Transition-metal Complexes of 1,3-Dienes. Part I. Synthesis and Structure of Rhodium(I) Complexes

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The preparation of a series of rhodium(I) complexes with halogen- or methyl-substituted 1,3-dienes by displacement of ethylene from $[(C_2H_4)_2RhCl]_2$ and $[(C_2H_4)_2Rh(acac)]$ (acac = acetylacetonato) is described. The corresponding π-cyclopentadienyl complexes have also been prepared. The complexes have been characterized by means of ^1H n.m.r., i.r., and mass spectra and by their chemical reactions. All the dienes studied co-ordinate to the metal in a chelate fashion with the exception of 4-methylpenta-1,3-diene which co-ordinates *via* the unsubstituted double bond only in the case of the chloro- and acetylacetonato-complexes. In solution the latter complexes exhibit temperature-dependent rotation of the co-ordinated diene about the rhodium–olefin bond axis. Possible reasons for the different co-ordination modes are discussed.

In contrast to rhodium(I) complexes of simple olefins, there are very few reports of rhodium(I) complexes of conjugated dienes. The present paper reports the preparation and structure of a number of new complexes of this class; a subsequent paper will describe isomerization reactions of the co-ordinated diene.

Porri and Lionetti[1,2] have described the preparation of some bis(diene) complexes [(diene)$_2$RhCl] (diene = butadiene, isoprene, *trans*-penta-1,3-diene, 2,3-dimethylbutadiene, and methyl hexa-2,4-dienoate), as well as some mixed complexes [(diene)(L)RhCl] (L = cyclooctene or *p*-toluidine). Winkhaus and Singer[3] have reported the binuclear complexes [(diene)RhCl]$_2$ (diene = 2,3-dimethylbutadiene and cyclohexa-1,3-diene). Bis(butadiene)rhodium(I) chloride has been shown by a single-crystal *X*-ray study[4] to be an approximate square pyramid, the centres of the four C=C bonds constituting the basal plane and the chlorine atom occupying the apical position. This complex excepted, our knowledge of the constitution of the remaining complexes is confined largely to i.r. spectra and some chemical reactions. From the absence of absorption in the 1 600—1 700 cm^{-1} region characteristic of free C=C bonds, it seems that all the known complexes contain diene bonded to the metal *via* both double bonds (bidentate co-ordination). Among the complexes to be described here are the first examples wherein the diene is co-ordinated to Rh^{I} *via* one double bond only (monodentate co-ordination).

RESULTS

The complexes prepared and their analytical data are listed in Table 1. The most convenient method of preparation of the chloro- and acetylacetonato-complexes was found to be displacement of ethylene from $[(C_2H_4)_2RhCl]_2$ and $[(C_2H_4)_2Rh(acac)]$, respectively, in diethyl ether. The latter complexes may alternatively be prepared from the corresponding chlorides by treatment with acetylacetone in the presence of K_2CO_3. The π-cyclopentadienyl (cp) derivatives were obtained from the corresponding chlorides in ether or tetrahydrofuran by stirring with thallium cyclopentadienide with purification of the crude product by vacuum sublimation. Details of the syntheses and variations on the above methods are given in the Experimental section. Structural characterization of the complexes was based on elemental analysis, i.r. and mass spectra, and, particularly, on ^1H n.m.r. spectra of solutions. Unfortunately, it was not possible to obtain n.m.r. spectra of all the chloro- and acetylacetonato-complexes either because of limited solubility or because of decomposition in solution; data are therefore most complete for the cp series, discussed first.

(π-Cyclopentadienyl)(π-diene)rhodium(I) *Complexes*.—^1H *N.M.R. spectra*. Assignments were made on the basis of published data on co-ordinated dienes and olefins in related systems. Particular use was made of the spectra of analogous tricarbonyl(diene)iron(0) complexes reported by Pettit and his co-workers.[5] The assignments are fully internally consistent for the whole range of complexes studied. Chemical shifts for the protons, labelled as shown below, are given in Table 2. Spectra of some of the complexes have been fully analysed with respect to proton–proton and rhodium–proton coupling with the aid, where necessary, of decoupling techniques. Table 3 lists rhodium–hydrogen coupling constants for a selection of the complexes and Figure 1 illustrates the application of proton decoupling to the case of [(isoprene)Rh(cp)] (cp = π-cyclopentadienyl).

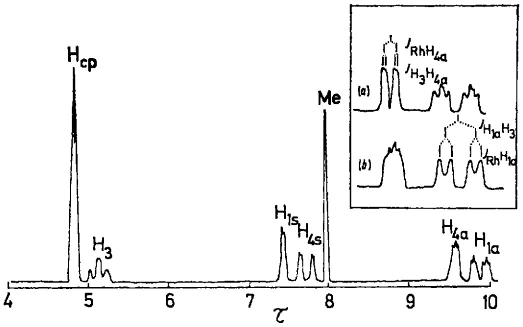
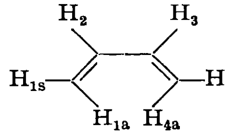


FIGURE 1 ^1H N.m.r. spectrum of the complex [(isoprene)Rh(cp)] in $CDCl_3$ at 25 °C showing (in inset) (*a*) proton H_{1s} decoupled and (*b*) proton H_{4s} decoupled



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[1] L. Porri, A. Lionetti, G. Allegra, and A. Immerzi, *Chem. Comm.*, 1965, 336.

[2] L. Porri and A. Lionetti, *J. Organometallic Chem.*, 1966, **6**, 422.

[3] G. Winkhaus and H. Singer, *Chem. Ber.*, 1966, **99**, 3602.

[4] A. Immerzi and G. Allegra, *Acta Cryst.*, 1969, **B25**, 120.

[5] G. F. Emmerson, J. E. Mahler, R. Kochlar, and R. Pettit, *J. Org. Chem.*, 1964, **29**, 3620.

J_{RhH} Values fell into three distinct ranges. *Anti*-protons ($H_{1a}H_{4a}$) coupled most strongly with Rh (J_{RhH} 1·9—2·8 Hz), central-proton (H_2,H_3) coupling constants were in the range 1·4—1·5 Hz, while *syn*-protons had the smallest coupling (J_{RhH} 0·5—1·1 Hz). This correlation of J_{RhH} with proton position has an obvious use in resonance assignment. Rhodium–proton coupling is in some cases transmitted through an extra carbon atom. Thus, the resonance of an *anti*-methyl group was split with J_{RhH} 0·8—1·0 Hz. No coupling between rhodium and *syn*- or central-methyl protons was detected. Cyclopentadienyl proton resonances occurred as doublets with J_{RhH} 0·9 Hz, a value within the range observed for *syn*-protons.

TABLE 1

Analytical data for rhodium(I)–diene complexes

Complex type	Diene	Colour	M.p. (*t*/°C)	Found (%)			Calc. (%)		
				C	H	Cl	C	H	Cl
[(diene)Rh(cp)]									
	Buta-1,3-diene	Yellow	83—84	48·6	4·9		48·7	5·0	
	2-Chlorobuta-1,3-diene	Yellow	35	41·9	3·8	13·6	42·1	3·9	13·8
	2,3-Dichlorobuta-1,3-diene	Orange	97—98	37·4	3·3	24·5	37·1	3·1	24·4
	2-Bromobuta-1,3-diene	Yellow	30	35·8	3·3	26·5 [a]	35·9	3·3	26·6 [a]
	Isoprene	Yellow	40	50·7	5·4		50·9	5·4	
	trans-Penta-1,3-diene	Yellow	Oil	50·8	5·5		50·9	5·4	
	cis-Penta-1,3-diene	Yellow	Oil	50·6	5·4		50·9	5·4	
	trans-2-Methylpenta-1,3-diene	Yellow	Oil	52·6	5·8		52·8	6·0	
	trans-3-Methylpenta-1,3-diene	Yellow	Oil	52·6	5·9		52·8	6·0	
	cis-3-Methylpenta-1,3-diene	Yellow	Oil	52·7	6·0		52·8	6·0	
	4-Methylpenta-1,3-diene	Yellow	Oil	52·7	6·0		52·8	6·0	
	trans,trans-Hexa-2,4-diene	Yellow	Oil	52·5	5·9		52·8	6·0	
	cis,trans-Hexa-2,4-diene	Yellow	Oil	52·7	5·9		52·8	6·0	
	2,3-Dimethylbuta-1,3-diene	Yellow	56—57	52·6	6·0		52·8	6·0	
	2,4-Dimethylpenta-1,3-diene	Yellow	Oil	54·3	6·3		54·5	6·4	
	trans,trans-1,4-Diphenylbuta-1,3-diene	Yellow	180	67·1	5·0		67·4	5·1	
[(diene)Rh(acac)]									
	2-Chlorobuta-1,3-diene	Red	99—102	37·2	4·1	12·2	37·1	4·2	12·2
	2,3-Dichlorobuta-1,3-diene	Yellow	156—159d	33·1	3·3	21·8	33·2	3·4	21·8
	trans-Penta-1,3-diene	Red	100—103d	44·1	5·5		44·4	5·6	
	cis-Penta-1,3-diene	Red	Oil	42·9	4·9		44·4	5·6	
	trans-2-Methylpenta-1,3-diene	Orange	85—88d	46·3	5·9		46·5	6·0	
	trans-3-Methylpenta-1,3-diene	Red	95—97d	46·4	5·9		46·5	6·0	
	cis-3-Methylpenta-1,3-diene	Red	65d	46·4	6·0		46·5	6·0	
	trans,trans-Hexa-2,4-diene	Orange	128—130d	46·2	5·9		46·5	6·0	
	cis,trans-Hexa-2,4-diene	Orange	40d	46·7	6·0		46·5	6·0	
	2,3-Dimethylbuta-1,3-diene	Orange		46·3	5·9		46·5	6·0	
	2,4-Dimethylpenta-1,3-diene	Red		48·1	6·2		48·3	6·4	
[(diene)$_2$Rh(acac)]									
	4-Methylpenta-1,3-diene	Red	55—56	55·4	7·4		55·7	7·4	
[(diene)$_2$RhCl]									
	Buta-1,3-diene [b]	Yellow	38·40	38·7	4·5	14·1	38·9	4·9	14·4
	2-Chlorobuta-1,3-diene	Orange	140—142d	30·5	3·1	33·8	30·5	3·1	33·9
	Isoprene [c]	Yellow	42d	43·3	5·5	13·1	43·6	5·8	12·9
	trans-Penta-1,3-diene [c]	Red	42—44d	43·7	5·8	12·8	53·6	5·8	12·9
	trans-2-Methylpenta-1,3-diene	Orange	135—137d	47·8	6·6	11·5	47·6	6·6	11·7
	trans-3-Methylpenta-1,3-diene	Orange	135—138d	47·4	6·6	11·8	47·6	6·6	11·7
[(diene)RhCl]$_2$									
	2,3-Dichlorobuta-1,3-diene	Orange	170—173d	18·4	1·5	40·7	18·4	1·5	40·7
	cis-3-Methylpenta-1,3-diene	Orange	120—124d	32·3	4·5	16·3	32·7	4·5	16·1
	trans,trans-Hexa-2,4-diene	Red	132—135d	32·7	4·5	16·3	32·7	4·5	16·1
	cis,trans-Hexa-2,4-diene	Red	40—44	32·1	4·0	15·6	32·7	4·5	16·1
	2,3-Dimethylbuta-1,3-diene [d]	Red	140d	32·4	4·4	16·0	32·7	4·5	16·1
	2,4-Dimethylpenta-1,3-diene	Orange	40d	35·6	4·9	14·8	35·8	5·1	15·1
	trans,trans-Diphenylbuta-1,3-diene	Red	228—231d	55·3	4·0	10·2	55·6	4·1	10·3
[(diene)$_2$RhCl]$_2$									
	4-Methylpenta-1,3-diene	Red	118—120d	47·5	6·7	11·7	47·5	6·6	11·7
Miscellaneous									
	[(2,3-Dichlorobuta-1,3-diene)RhBr]$_2$	Orange	125—128d	15·5	1·2		15·7	1·3	
	[(2,3-Dichlorobuta-1,3-diene)Rh(NCS)]$_2$	Red	101—102d	21·0	1·2	24·9	21·1	1·4	25·0
	[(2,3-Dichlorobuta-1,3-diene)(*p*-toluidine)-RhCl] [e]	Yellow		35·3	3·5	28·9	35·8	3·6	28·9

[a] Br analysis. [b] Previously prepared by displacement of cyclo-octene from the complex [(cyclo-octene)$_2$RhCl]$_2$ or from $RhCl_3$,-$x$$H_2O$ (ref. 1). [c] Previously prepared by displacement of butadiene from the complex [$(C_4H_6)_2$RhCl] (ref. 2). [d] Previously prepared (ref. 3). [e] N analysis: found, 3·8; calc. 3·8%.

I.r. spectra. Symmetrically bonded cp complexes have seven i.r.-active vibrations in the range 3 200—700 cm^{-1} and the simultaneous appearance of at least five of these is strong evidence for a π-bonded cyclopentadienyl ring.[6] All the complexes isolated in the present study exhibited at least five of the characteristic vibrations within the frequency and intensity ranges documented by Fritz.[7] In addition, from two to three bands occurred in the 1 400—1 500 cm^{-1} region characteristic of co-ordinated diene. None of the complexes absorbed in the 1 600—1 700 cm^{-1} range where absorption due to uncomplexed olefinic functions is expected.

Mass spectra. In all cases the parent-ion peak was observed. This formed the ion $[(cp)Rh]^+$ by loss of diene in a single step and the latter fragmented to the Rh^+ ion by cleavage of the π-bond. The fragmentation pattern was the same as that observed by King [8] for π-cyclopentadienylrhodium(I) complexes of ethylene and cyclo-octa-1,5-diene.

TABLE 2

Proton chemical shifts (τ) for [(diene)Rh(cp)] complexes

Diene	H_{cp}	H_{1a}	H_{1s}	H_2	H_3	H_{4s}	H_{4a}
Buta-1,3-diene	4·73d	9·66dt	7·55dd	5·08t	7·55dd	7·55dd	9·66dt
2-Chlorobuta-1,3-diene	4·70d	9·47dt	7·10dt	Cl	4·70m	7·70dq	10·00dt
2,3-Dichlorobuta-1,3-diene	4·64d	9·62t	7·08dd	Cl	Cl	7·08dd	9·62t
2-Bromobuta-1,3-diene	4·66d	9·65dt	6·94dt	Br	4·66m	7·64dq	9·85dt
Isoprene	4·78d	9·68t	7·45	7·89s (Me)	5·08t	7·68dd	9·85dt
trans-Penta-1,3-diene	4·80d	9·72dt	7·70dd	5·20	5·00m	8·62s (Me)	8·62m
cis-Penta-1,3-diene	4·73d	8·62dt	7·43dd	5·20	5·00m	6·66t	9·06dd (Me)
trans-2-Methylpenta-1,3-diene	4·84d	9·74t	7·62m	8·00s (Me)	5·22d	8·62d (Me)	9·02m
trans-3-Methylpenta-1,3-diene	4·88d	9·78dt	7·82dd	5 27t	7·93s (Me)	8·55d (Me)	8 96m
cis-3-Methylpenta-1,3-diene	4·82d	8·72dt	7·65d	5·03t	7·98s (Me)	6·60dd	9·06dd (Me)
4-Methylpenta-1,3-diene	4·93d	8·55dt	7·70d	5·3	5·1m	8·55s (Me)	9·00d (Me)
trans,trans-Hexa-2,4-diene	4·84d	8·70m	8·69s (Me)	5·38dd	5·38dd	8·69s (Me)	8·70m
cis,trans-Hexa-2,4-diene	4·82d	9·04dd (Me)	6·78t	5·50	5·20m	8·60d (Me)	7·70m
2,3-Dimethylbuta-1,3-diene	4·85d	9·80dd	7·58d	7·90s (Me)	7·90s (Me)	7·58d	9·80dd
2,4-Dimethylpenta-1,3-diene	4·86d	8·60m	7·58d	7·98s (Me)	5·32bs	8·50s (Me)	9·00d (Me))
trans,trans-1,4-Diphenylbuta-1,3-diene	5·25d	7·65dd	2·5—2·9 (Ph)	4·6dd	4·6dd	2·5—2·9 (Ph)	7·65sd

b = Broad, d = doublet, dd = doublet of doublets, s = singlet, t = triplet, and dt = doublet of triplets.

TABLE 3

Rhodium–proton coupling constants (Hz) for some [(diene)Rh(cp)] complexes [a]

Diene	$J_{\mathrm{RhH_{1a}}}$	$J_{\mathrm{Rhh_{1s}}}$	$J_{\mathrm{RhH_2}}$	$J_{\mathrm{RhH_3}}$	$J_{\mathrm{RhH_{4s}}}$	$J_{\mathrm{RhH_{4a}}}$
Buta-1,3-diene	2·5	0·9	1·4	1·4	0·9	2·5
2-Chlorobuta-1,3-diene	2·7	1·1	Cl	*b*	0·9	2·4
2,3-Dichlorobuta-1,3-diene	2·5	0·9	Cl	Cl	0·9	2·5
2-Bromobuta-1,3-diene	2·8	1·1	Br	*b*	0·9	2·4
Isoprene	2·4	0·9	Me	*b*	0·5	2·3
trans-Penta-1,3-diene	2·4	1·0	*b*	*b*	Me	*b*
4-Methylpenta-1,3-diene	*b*	1·0	*b*	*b*	Me	Me, 0·9
trans,trans-Hexa-2,4-diene	*b*	Me	1·4	1·4	Me	*b*
2,3-Dimethylbuta-1,3-diene	1·9	0·5	Me	Me	0·5	1·9
trans,trans-1,4-Diphenylbuta-1,3-diene	2·2	Ph	1·5	1·5	Ph	2·2

[a] $J_{\mathrm{RhH_{cp}}}$ 0·9 Hz in all cases. [b] Not resolved.

We recently reported [9] single-crystal *X*-ray analyses of two of the complexes of this class, *viz.* those where diene = 2,3-dichlorobuta-1,3-diene and 2,3-dimethylbuta-1,3-diene. In both molecules the cyclopentadiene ring and the butadiene group are both planar to within experimental error, and approximate mirror planes run through one carbon atom C(1) of the ring and the midpoints of the C(3)–C(4) ring bond opposite to it and the internal C–C bond of the diene. The C(1) end of the ring is tilted slightly towards the plane of the diene and there is evidence, in the case of the dichloro-complex, for a small degree of localized bonding within the ring. The close similarity in the spectroscopic properties of all the complexes of this class with the two members whose *X*-ray structures have been determined is strong evidence for an essentially common structure for them all.

Acetylacetonato(π-diene)rhodium(I) *Complexes.*—These are orange-red solids which do not visibly deteriorate when stored under an atmosphere of nitrogen. They are less stable in solution in organic solvents, however, than corresponding cp complexes. With one exception [(4-methylpenta-1,3-diene)$_2$Rh(acac)] (considered separately), all complexes in this class have the stoicheiometry [(diene)Rh(acac)]. The different constitution of the two types of complex is not a consequence of different preparative conditions or variations in reactant ratio.

^{1}H *N.M.R. spectra.* Chemical shifts for those complexes which do not decompose in solution are given in Table **4**; other complexes showed only resonances of co-ordinated acetylacetone and free diene. From a comparison of the data in Tables 2 and 3, it can be seen that the olefinic protons resonate at slightly lower fields in the complex [(diene)Rh(acac)] than in [(diene)Rh(cp)]. Although the spectra of the [(diene)Rh(acac)] complexes have not all been fully analysed for spin–spin coupling, in the cases where J_{RhH} has been measured, values very close to those found for the [(diene)Rh(cp)] derivatives were obtained. For example, $J_{\mathrm{RhH_{1a}}}$ and $J_{\mathrm{RhH_{1s}}}$ are 2·2 and 0·8 Hz in [(2,3-dichlorobuta-1,3-diene)Rh(acac)] as compared with 2·5 and 0·9 Hz, respectively, in the cp complex.

I.r. spectra. All the [(diene)Rh(acac)] complexes showed strong multiple absorption in the 1 400—1 600 cm^{-1} region,

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[6] D. M. Adams, 'Metal Ligand and Related Vibrations,' Arnold, London, 1967.

[7] H. P. Fritz, *Adv. Organometallic Chem.*, 1964, **1**, 240.

[8] R. B. King, *J. Organometallic Chem.*, 1968, **14**, 19.

[9] M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Organometallic Chem.*, 1972, **39**, C9.

as expected for co-ordinated diene and acetylacetone. The highest-energy band was observed at 1605 cm^{-1} in the complex of 2,3-dichlorobuta-1,3-diene. This complex excepted, no absorption occurred in the 1 600—1 700 cm^{-1} region.

There is good correspondence with the spectra of corresponding acac and cp complexes.

All the complexes also had i.r. spectra closely similar to those of corresponding acac and cp complexes when allowance was made for absorption due to the counter ligands.

TABLE 4

Proton chemical shifts (τ) for [(diene)Rh(acac)] complexes [a]

Diene	H_{1a}	H_{1s}	H_2	H_3	H_{4s}	H_{4a}
2,3-Dichlorobuta-1,3-diene	9·07t	6·98dd	Cl	Cl	6·98dd	9·07t
trans-Penta-1,3-diene	9·10dt	7·06d	5·00	5·20m	8·78d (Me)	9·28m
trans-2-Methylpenta-1,3-diene	9·26bs	7·50bs	7·83s (Me)	5·44d	8·83d (Me)	8·33m
trans-3-Methylpenta-1,3-diene	9·17dt	7·40d	5·10t	7·98s (Me)	8·82d (Me)	8·42d
trans,trans-Hexa-2,4-diene	8·33m	8·86d (Me)	5·33d	5·33dd	8·86d (Me)	8·33
2,3-Dimethylbuta-1,3-diene	9·28t	7·44bs	7·98s (Me)	7·98s (Me)	7·44bs	9·28t
2,4-Dimethylpenta-1,3-diene	8·10bs	7·34s	7·88s (Me)	5·65bs	8·72s	9·07s

[a] acac Proton resonances occur at τ 4·5—4·6 (H) and 7·9—8·0 (Me); abbreviations as in footnote to Table 2.

TABLE 5

Proton chemical shifts (τ) for some $[(diene)RhCl]_2$ complexes

Diene	H_{1a}	H_{1s}	H_2	H_3	H_{4s}	H_{4a}
2,3-Dichlorobuta-1,3-diene	9·45dd	7·28d	Cl	Cl	7·28d	9·45dd
trans,trans-Hexa-2,4-diene	8·45dd	8·95d (Me)	5·25d	5·25d	8·95d (Me)	8·45dd
2,3-Dimethylbuta-1,3-diene	9·86t	7·87bs	8·09s (Me)	8·09s (Me)	7·87bs	9·86t
2,4-Dimethylpenta-1,3-diene	8·33m	7·98s	7·98s (Me)	5·54s	8·78s (Me)	9·20s (Me)

Abbreviations as in footnote to Table 2.

Mass spectra. These showed peaks corresponding to the ions $[(diene)Rh(acac)]^+$, $[(diene)Rh]^+$, and Rh^+. No peak corresponding to $[Rh(acac)]^+$ was observed.

All the properties above of the [(diene)Rh(acac)] complexes are consistent with a four-co-ordinate, mononuclear, structure involving bidentate acetylacetonate and bidentate diene.

Chlorobis(diene)rhodium(I) *and Di-μ-chloro(diene)rhodium*(I) *Complexes*.—Both types of complex are stable in the solid state under an atmosphere of nitrogen, but the bis(diene) complexes decompose in solution in organic solvents. For a given diene only $[(diene)_2RhCl]$ or $[(diene)RhCl]_2$, but not both, could be isolated whatever the reactant ratio. It is interesting that reaction of 2,3-dimethylbuta-1,3-diene with $[(C_2H_4)_2RhCl]_2$ gives the chloro-bridged complex $[(diene)RhCl]_2$ and not $[(diene)_2RhCl]$, reported by Porri and Lionetti [2] as the product of displacement of butadiene from $[(butadiene)_2RhCl]$. Indeed, attempts to prepare this complex by the latter method yielded only $[(diene)RhCl]_2$; our results are therefore in agreement with the findings of Winkhaus and Singer.[3]

The reason why a particular diene forms one type of chloro-complex and not the other is not understood; there is no obvious correlation of the type of complex formed and either the nature or the position of the diene substituents.

The $[(diene)_2RhCl]$ complexes may reasonably be assumed to have the same mononuclear, formally five-co-ordinate, structure known for $[(butadiene)_2RhCl]$,[4] and the $[(diene)RhCl]_2$ complexes to have a binuclear, formally four-coordinate, chloro-bridged structure analogous to $[(C_2H_4)_2RhCl]_2$ [10] but containing diene bidentately bonded to each metal atom in place of two molecules of ethylene. Available evidence supports these formulations.

^{1}H N.M.R. and i.r. spectra. Some of the complexes that did not decompose in solutions were poorly soluble. Such n.m.r. data as could be obtained are given in Table 5. The 4-methyl-penta-1,3-diene complex excepted, none absorbed in the 1 600—1 700 cm^{-1} region. All the chloro-compexes exhibited one or more bands in the 200—300 cm^{-1} region, not shown by complexes of other counter ligands.

TABLE 6

Rhodium–chlorine stretching wavenumbers (cm^{-1})

Complex type	Diene	Cl	
		terminal	bridging
$[(diene)_2RhCl]$			
	2-Chlorobuta-1,3-diene	233s	
	Isoprene	228s	
	trans-Penta-1,3-diene	225s	
	trans-2-Methylpenta-1,3-diene	235s	
	trans-3-Methylpenta-1,3-diene	244s	
$[(diene)RhCl]_2$			
	2,3-Dichlorobuta-1,3-diene		233s
	cis-3-Methylpenta-1,3-diene		220s
	trans,trans-Hexa-2,4-diene		278w, 247m, 220s
	cis,trans-Hexa-2,4-diene		236s
	2,3-Dimethylbuta-1,3-diene		227s
	2,4-Dimethylpenta-1,3-diene		215s
	trans,trans-1,4-Diphenylbuta-1,3-diene		270s
$([diene)_2RhCl]_2$			
	4-Methylpenta-1,3-diene		280m, 255s, 243s

m = Medium, s = strong, and w = weak.

By analogy with similar Rh^I complexes, these bands are assigned to Rh–Cl stretching vibrations,[11,12] though no correlation of the number of bands with structure was observed (Table 6).

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[10] K. Klanderman, *Diss. Abs.*, 1965, **25**, 6253.

[11] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, 1967, **6**, 1647.

[12] D. M. Adams and P. J. Chandler, *J. Chem. Soc.* (*A*), 1969, 588.

As a test of the correctness of assignment of a di-μ-chloro-structure to the complexes of stoicheiometry [(diene)RhCl], which showed a single band only in the 200—300 cm^{-1} region in the i.r. spectrum, a number of bridge-replacement and -splitting reactions were attempted for one of the complexes, that containing 2,3-dichlorobuta-1,3-diene. When treated with LiBr in acetone a complex of empirical formula $[(C_4H_4Cl_2)RhBr]$ was isolated. The i.r. spectrum was identical to that of the chloride except for absence of the band at 233 cm^{-1} attributed to bridging Rh–Cl. Treatment with KNCS led to isolation of the complex $[(C_4H_4Cl_2)$-Rh(NCS)]. As before the 233 cm^{-1} band was absent but the i.r. spectrum showed a strong band at 2 160 cm^{-1}, *i.e.* in the range associated with bridging thiocyanate.[13] Reaction with NaN_3 in methanol gave a mixture of an azido-complex and starting material. When longer reaction times were employed, in an attempt to achieve complete replacement of Cl by N_3, no product was isolated, extensive decomposition occurring. However, the impure azido-complex showed absorptions at 2 062, 1 280, and 625 cm^{-1}. These are characteristic, respectively, of the asymmetric stretch, symmetric stretch, and bending mode of the azido-group when bridging two metal atoms *via* one nitrogen atom.[14,15] Triphenylphosphine and pyridine displaced diene from the complex $[(C_4H_4Cl_2)RhCl]$, but *p*-toluidine (ptol) gave $[(C_4H_4Cl_2)(ptol)RhCl]$.

These reactions, which are typical of chloro-bridged binuclear complexes of non-conjugated dienes,[2,15] *e.g.* cycloocta-1,5-diene, serve as support for a di-μ-chloro-structure in these complexes.

Complexes containing Monodentately Co-ordinated Diene.— In contrast to its cp complex, 4-methylpenta-1,3-diene in $[(diene)_2Rh(acac)]$ and in $[(diene)_2RhCl]_2$ is linked to the rhodium atom *via* one double bond only. This conclusion, originally indicated by stoicheiometry, is supported by i.r. and ^1H n.m.r. spectra and proven, in the case of the chloride, by single-crystal *X*-ray analysis.[16] Both complexes exhibited a strong band at 1 646 cm^{-1} in the i.r. spectra, not show by any other complex. This is in the region of expected absorption for unco-ordinated olefinic functions.

The ^1H n.m.r. spectra of both complexes were temperature dependent. Figure 2 shows the spectra of the acetylacetonate at −60 and +50 °C. Protons are labelled as shown. Those on the unco-ordinated C=C bond (H_{uc} multiplet at τ 4·7—4·8; Me_0 and Me_i at τ 8·19 and 8·37) occurred at almost the same field as in the free diene, whereas protons on the co-ordinated double bond (H_c) resonated at higher field. The higher-field methyl resonance (τ 8·37) is tentatively assigned to protons on the ' inside ' methyl group since these might be expected to have the greater long-range shielding. Increasing the temperature from −60 to 50 °C causes the H_c resonances to broaden and coalesce; the two singlets due to Me_0 and Me_i also began to coalesce. These observations can be explained in terms of rotation of the diene about the metal–olefin bond axis as demonstrated by Cramer[17] for co-ordinated ethylene in $[(C_2H_4)_2Rh(cp)]$. Attempts to measure the energy barrier to rotation, by determining the coalescence temperature of the Me_0 and Me_i resonances, were unsuccessful as above 60 °C the spectrum began to display time-dependent and irreversible changes. A similar effect was observed for spectra of the chloro-complex above 40 °C. Separate experiments have shown that these changes, to be discussed in Part II, are associated with diene isomerization.

Although 4-methylpenta-1,3-diene is the only conjugated diolefin to exhibit monodentate co-ordination in a complex isolable in the solid state, evidence was obtained for the existence of an analogously constituted complex in solution at low temperatures in the case of *cis*-penta-1,3-diene. When excess of *cis*-penta-1,3-diene was reacted with the complex $[(C_2H_4)_2Rh(acac)]$ in ether at room temperature no product could be isolated even on cooling to −78 °C. Removal of solvent and excess of diene at room temperature gave a red oil which was identified from elemental analysis and i.r. and mass spectra as the complex [(*cis*-penta-1,3-diene)Rh(acac)] wherein the diene is bonded bidentately; this complex decomposes in solution. However, removal of solvent at −20 °C and examination of the residual red oil in $CDCl_3$, also at −20 °C, gave the spectrum shown in Figure 3. This is similar to spectra of the 4-methylpenta-1,3-diene complexes discussed above, showing clear evidence for both co-ordinated and unco-ordinated olefinic functions. Warming the solution to room temperature resulted in decomposition of the bis(diene) complex as judged by irreversible changes in the spectrum and the appearance of resonances due to free diene.

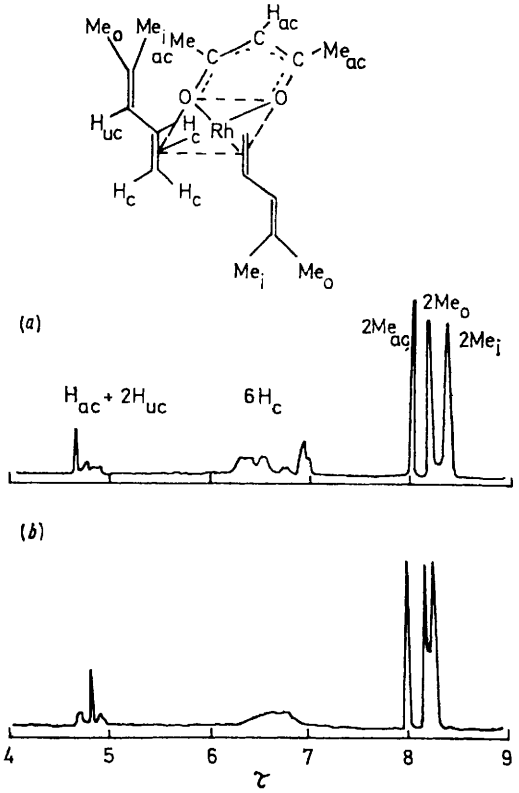

FIGURE 2 ^1H N.m.r. spectrum of the complex [(4-methylpenta-1,5-diene)$_2$Rh(acac)] in $CDCl_3$ at (*a*) −60 and (*b*) 50 °C

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[13] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1960, 1912.

[14] J. Nelson and S. M. Nelson, *J. Chem. Soc.* (*A*), 1969, 1597.

[15] L. Busetto, A. Palazzi, and R. Ros, *Inorg. Chem.*, 1970, **9**, 2792.

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

[17] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217.

DISCUSSION

The foregoing results have demonstrated both bidentate and monodentate co-ordination modes for 1,3-dienes both in solution and in the solid state. However, the rare occurrence of the latter mode makes it clear that 1,3-dienes have a marked preference for chelation. The present examples excepted, monodentately co-ordinated 1,3-diolefin is virtually unknown in stable complexes though it is often postulated in reaction intermediates. Butadienetetracarbonyliron(0) is one example,[18] but this readily loses one molecule of CO with accompanying chelation. The preference for a chelating structure can presumably be related to improved $d_\pi \longrightarrow p_\pi{}^*$ overlap as a consequence of the greater electron delocalization possible in conjugated systems. The observation that no monodentate structures were found when the counter ligand was cp is consistent with the separate deduction from n.m.r. spectra that in these complexes the rhodium atom is a better π-donor to the diene. Thus, monodentate co-ordination must be considered exceptional, requiring a special explanation.

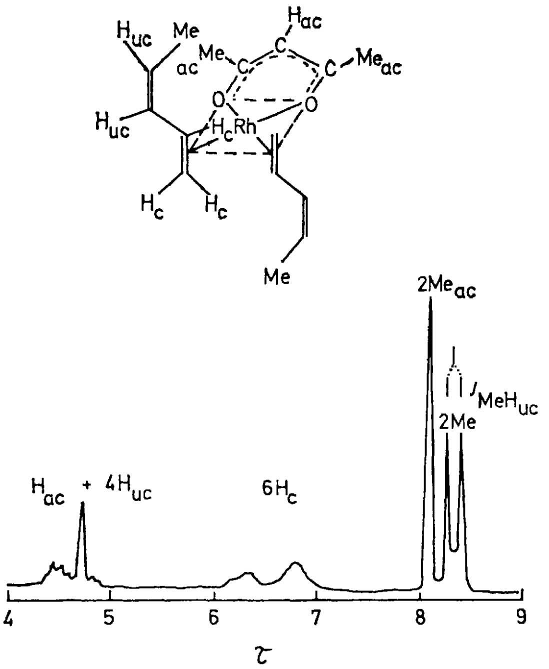
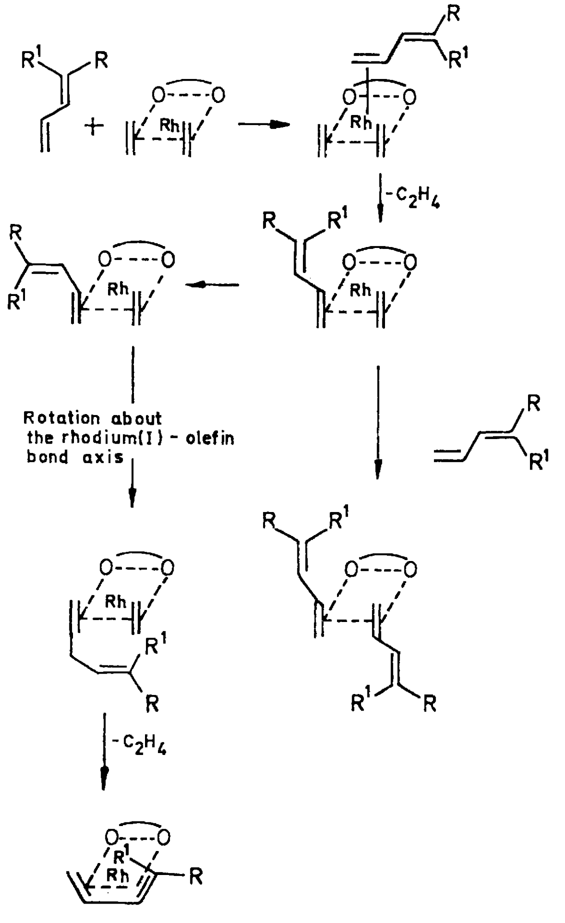


FIGURE 3 ^{1}H N.m.r. spectrum of the complex [(*cis*-penta-1,3-diene)$_2$Rh(acac)] in CDCl$_3$ at -20 °C

From stability-constant measurements of the displacement of ethylene in the complex [(C$_2$H$_4$)$_2$Rh(acac)] by substituted ethylenes, Cramer[19] has shown that both steric and electronic effects are involved. These may be opposing or reinforcing. The steric effect of any substituent is to weaken the metal–olefin bond, while the effect of an electron-withdrawing substituent, through improved $d_\pi \longrightarrow p_\pi{}^*$ overlap, is a compensating one. It was further shown that the position of substitution is important. Thus, *trans*-1,2-dialkyl-substituted olefins form less stable complexes than *cis*-1,2-disubstituted olefins, and stability is lowered further if both substituents are on the same carbon atom. Analogous information on the effects of substitution on metal–diene stability is lacking, but we may reasonably assume that the same effects apply, qualitatively, even after allowance is made for differences in geometry. If this is accepted we can now rationalize the exceptional behaviour of 4-methylpenta-1,3-diene in terms of the relative co-ordinating tendencies of the two C=C bonds.

The Scheme below illustrates the sequence of proposed steps in the displacement of ethylene in the complex [(C$_2$H$_4$)$_2$Rh(acac)] by an alkyl-substituted diene, CH$_2$=CH–CH=CRR′ (R = Me; R′ = Me or H). Since the reactant complex is co-ordinatively unsaturated, the first step is probably S_N2 nucleophilic attack of the unsubstituted double bond on the metal giving a five-co-ordinate intermediate.[19] This is followed by dissociation of one molecule of ethylene. As shown in the Scheme two possible routes are open to this intermediate in the presence of diene.[20] Thus, the type of product complex obtained is determined by the relative co-ordinating capabilities of the two C=C bonds of the diene.



SCHEME

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[18] H. Murdock and E. Weiss, *Helv. Chim. Acta*, 1962, **45**, 1156.
[19] R. Cramer, *J. Amer. Chem. Soc.*, 1967, **89**, 4621.
[20] S. M. Nelson and M. Sloan, *J.C.S. Chem. Comm.*, 1972, 745.

For the present series of dienes the difference in co-ordinating capacity is maximized in 4-methylpenta-1,3-diene and the normal stability advantage conferred by 1,3-diene chelation is in this case sufficient. In all other dienes the component C=C bonds differ less in co-ordinating tendency and chelate-complexes are preferred. The stability balance between the two alternative co-ordination modes is altered by changing the counter ligand, cyclopentadiene favouring the path that leads to chelation. Similar reaction sequences can be written for chloro- and cyclopentadienyl complexes. In the case of the latter, however, which have an effective atomic number of 18, the initial step is likely to be S_N1 dissociation of ethylene.

EXPERIMENTAL

The complexes were prepared by displacement of C_2H_4 from $[(C_2H_4)_2RhCl]_2$ and $[(C_2H_4)_2Rh(acac)]$ by the general methods given below. The chlorobuta-1,3-dienes were gifts from Du Pont Co. (U.K.) Ltd. 2-Bromobuta-1,3-diene was prepared by the method of Carothers.[21] Other butadienes were purchased from R. Emmanuel Ltd. or Pfaltz Bauer Ltd. The complexes $[(C_2H_4)_2RhCl]_2$ and $[(C_2H_4)_2Rh(acac)]$ were prepared by the methods of Cramer.[17,22] and $[(C_4H_6)_2RhCl]$ by the method of Porri *et al.*[1] Thallous cyclopentadienide was prepared as described by Cotton and Reynolds.[23] All operations were carried out under an atmosphere of nitrogen and all solvents were dried and deoxygenated before use.

Preparation of Complexes.—[(diene)$_2$RhCl], [(diene)RhCl]$_2$, *and* [(diene)$_2$RhCl]$_2$. An excess of the appropriate diene (2—10 mmol) was added to a suspension of the complex $[(C_2H_4)_2RhCl]_2$ (1 mmol) in diethyl ether (30 cm^3) and heated under reflux for 5 min; C_2H_4 was evolved. The red filtrate was concentrated to 5—10 cm^3 and usually the product separated at this stage. If not, the solution was cooled to −78 °C and if this did not initiate precipitation all the solvent was removed leaving a red oil which was triturated with cold pentane. Recrystallization was from pentane–diethyl ether (1 : 1).

The complex [(2-chlorobuta-1,3-diene)$_2$RhCl] was also synthesized by displacing butadiene from $[(C_4H_6)_2RhCl]$ but in only 32% yield as compared with 92% by the above method.

[(diene)Rh(acac)] *and* [(diene)$_2$Rh(acac)]. An excess of diene (2—12 mmol) was added to a solution of the complex $(C_2H_4)_2Rh(acac)]$ in diethyl ether and stirred for 2 h. The red filtrate was concentrated and in some cases a red solid separated. If not, the solvent was pumped off leaving a red oil which was then triturated with cold pentane. Recrystallization was from pentane–diethyl ether. Several of the complexes were alternatively prepared by addition of acetylacetone (0·2—0·3 cm^3) and anhydrous K_2CO_3 (200 mg) to a suspension of the chloro-complex (1 mmol) in petroleum ether (30 cm^3; b.p. 40—60 °C) and stirring for 1 h. The solid obtained on filtration was separated from K_2CO_3 by extraction with dichloromethane (3 × 20 cm^3). On concentrating the combined extracts to 10 cm^3, a yellow solid separated. Recrystallization was from dichloromethane–pentane (4 : 1).

[(diene)Rh(cp)]. These were prepared by treating the appropriate complex [(diene)$_2$RhCl] (1 mmol) or [(diene)-RhCl]$_2$ (0·5 mmol) with thallous cyclopentadienide (1 mmol) in diethyl ether or tetrahydrofuran (30 cm^3) and stirring for 2 h. Removal of solvent under reduced pressure from the orange filtrate left a brown solid or oil. Sublimation (100 °C, 0·2 mmHg) into a Drikold–acetone cold-finger gave yellow solids which, in some cases, melted to yellow oils on warming to room temperature.

In general, yields were high and rarely below 70%. An exception was the complex [(*cis,trans*-hexa-2,4-diene)RhCl]$_2$ which was obtained in only 12% yield. Extensive decomposition occurred on concentrating the ether filtrate, rhodium metal being deposited on the sides of the flask. Similar difficulty was experienced in the reaction of *cis*-penta-1,3-diene with the complex $[(C_2H_4)_2RhCl]_2$ and in this case no pure solid product was isolated, but the solution was used successfully in the preparation of the cp derivative. Likewise, the acac complex of the same diene was obtained only as a red oil which gave poor elemental analysis and was unstable in solution. The isoprene complex [(diene)$_2$RhCl] was obtained initially as a yellow oil which failed to solidify on trituration with pentane or setting aside. It was finally isolated as a solid by setting aside under pentane for 48 h at 0 °C. No attempt was made to recrystallize it. The complex [(1,4-diphenylbuta-1,3-diene)RhCl]$_2$ was also not recrystallized. This complex is insoluble in diethyl ether.

I.r. spectra were measured over the range 4 000—300 cm^{-1}, using a Perkin-Elmer 457 grating spectrophotometer, and over the range 300—200 cm^{-1}, using a Grubb–Parsons ' Spectromaster ' grating spectrometer. Solids were examined either as KBr or CsI discs or as Nujol mulls. Liquids were measured as thin films between KBr or CsI plates. Generally, ^1H n.m.r. spectra were recorded using an A-60D spectrometer at 37 °C. Some spectra, including spin–spin decoupling experiments, were carried out using a Varian HA-100 instrument. $CDCl_3$ was used as solvent in almost all cases. Mass spectra were obtained using an A.E.I. MS902 model at an ionizing voltage of 70 eV.

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[3/622 *Received*, 26*th March*, 1973]

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[21] W. H. Carothers, ' Collected Papers of W. H. Carothers on Polymerization,' vol. 1, Interscience, New York, 1940.

[22] R. Cramer, *Inorg. Chem.*, 1962, **1**, 722.

[23] F. A. Cotton and L. T. Reynolds, *J. Amer. Chem. Soc.*, 1958, **80**, 269.