ^e Found: S, 9.35. Calc.: 9.35%.

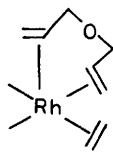
mode of co-ordination to platinum is firmly established as (2a).^{3,4} Olefin rotation⁹ about the square-planar platinum atom in (2a; M = PtCl₂) is precluded by the geometrical constraints of the ligand, but there is a



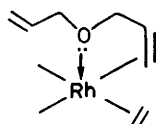
(6)



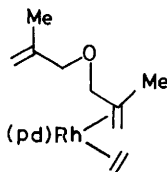
(7)



(8)



(9)



(10)

possibility that the presence of the ether oxygen atom as a potential donor atom might promote interconversion of both the complexes of platinum, (1) \rightleftharpoons (2a) (M = PtCl₂), and the corresponding rhodium analogues since both types of complexes are 16-electron systems. How-

⁸ M. G. B. Drew, S. M. Nelson, and M. Sloan, *J.C.S. Dalton*, 1973, 1484.

complexes was resolved by a single-crystal X-ray structure of the rhodium(I) complex of (5).

Crystal-structure Determination.—Cell parameters were first found from oscillation and Weissenberg photographs and then by least squares from the setting angles of 20 reflections on a Hilger-Watt four-circle diffractometer.

Crystal data. C₁₃H₂₁O₃Rh, *M* = 328.1, Monoclinic, *a* = 11.607(2), *b* = 16.878(3), *c* = 7.068(2) Å, β = 95.85(1)°, *U* = 1 377.4 Å³, *D*_c = 1.582 g cm⁻³, *Z* = 4, *D*_m = 1.57 g cm⁻³, *F*(000) = 692, space group *P*2₁/*c* from systematic absences, Mo-*K*_α radiation (graphite monochromator), λ = 0.710 69 Å, μ = 12.02 cm⁻¹.

Reflections were scanned (ω-2θ mode) for θ ≤ 25°. 1 988 Reflections in this range had a net count ≥ σ and were deemed observed. Lorentz polarisation, but not absorption, corrections were made. The structure was solved routinely by the heavy-atom method, and refined by full-matrix least squares. In the later stages of refinement all the hydrogen atoms were located on a difference map and included in the calculations with *U* = 0.05, but were not refined. The weighting scheme used in the final stages of refinement was *w* = 1 for reflections with *F*_o ≤ 45.0 and *w* = (45.0/*F*_o)² for stronger reflec-

⁹ C. E. Holloway, G. Hulley, B. F. G. Johnston, and J. Lewis, *J. Chem. Soc. (A)*, 1970, 1653; R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217; 1969, **91**, 2519; J. Kriz and K. Bouchal, *J. Organometallic Chem.*, 1974, **64**, 255; H. Alt, M. Herberhold, C. G. Kreiter, and H. Strack, *ibid.*, vol. **77**, p. 353; J. W. Faller and B. V. Johnson, *ibid.*, 1975, **88**, 101.

tions. At convergence the maximum positional shift was 0.03σ and R was 0.045 .

TABLE 2

Fractional co-ordinates with standard deviations in parentheses for (but-2-enyl 1-methylallyl ether)pentane-2,4-dionatorrhodium

Atom	x/a	y/b	z/c
Rh(1)	0.215 50(4)	0.062 59(3)	0.113 61(6)
C(1)	0.016 2(6)	0.164 0(4)	-0.079 1(8)
C(2)	0.142 7(6)	0.150 3(4)	-0.076 5(9)
C(3)	0.225 5(6)	0.185 6(4)	0.047 4(9)
C(4)	0.345 0(6)	0.208 2(5)	0.004 1
C(5)	-0.039 6(6)	0.102 6(4)	0.200 5(9)
C(6)	0.070 3(5)	0.060 8(4)	0.271 8(9)
C(7)	0.163 6(6)	0.097 9(4)	0.378 0(9)
C(8)	-0.111 7(6)	0.121 8(5)	0.359 1
C(9)	0.430 2(7)	-0.034 3(5)	-0.296 1
C(10)	0.364 4(6)	-0.030 8(5)	-0.122 1
C(11)	0.364 7(6)	-0.095 3(4)	-0.005 1
C(12)	0.310 0(6)	-0.100 9(4)	0.162 1
C(13)	0.316 7(8)	-0.177 9(5)	0.272 1
O(1)	-0.020 7(4)	0.176 1(2)	0.103 9(6)
O(2)	0.312 5(4)	0.034 6(3)	-0.105 4(7)
O(3)	0.252 4(4)	-0.046 5(2)	0.234 0(6)
HA(1)	-0.029 6	0.116 3	-0.135 0
HB(1)	-0.002 1	0.206 6	-0.160 6
H(2)	0.166 2	0.124 6	-0.194 0
H(3)	0.203 7	0.212 3	0.172 0
HA(4)	0.402 4	0.199 4	0.119 0
HB(4)	0.352 7	0.271 1	-0.026 9
HC(4)	0.388 0	0.182 8	-0.095 5
H(5)	-0.088 3	0.061 1	0.117 3
H(6)	0.048 6	0.001 6	0.300 7
HA(7)	0.215 5	0.062 9	0.470 3
HB(7)	0.155 9	0.155 1	0.392 4
HA(8)	-0.127 7	0.068 6	0.441 7
HB(8)	-0.057 9	0.156 9	0.449 2
HC(8)	-0.190 3	0.145 4	0.317 8
HA(9)	0.449 3	0.017 1	-0.339 9
HB(9)	0.370 8	-0.058 7	-0.394 3
HC(9)	0.499 2	-0.062 8	-0.303 6
H(11)	0.405 8	-0.141 2	-0.047 0
HA(13)	0.378 9	-0.210 3	0.220 9
HB(13)	0.343 0	-0.163 3	0.408 1
HC(13)	0.240 0	-0.214 1	0.272 0

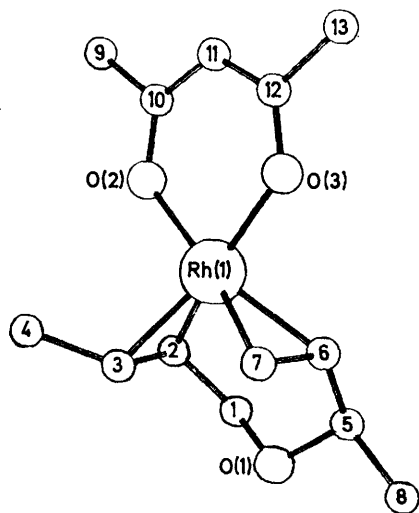


FIGURE 1 Perspective drawing and crystallographic numbering of (but-2-enyl 1-methylallyl ether)pentane-2,4-dionatorrhodium

Table 2 shows the fractional co-ordinates of the atoms, and Table 3 the bond lengths and angles not involving hydrogen. Figure 1 is a perspective drawing of the

molecule * and shows the crystallographic numbering. A list of observed and calculated structure factors, the thermal parameters of the non-hydrogen atoms, and the bond lengths and angles involving hydrogen are available as Supplementary Publication No. SUP 22166 (21 pp.).† All the computations were carried out using the Oxford CRYSTALS package.‡

The structure of the rhodium complex (Figure 1) is thus analogous to that of the related platinum complex (2a; $M = \text{PtCl}_2$, $R = \text{Me}$). The rhodium atom, the

TABLE 3

Bond lengths (Å) and angles (°) not involving hydrogen, with standard deviations in parentheses

Rh(1)-O(2)	2.061(4)	C(12)-C(13)	1.514(10)
Rh(1)-O(3)	2.055(4)	C(12)-O(3)	1.274(8)
Rh(1)-C(2)	2.116(6)	O(1)-C(1)	1.419(7)
Rh(1)-C(3)	2.135(6)	O(1)-C(5)	1.444(7)
Rh(1)-C(6)	2.116(6)	C(1)-C(2)	1.484(9)
Rh(1)-C(7)	2.108(6)	C(2)-C(3)	1.368(9)
O(2)-C(10)	1.269(8)	C(3)-C(4)	1.500(9)
C(10)-C(9)	1.516(10)	C(5)-C(6)	1.459(9)
C(10)-C(11)	1.368(11)	C(5)-C(8)	1.503(9)
C(11)-C(12)	1.397(10)	C(6)-C(7)	1.400(9)
O(2)-Rh(1)-O(3)	90.0(2)	C(1)-C(2)-C(3)	124.7(6)
O(2)-Rh(1)-C(3)	90.7(2)	O(1)-C(1)-C(2)	113.7(5)
O(2)-Rh(1)-C(6)	84.1(2)	C(1)-O(1)-C(5)	112.4(5)
O(2)-Rh(1)-C(7)	156.9(2)	O(1)-C(5)-C(6)	113.5(5)
O(2)-Rh(1)-C(10)	163.6(2)	O(1)-C(5)-C(8)	106.9(5)
C(3)-Rh(1)-C(2)	37.5(3)	C(6)-C(5)-C(8)	111.8(5)
C(3)-Rh(1)-C(6)	101.2(2)	Rh(1)-C(6)-C(5)	120.8(4)
C(3)-Rh(1)-C(7)	86.9(3)	Rh(1)-C(6)-C(7)	70.4(4)
C(3)-Rh(1)-O(3)	161.6(2)	C(5)-C(6)-C(7)	123.6(6)
C(2)-Rh(1)-C(6)	93.3(2)	Rh(1)-C(7)-C(6)	70.9(4)
C(2)-Rh(1)-C(7)	103.5(3)	Rh(1)-O(2)-C(10)	124.7(5)
C(2)-Rh(1)-O(3)	160.5(2)	O(2)-C(10)-C(9)	113.1(7)
C(6)-Rh(1)-C(7)	38.7(3)	O(2)-C(10)-C(11)	127.6(6)
C(6)-Rh(1)-O(3)	84.9(2)	C(9)-C(10)-C(11)	119.3(7)
C(7)-Rh(1)-O(3)	87.3(2)	C(10)-C(11)-C(12)	126.2(6)
Rh(1)-C(3)-C(4)	111.4(5)	C(11)-C(12)-C(13)	119.2(6)
Rh(1)-C(3)-C(2)	70.5(4)	C(11)-C(12)-O(3)	126.4(7)
C(2)-C(3)-C(4)	125.7(6)	C(13)-C(12)-O(3)	114.4(7)
Rh(1)-C(2)-C(3)	72.0(4)	Rh(1)-O(3)-C(12)	125.1(4)
Rh(1)-C(2)-C(1)	116.5(4)		

oxygen atoms of the pd ligand, and the midpoints of the double bonds are planar with no atom deviating by $>0.03 \text{ \AA}$ from the mean plane. The C(2)-C(3) and C(6)-C(7) bond lengths [1.368(9) and 1.400(9) Å] lie within the range 1.358(9)–1.44(7) Å found for coordinated double bonds in related systems,¹⁰ and both double bonds are approximately perpendicular to the plane of co-ordination with the Rh-C(2)-C(3) and Rh-C(6)-C(7) planes at an angle of 97.3° . The angle between the Rh-C(2)-C(3) plane and the plane of co-ordination is 81.2° , whilst the angle between the Rh-C(6)-C(7) plane and the plane of co-ordination is 86.4° .

Hydrogen-1 N.M.R. Spectra.—The spectra of the

* Program PLUTO, Cambridge Data Centre, W. D. S. Motherwell, personal communication

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

‡ W. R. Carruthers, personal communication.

¹⁰ J. A. Ibers and R. G. Snyder, *Acta Cryst.*, 1962, **15**, 923; L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, 1965, **42**, 2683; J. Coetzer and G. Gafner, *Acta Cryst.*, 1970, **B26**, 985; L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, 1972, **94**, 3779.

diallyl ether complexes are collected in Table 4. Assignments are made on the basis of published data on related olefin complexes. In all cases of complexes of unsymmetrical diallyl ethers the two methyl groups of the pd ligand give separate signals. The ^1H n.m.r. spectrum



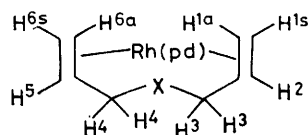
(11a) X = O

(11b) X = C(COMe)₂

of the rhodium(I) complex of 4,4-diacetylhepta-1,6-diene was of interest in that the methyl signals for the two

However, conformer [2b; M = Rh(pd), R = H] is analogous to the solid-state conformations found for (2a; M = PtCl₂, R = Me) and our rhodium complex (Figure 1), and models suggest that conformer [2b; M = Rh(pd), R = H] maximises the difference in proximity of the 'axial' and 'equatorial' protons of the methylene groups to the rhodium. The large difference in chemical shift of the methylene protons (τ 7.30 and 8.94) may be due to a conformational preference for [2b; M = Rh(pd); R = H] or may be due to an unsymmetrical shielding effect of the acetyl groups on the neighbouring protons.¹¹ In contrast to the 4,4-diacetylhepta-1,6-diene complex, the protons of the methylene groups of the diallyl ether complexes are very similar in chemical shift (Table 4) and here again an analogous conformational equilibrium [2a; M = Rh(pd)] \rightleftharpoons (11a) is possible.*

TABLE 4
Proton chemical shifts (τ) for [Rh(diene)(pd)] complexes in CDCl₃



Diene	X					pd	
		H ^{1a} , H ^{6a}	H ^{1s} , H ^{6s}	H ² , H ⁵	H ³ , H ⁴	H	Me
Diallyl ether	O	7.54(d)	6.36	6.10(brm)	6.36	4.70	8.02
Allyl but-2-enyl ether	O	7.77(d)	6.50	6.10	6.36	4.75	8.08
Allyl 2-methylallyl ether	O	6.89	8.40(d)(Me)	6.26			8.10
		7.30(m)	6.40—	6.40—	6.30(dd)	4.75	8.02
Bis(but-2-enyl) ether	O	7.57	6.80(m)	6.80(m)			8.04
		7.13(m)	8.36(d)(Me)	6.24(m)	6.30(m)	4.75	8.04
But-2-enyl 2-methylallyl ether	O	6.64	6.70	6.70	6.30	4.78	8.08
		7.82(s)	8.65(d)(Me)	8.45(s)(Me)	6.70(dd)		8.10
But-2-enyl 1-methylallyl ether	O	6.88(m)	6.63(dd)	6.30	6.30	4.78	8.08
		7.75(d)	8.40(d)(Me)		6.0(m), 8.79(d)(Me)		8.10
Bis(2-methylallyl) ether	O	7.29(br s)	6.60(s)	8.56(Me)	6.35(br)	4.78	8.08
					6.50(br)		
Bis(1-methylallyl) ether	O	7.54(d)	6.58(dd)	6.05(n)	6.05(m)	4.70	8.03
					8.79(d)(Me)		
Allyl cinnamyl ether	O	5.88(d)	6.40	5.96	6.17—6.25	4.90	8.15
		7.40(d)	2.44(m), 2.80(m)(Ph)	5.43(dt)			8.23
Cinnamyl 2-methylallyl ether	O	5.77(d)	2.46(m), 2.82(m)(Ph)	5.77(d)	6.16(s)	5.0	8.22
		7.50(s)	6.50(s)	8.62(s)(Me)	6.54(dd)		8.31
But-2-enyl cinnamyl ether	O	6.70(m)	8.19(d)(Me)	6.1—6.3	6.1—6.3	4.9	8.18
		6.10	2.44(m), 2.80(m)(Ph)				8.32
Dicinnamyl ether	O	5.80(d)	2.36(m), 2.77(m)(Ph)	5.31(dq)	6.09(br s)	5.1	8.37
Diallylamine	NH	7.50(d)	5.98(br d)	5.98(d)	7.09(m)	4.72	8.05
Diallyl(2,3-epoxypropyl)amine	N(C ₃ H ₅ O)	7.57(m)	6.52(dt)	6.00(m)	7.40(m)	4.72	8.05
Allyl acrylate	O	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i> , C=O	4.57	7.99(s)
Diallyl sulphone	SO ₂	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	4.58	7.96(d)
Diallyl(methyl)amine	NMe	7.50(d)	6.52(br d)	6.00(m)	7.60(m)	4.62	8.12
4,4-Diacetylhepta-1,6-diene	C(COMe) ₂ ^b	7.80(d)	6.21(dd)	5.71(m)	7.30(q)	4.73	8.06
					8.94(q)	4.79	8.09

^a Complex spectra; firm assignments not attempted. ^b Methyls of X at τ 7.52 and 7.83.

acetyl substituents, and the signals of the protons of the methylene groups, were significantly different. There are two possible conformations of the co-ordinated 1,6-diene [2b; M = Rh(pd), R = H] and (11b) corresponding to the chair and boat conformation in cyclohexanes. The 'boat' conformation (11b) enables one of the acetyl oxygen atoms to co-ordinate to the rhodium, which might confer extra stability on this conformer.

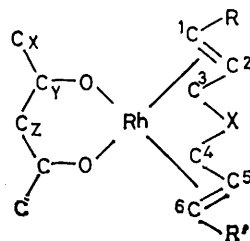
Carbon-13 N.M.R. Spectra.—The ¹³C n.m.r. spectra of several of the rhodium complexes were measured and are collected in Table 5. The assignments were made with the assistance of off-resonance spectra. The ¹⁰³Rh-¹³C

* Variable-temperature studies of these and related complexes, *i.e.* [2; M = Rh(pd), R = H, X = CHR'], are in progress to resolve these points.

¹¹ R. F. Zurcher, *Progr. N.M.R. Spectroscopy*, 1967, 2, 205.

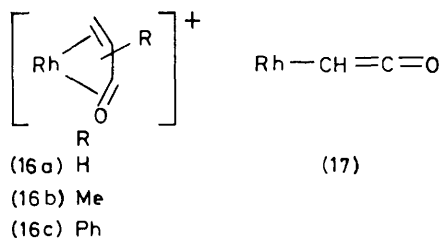
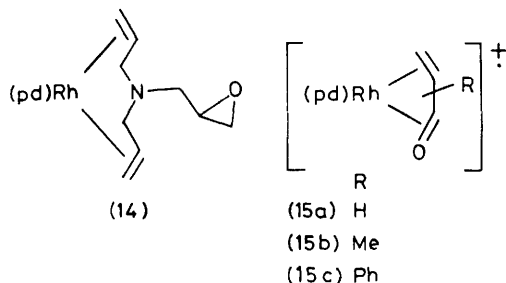
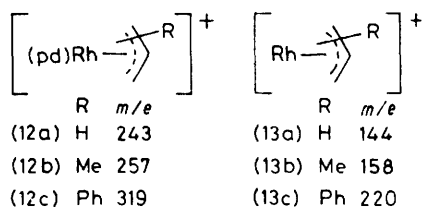
TABLE 5

Carbon-13 chemical shifts (δ /p.p.m.) relative to internal SiMe₄ for [Rh(diene)(pd)] complexes in CDCl₃. Coupling constants [J (Rh-C)/Hz] are given in parentheses



Diene	C ¹ , C ⁶	C ² , C ⁵	C ³ , C ⁴	R, R'	pd	X		
Allyl cinnamyl ether (R = H, R' = Ph)	54.72(d) (11.7)	70.71(d) (11.8)	71.16	140.6 128.61 127.77 126.66	C _x 27.1 C _y 186.13 C _z 98.59			
	63.30(d) (14.7)							
Dicinnamyl ether (R = R' = Ph)	64.63(d) (14.7)	70.91(d) (11.8)	71.16	140.90 128.55 127.71 126.11	C _x 26.7 C _y 185.61 C _z 98.33			
Diallyl(methyl)-amine (R = R' = H)	55.40(d) (13.3)	70.71(d) (14.8)	59.76		C _x 27.36 C _y 186.72 C _z 96.85	47.31 (NMe ₃)		
Diallyl(2,3-epoxypropyl)amine (R = R' = H)	55.33(d) (13.2)	58.86(d) (16.2)	50.88		C _x 27.43 C _y 186.72 C _z 98.90	44.71 (NCH ₃)	60.83 CH	70.58 CH ₂
4,4-Diacetylhepta-1,6-diene (R = R' = H)	61.89(d) (14.7)	69.96(d) (13.2)	36.54		C _x 27.29 C _y 186.59 C _z 98.72	74.05 (>C=O)	206.89 206.28	26.19 28.98 (2Me)

coupling constants vary between 11.7 and 16.2 Hz, and for the diallyl ether and hepta-1,6-diene complexes the



¹⁰³Rh-¹³C coupling constants for C¹ and C⁶ are greater than those for C² and C⁵, except for the terminal allyl carbon of the allyl cinnamyl ether complex where the ¹⁰³Rh-¹³C coupling constants for C¹ and C² are equal. In contrast, in the diallylamine complexes the ¹⁰³Rh-¹³C coupling constants for C¹ and C⁶ are smaller than those for C² and C⁵. The range of values for the ¹⁰³Rh-¹³C coupling constants is similar to that reported for related rhodium complexes.¹² The interpretation of ¹⁰³Rh-¹³C coupling constants is a matter of continuing debate.^{12,13}

Mass Spectra.—Parent-ion peaks were observed for all the rhodium complexes together with two series of peaks for Rh(η -allyl)(pd) (12a)—(12c) and Rh(η -allyl) species (13a)—(13c). In all cases except one the peaks due to Rh(η -allyl) species were substantially stronger than those due to the Rh(η -allyl)(pd) species (Table 6).

The base peak in the mass spectrum of the diallylamine complex (14) corresponds to the η -allyl species (13a). In the mass spectra of the phenyl-substituted diallyl ether complexes, fragmentation to the η -allyl species (12c) and (13c) is less important and the strongest fragmentation peak occurs at m/e 117 (PhCH=CH- $\dot{\text{C}}\text{H}_2$). The mass spectrum of the one example in Table 6 where the Rh(η -allyl)(pd) species predominates over the Rh(η -allyl) species is shown in Figure 2 and the spectrum of an isomeric complex (Figure 3) shows the influence of

¹² G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Comm.*, 1970, 1530.

¹³ D. E. Axelson, C. E. Holloway, and A. J. Oliver, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 885.

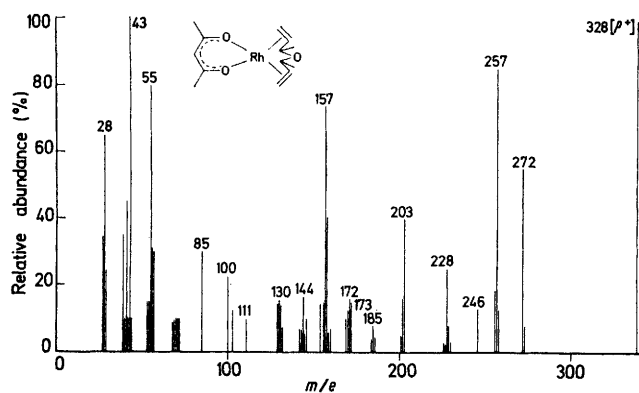


FIGURE 2 Mass spectrum of [bis(1-methylallyl) ether]pentane-2,4-dionatorrhodium

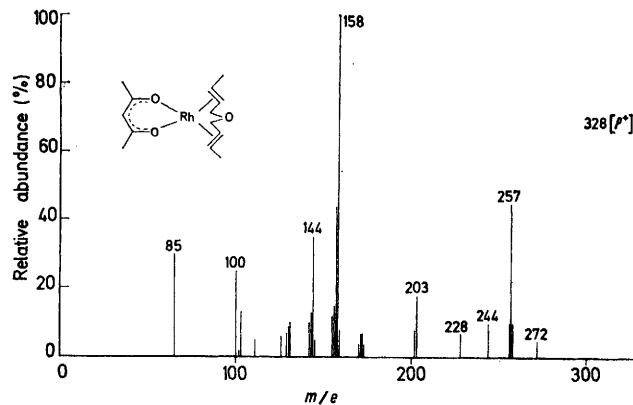
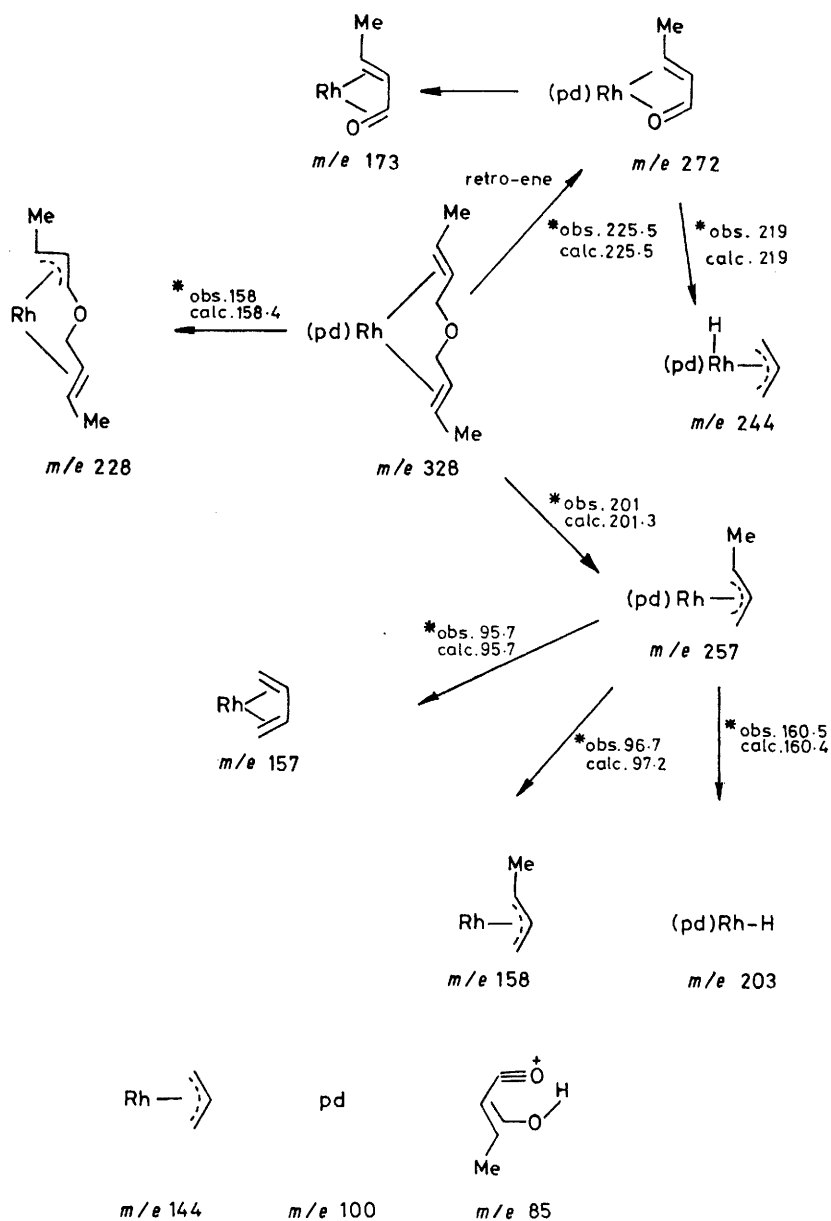


FIGURE 3 Mass spectrum of [bis(but-2-enyl) ether]pentane-2,4-dionatorrhodium



SCHEME Fragmentation paths for [bis(but-2-enyl) ether]pentane-2,4-dionatorrhodium

methyl substitution on the fragmentation path. Small peaks (<10% abundance) attributable to a formal

TABLE 6

Percentage abundance * of η -allyl species in the mass spectra of [Rh(diallyl ether)(pd)] complexes

Ether	Rh(η -allyl)(pd) species (12a)—(12c)	Rh(η -allyl) species (13a)—(13c)
	243(50)	144(100)
	243(16), 257(31)	144(100), 158(65)
	243(35), 257(32)	144(100), 158(65)
	257(85)	144(16), 158(40)
	257(45)	144(35), 158(100)
	257(6)	158(10)
	257(55)	144(33), 158(100)
	243(8), 319(15)	144(20), 220(27)
	319(20)	158(17), 220(23)
	319(12)	158(10), 220(16)
	319(20)	220(24)

* Peaks having less than 5% abundance are not recorded.

retro-ene reaction giving rise to (15a)—(15c) and (16a)—(16c) are observable in most of the spectra but in one case (Figure 2) this fragmentation is more favoured. The

Scheme rationalises the fragmentation pattern of Figure 3. Almost all the suggested fragmentation paths are supported by appropriate metastable peaks and it is of interest that an accurate mass measurement shows the peak at m/e 144 to be wholly due to Rh(C₃H₃) [*i.e.* (13a)] with no contribution from Rh(C₂HO), a possible rhodium ketene derivative, (17).

EXPERIMENTAL

Melting points were determined with a Kofler hot-stage apparatus. N.m.r. spectra were obtained for solutions in CDCl₃ with Varian HA100 or Bruker WP90 instruments, and mass spectra with an A.E.I. MS902 spectrometer operating at 70 eV.* The complexes were prepared by the general method given below.

Preparation of Complexes.—An excess of diene (2–10 mmol) was added to a stirred solution of [Rh(C₂H₄)₂(pd)]¹⁴ (1 mmol) in n-pentane (5–15 cm³) at room temperature. The reaction was allowed to proceed for the time given in Table 1. The solid complex was then removed by filtration, the filtrate concentrated, and the residue triturated with a little cold pentane to give more of the complex. The solvent used for crystallisation is given in Table 1. Some of the complexes were purified by sublimation.

Isolation of [Bis(2-methylallyl) ether]ethylene(pentane-2,4-dionato)rhodium, (10).—Bis(2-methylallyl) ether (1 g, 8 mmol) was added to a stirred solution of [Rh(C₂H₄)₂(pd)] (1 g, 3 mmol) in n-pentane (15 cm³). After 15 h the precipitated orange complex (0.52 g, 38%), m.p. 154 °C (decomp.), was removed by filtration, m/e 356 (P^+); τ 4.55 (s, 1 H, pd), 4.7, 6.35, and 7.25 (all br, CH₂), 7.7 (br s, co-ordinated C₂H₄), 7.98 (s, 3 H, Me on unco-ordinated double bond), 8.18, 9.22 (both s, 2 × 3 H, pd Me), and 8.5 (s, 3 H, Me on co-ordinated double bond). Attempts to recrystallise this material resulted in decomposition.

[7/672 Received, 22nd April, 1977]

* Throughout this paper: 1 eV \approx 1.60 × 10⁻¹⁹ J.

¹⁴ R. Cramer, *Inorg. Synth.*, 1975, **16**, 16.