Cationic Transition-metal Complexes. Part V.[1] Synthesis, Structure, and Dynamic Behaviour of Bis(π-allyl)-rhodium(III) and -iridium(III) Cations

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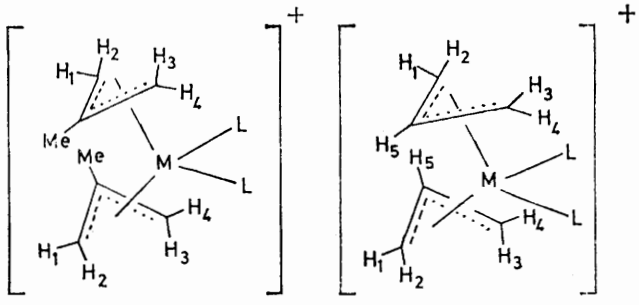
The synthesis and characterisation of cationic bis-(π-allyl) or -(π-2-methylallyl) complexes $[M(all)_2L_2]BF_4$ (M = Rh or Ir; L = phosphine, phosphites, arsine, pyridines, and MeCN), and of the neutral complexes $[M(all)_2(tpl)]$ (M = Rh or Ir; tpl = tropolonate) and $[Rh(all)_2(pyc)]$ (pyc = pyridine-2-carboxylate) is described. ^1H N.m.r. spectra of these complexes show that two equivalently bonded π-allyl ligands are asymmetrically bonded to each metal atom. The dynamic behaviour of these complexes in solution has been studied by variable-temperature ^1H n.m.r. spectroscopy. In the case of the cationic complexes it is concluded that a left-to-right exchange process occurs *via* initial dissociation of a neutral ligand (L) followed by Berry pseudo-rotation of the resultant five-co-ordinate species. The neutral complexes undergo left-to-right exchange and concomitant *syn–anti*-exchange *via* rupture of a metal–carbon bond.

VARIABLE-TEMPERATURE ^1H n.m.r. measurements combined with double-irradiation experiments with the complex bis(π-allyl)dicarbonylruthenium have provided evidence for a left-to-right exchange process.[2] The absence [3] of exchange between ^{13}CO and $[Ru(\pi\text{-}C_3H_5)_2(CO)_2]$ suggested that this formally six-co-ordinate

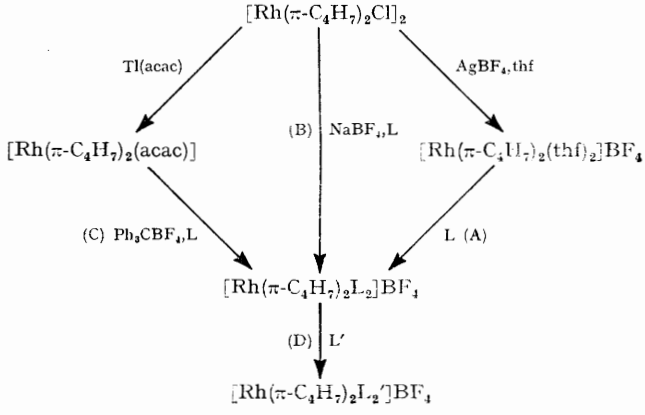


[I; M = Rh, L = $P(OMe)_3$]
[II; M = Rh, L = $P(OPr^i)_3$]
(III; M = Rh, L = Me_2PhP)
(IV; M = Rh, L = C_5H_5N)
(V; M = Rh, L = 2-picoline)
(VI; M = Rh, L = 3-picoline)
(VII; M = Rh, L = 4-picoline)
(VIII; M = Rh, L = MeCN)
[IX; M = Rh, L_2 = $(Ph_2PCH_2)_2$]
[X; M = Rh, L_2 = $(Ph_2AsCH_2)_2$]
[XI; M = Rh, L_2 = $(Me_2As)_2C_6H_4$]
(XII; M = Rh, L_2 = bipyridyl)
[XIII; M = Rh, L_2 = $(CNCH_2CH_2)_2$]
(XIV; M = Rh, L = C_5H_5N)
(XV; M = Rh, L = 2-picoline)
(XVI; M = Rh, L = 3-picoline)
(XVII; M = Rh, L = 4-picoline)
(XVIII; M = Rh, L = MeCN)
(XIX; M = Rh, L_2 = bipyridyl)
(XX; M = Ir, L = Ph_3P)
(XXI; M = Ir, L = C_5H_5N)
(XXII; M = Ir, L = 2-picoline)
(XXIII; M = Ir, L = MeCN)

Ru^{II} system might be undergoing a low-activation-energy twist process. Since such intramolecular rearrangements of six-co-ordinate species are still rare [4,5] and the factors governing such processes not well understood, we have examined the stereochemical stability of the isoelectronic and isostructural cationic species $[M(all)_2L_2]BF_4$ (M = Rh or Ir), and have found that with these systems a dissociative process is important.

RESULTS AND DISCUSSION

Synthesis and Structure.—Previously, Powell and Shaw, in their important studies [6] with the complexes $[Rh(all)_2Cl]_2$ (all = $\pi\text{-}C_3H_5$ or $\pi\text{-}C_4H_7$), isolated the cations $[Rh(all)_2L_2]^+$ (L = pyridine, L_2 = 2,2′-bipyridyl) as tetraphenylborate salts. However, the low solubility of these complexes precluded n.m.r. studies. We avoided this difficulty by preparing tetrafluoroborate salts; the methods used to prepare the rhodium and iridium complexes (I)—(XXIII) are shown in Scheme 1



SCHEME 1

for the 2-methylallyl system. Method (A), which proved to be the most useful, involved addition of a

[1] Part IV, M. Green and Susan H. Taylor, *J.C.S. Dalton*, 1972, 2629.
[2] M. Cooke, M. Green, R. J. Goodfellow, and G. J. Parker, *J. Chem. Soc.* (*A*), 1971, 16.
[3] G. J. Parker, Ph.D. Thesis, University of Bristol, 1972.
[4] S. S. Eaton, J. R. Hutchinson, R. H. Holm, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 6411; S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *ibid.*, 1973, **95**, 1116 and references therein.
[5] P. K. Pomeroy and W. A. Graham, *J. Amer. Chem. Soc.*, 1972, **94**, 274.
[6] J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 583.

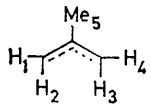
stoicheiometric amount of silver(I) tetrafluoroborate to a solution of the complex $[Rh(all)_2Cl]_2$ in tetrahydrofuran (thf), followed by removal of the precipitate of silver(I) chloride and addition of the ligand L. Method (B) was only feasible for the stronger ligands, while route (C) required isolation of the intermediate acetylacetonate complex. The more weakly bonded ligands, such as acetonitrile, can be readily displaced by other ligands [route (D)].

The iridium cations $[Ir(\pi\text{-}C_3H_5)_2L_2]BF_4$ (XX)—(XXIII) were prepared by route (A); the intermediate $[Ir(\pi\text{-}C_3H_5)_2Cl]_2$ was formed by reaction of the known [7] tris(allyl) complex $[Ir(\pi\text{-}C_3H_5)_3]$, with an ethereal solution of hydrogen chloride. Although attempts to prepare $[Rh(\pi\text{-}C_3H_5)_2(PPh_3)_2]BF_4$ were unsuccessful, due to formation of $[Rh(PPh_3)_4]BF_4$ by reductive dimerisation of the allyl ligands, the complex $[Ir(\pi\text{-}C_3H_5)_2(PPh_3)_2]BF_4$ was easily prepared, even in the presence of an excess of triphenylphosphine. Thus, mainly *via* route (A), the cationic complexes were obtained as crystalline materials which were characterised by elemental analysis, and i.r. and n.m.r. spectroscopy.

The structure of the neutral complex bis(π-2-methylallyl)bis(trimethyl phosphite)ruthenium has been established [8] by *X*-ray crystallography; the crystal structure confirms that the 2-methylallyl ligands are equivalent but asymmetrically bonded with the ruthenium atom octahedrally co-ordinated and the phosphite ligands mutually *cis*. Comparison of the ^1H n.m.r. spectra of the ruthenium complex [2] with that of the cation (I), and allowing for the expected downfield shift (1·5 p.p.m.) due the presence of a positive charge, suggests that these complexes are isostructural. The assignments for the rhodium cation (I) (Table 1) were made on the basis of the magnitudes of the ^1H–^1H and ^1H–^{31}P couplings. In addition a heteronuclear double-resonance experiment with (I) showed that all four types of terminal allyl protons, and the phosphite methyl protons, are strongly coupled to the ^{31}P nuclei. Simultaneous homonuclear double irradiation of the signal at τ 6·35 showed that there is a coupling (J_{14} 3·0 Hz) between the signals at τ 6·35 and 7·48, and that there is a small coupling between the resonances at τ 7·48 and 7·60. The resonance at τ 7·93 due to the 2-methyl group of each

TABLE 1

^1H N.m.r. data for the complex $[Rh(\pi\text{-}C_4H_7)_2L_2]BF_4$: chemical shifts [a] as τ values, coupling constants in Hz



Complex	L	τ_1	τ_4	τ_2	τ_3	τ_5	J_{RhH_5}	J_{14}
(I)	$P(OMe)_3$ [b]	6·35	7·48	7·31	7·60	7·93	<1	3·0
(II)	$P(OPr^i)_3$ [c]	6·49	7·5 [d]		7·9 [d]		<1	2·8
(III)	PMe_2Ph [e]	6·34	7·52	7·84	8·13	7·94	<1	2·8
(IV)	Pyridine [f]	5·44	7·59	7·11	8·10	7·68	2·1	1·8
(V)	2-Picoline [g]	5·22	7·55	7·18	8·11	7·77	1·9	2·0
(VI)	3-Picoline [h]	5·51	7·6	7·14	8·12	7·75	1·8	1·9
(VII)	4-Picoline [i]	5·52	7·62	7·18	8·14	7·77	1·7	2·0
(VIII)	MeCN [j]	5·58	7·9	6·86	7·9	7·99	2·1	1·0
(IX)	½ dppe [k]	7·06	7·37	7·04	8·59	7·80	<1	3·0
(X)	½ dpae [l]	6·71	7·3		8·54	7·76	<1	2·9
(XI)	½ diars [m]	6·69	7·46	7·59	8·20	7·86	1·4	2·4
(XII)	½ bipy [n]	6·10	7·38	6·88	6·95	7·83	1·8	2·6
(XIII)	$CN(CH_2)_4CN$ [o]	6·82	7·84		7·99		2·1	

[a] Measured at 27 °C in $CDCl_3$ unless otherwise stated. [b] Phosphite protons τ 6·21. [c] Phosphite protons τ 5·42, 8·63, and 8·71. [d] Approximate values due to coincidence. [e] Phosphine methyl resonance τ 8·30. [f] Pyridine protons at τ 1·54(d), 2·20(t), and 2·53(t). [g] Measured at −55 °C. [h] Picoline protons at τ 1·74(d), 1·78(s), 2·29(t), 2·64(dd), and 7·64(s). [i] Picoline protons at τ 1·72(d), 2·72(d), and 7·57(s). [j] Measured at −58°; MeCN resonance τ 7·60(s). [k] Phosphine CH_2 protons τ 7·8(m). [l] Arsine CH_2 protons τ 7·68(s) and 7·8(s). [m] diars Resonances at τ 2·37(A_2B_2), 8·08(s), and 8·60(s). [n] bipy Resonances at τ 1·43(m), 1·83(m), and 2·33(m). [o] In CH_2Cl_2 solution at −20 °C, ligand resonances at τ 7·20 and 8·12.

π-allyl ligand is a doublet (^{103}Rh coupling), which indicates that both methylallyl fragments are in equivalent environments, and that there is no significant coupling from the methyl group to either the terminal allyl protons or the ^{31}P nuclei. As in the ruthenium system it is probable that the more weakly bonded carbon atoms of the π-2-methylallyl ligand are *trans* to the phosphite ligands, the relative configuration of which was confirmed by the appearance of the CH_3OP resonance as an apparent doublet with evidence of an inner-line pattern.

The structures of the related cations (II)—(XXIII) follows from the relative chemical shifts of the allyl protons and the magnitude of the ^1H–^1H couplings (Tables 1 and 2). The largest coupling found is generally between the proton at lowest field and another proton. This is the long range *syn–syn*-coupling (J_{14}). A smaller coupling (J 1 Hz) was also observed in some cases between the high-field *syn*-proton (H_4) and the high-field *anti*-proton, and as a coupling between H_2 and H_4

[7] P. Chini and S. Martinengo, *Inorg. Chem.*, 1967, **6**, 837.
[8] J. Howard, R. A. Marsh, and P. Woodward, *J.C.S. Dalton*, 1973, 778.

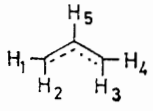
is improbable this must be the geminal coupling between H_3 and H_4.[9,10] As the signal due to the other *anti*-proton (H_2) is a sharp singlet a difference in the H–C–H bond angles at each end of the π-allyl ligand is indicated,[11] and the asymmetry of the bonding must result in a slight difference in the hybridisation at C_1 and C_3.

In the spectrum of complex (II) the non-equivalence of the phosphite methyl groups is consistent with the absence of a plane of symmetry passing through the phosphorus atoms. A similar effect should be observed with the dimethylphenylphosphine complex (III); however, the situation is complicated by the likelihood of ^{103}Rh coupling, and no definite evidence for prochiral non-equivalence of the methyl resonances could be obtained.

The pale yellow 2-picoline complex (V) could not be obtained in an analytically pure state; the complex also prepared, and the ^{1}H n.m.r. spectra of these cations illustrates the rather different steric properties imposed by these ligands on the complex. The assignments of the signals in these spectra were made on the basis of the coupling constants J_{14}, J_{34}, and J_{PH} only, as some unusual chemical shifts were observed. Thus, in the ^{1}H spectrum of the yellow crystalline complexes (IX) (Table 1), the chemical shift of the low-field *anti*-protons, H_2, is slightly lower, at τ 7·04, than that of the *syn*-protons, H_1, also bonded to C_1. Comparison of the chemical shifts of the protons in complex (IX) with those in (III), where the two PMe_2Ph ligands can be assumed to have approximately the same donor properties as the bis(diphenylphosphino)ethane (dppe) ligand, suggests that the chelating ligand increases the chemical shifts of H_1 (+0·7 p.p.m.) and H_3 (+0·5), but decreases the shifts of H_2 (−0·8) and H_4 (−0·2)

TABLE 2

^{1}H N.m.r. data [a] for the complexes $[M(\pi\text{-}C_3H_5)_2L_2]BF_4$ (M = Rh or Ir): chemical shifts as τ values, coupling constants in Hz



Complex	M	L	τ_1	τ_4	τ_2	τ_3	τ_5	J_{15}	J_{45}	J_{25}	J_{35}	J_{14}	J_{34}
(XIV)	Rh	Pyridine [b]	5·14	7·11	6·93	8·33	4·58	7·3	6·8	12·0	11·0	1·3	0·8
(XV)	Rh	2-Pyridine [c]	4·80	6·91	7·31	8·50	4·58	7·0	6·0	12·0	11·0	<2	<1
(XVI)	Rh	3-Picoline [d]	5·13	7·05	6·93	8·40	4·51	7·3	7·0	12·4	11·2	1·7	<1
(XVII)	Rh	4-Picoline [e]	5·12	7·14	7·00	8·47	4·60	7·3	6·8	12·0	11·2	1·9	1
(XVIII)	Rh	MeCN [f]	5·16	7·50	6·54	8·22	5·1		6·5	12·0	10·0		<1
(XIX)	Rh	½ bipy [g]	5·72	6·94	7·43	8·28	4·72	6·8	6·4	12·0	10·8	1·8	1
(XX)	Ir	PPh_3 [h]		6·3		8·14	8·57	4·64		9·5		10·8	
(XXI)	Ir	Pyridine [i]	5·62	7·16	7·63	8·67	4·90	6·8	9·8	6·3	10·2	1·6	1·9
(XXII)	Ir	2-Picoline [j]	5·28	7·04	8·05	8·74	5·04	7·2	9·5	6·5	10·4	2·0	1·7
(XXIII)	Ir	MeCN [k]	5·63	7·16	7·63	8·67	5·42	6·9	9·8	6·2	10·8	2·1	2·3

[a] Measured at 27 °C in $CDCl_3$ unless otherwise stated. [b] Pyridine resonances at τ 1·52(d), 2·17(t), and 2·44(t). [c] At −55 °C, 2-picoline resonances at τ 1·56(d), 2·24(t), 2·59(d), 2·84(t), and 7·12(s). [d] Picoline resonances τ 1·61(s), 1·72(d), 2·25(d), 2·61(dd), and 7·59(s). [e] Picoline resonances τ 1·71(d), 2·73(d), and 7·57(s). [f] Measured at −50 °C, *Me*CN resonances at τ 7·57(s). [g] bipy Multiplets at τ 1·35, 1·50, 1·82, and 2·35. [h] Due to complexity of spectrum most coupling constants are not measurable: $N_2 = |J_{P2} + J_{P'2}| = 17$; $N_3 = 13$ Hz. [i] Pyridine resonances at τ 1·44(d), 2·05(t), and 2·25(t). [j] Picoline resonances at τ 1·87(d), 2·24(t), 2·50(d), 2·93(t), and 7·11(s). [k] *Me*CN resonance at τ 7·41(s).

rapidly dissociates in solution at 10 °C. By forming this complex at low temperature (−80 °C) and measuring the ^{1}H n.m.r. spectrum at −55 °C, a spectrum was obtained, which apart from some small differences in chemical shift, corresponded closely to that of the more stable isomeric cations (VI) and (VII).

As shown by the data in Tables 1 and 2, the nature of the ligand L has a considerable influence on the chemical shifts of all allyl protons. Although it is reasonable to expect that steric interactions will play a part in determining these chemical shifts, H_1 and H_2 appear to become more shielded and H_3 and H_4 less shielded as the ligand becomes more strongly bonded to the metal. Similarly, the value of J_{14} increases while that of J(Rh–Me) decreases.

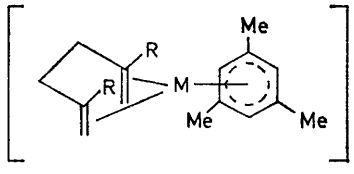
Several complexes containing bidentate ligands were relative to the two PMe_2Ph ligands. Inspection of molecular models shows that there will be considerable steric interactions between the phenyl groups of the dppe ligand and some of the allyl protons. Similar effects were observed in the spectrum of the bis(diphenylarsino)ethane (dpae) complex (X), although the observed magnitude of the shifts indicates the presence of less steric interaction, presumably, due to the longer Rh–L bond in the arsine complex. A more precise explanation of these effects is that the ring currents of the phenyl groups have an influence on the allyl protons.

Examination of molecular models of the *o*-phenylenebis(dimethylarsine) (diars) complex (XI) shows that there will be no significant interactions between the diars and π-allyl ligands. However, unless there is a large distortion, possibly due to interaction between

[9] M. Barfield, *J. Chem. Phys.*, 1964, **41**, 3825.
[10] S. Sternhell, *Pure Rev. Appl. Chem.*, 1964, **14**, 15.
[11] H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, 1959, **31**, 1278.

the $AsMe_2$ groups, the two arsenic atoms and the benzene ring of the diars ligand will be coplanar. This should result in the two π-2-methylallyl ligands being inequivalent because the arene ring will not lie in the ($Rh \cdots As_1 \cdots As_2$) plane. Thus, small chemical-shift differences could occur between pairs of protons, *e.g.* H_3 and H_3'; however, only in the case of the H_2 resonance was any evidence of non-equivalence observed.

The scope of the synthetic route (A), involving formation of the intermediate $[Rh(all)_2(thf)_2]BF_4$, was also examined. However, the unknown complexes $[Rh(all)_2(1,3\text{-diene})]BF_4$ could not be obtained, and addition of cyclo-octa-1,5-diene (cod) or norbornadiene (nbd) resulted in formation of the known [12] cations $[Rh(diene)_2]^+$ (diene = cod or nbd). The addition of the arenes, mesitylene, hexamethylbenzene, or, 1,2-dimethoxybenzene to solutions of the Rh^{III} species $[Rh(\pi\text{-allyl})_2(thf)_2]BF_4$ afforded the stable Rh^{I} arene complexes (XXIV)—(XXIX). The same kind of complex was also obtained by method (C), and in this way the arene cationic complexes (XXVI) and (XXVIII) were formed. These yellow stable crystalline complexes



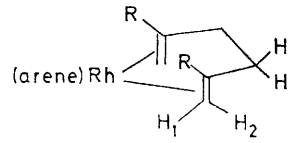
(XXIV; M = Rh, R = H)
(XXV; M = Rh, R = H, arene = C_6Me_6)
[XXVI; M = Rh, R = H, arene = $1,2\text{-}C_6H_2(OMe)_2$]
(XXVII; M = Rh, R = Me, arene = $1,3,5\text{-}C_6H_3Me_3$)
[XXVIII; M = Rh, R = Me, arene = $1,2\text{-}C_6H_4(OMe)_2$]
(XXIX; M = Rh, R = Me, arene = C_6Me_6)

were characterised by elemental analysis, and i.r. and n.m.r. spectroscopy. The ^1H n.m.r. spectra (Table 3) clearly showed that these complexes contain co-ordinated hexa-1,5-dienes formed by reductive dimerisation of the π-allylic ligands. Previously [13] the arene complexes $[Rh(cod)(arene)]^+$ and $[Rh(nbd)(arene)]^+$ have been described, and it is probable that the cations (XXIV)—(XXIX) are also best depicted as 18-electron systems.

For purposes of comparison with the cationic species $[M(all)_2L_2]^+$ (M = Rh or Ir), the neutral bis(π-allyl) complexes (XXX)—(XXXII) were synthesised by reaction of the corresponding chloro-species $[M(all)_2Cl]_2$ with tropolone in the presence of a base (KOH). The rhodium complex (XXXIII) was also prepared by reaction of $[Rh(\pi\text{-2-methylallyl})_2Cl]_2$ with 2-picolinic acid and base. The static ^1H n.m.r. spectra of these

TABLE 3

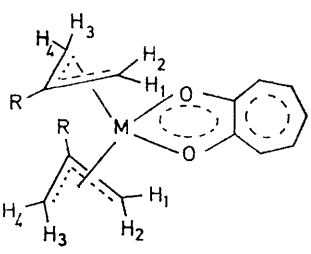
^1H N.m.r. data [a] for arene rhodium tetrafluoroborate complexes: chemical shifts as τ values, coupling constants in Hz



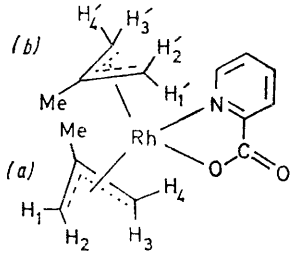
	Chemical shifts						Coupling constants			
	diene				arene					
Complex	τ_1	τ_2	τ_R	τ_{CH_2} [b]	τ	τ_{Me}	$J(RH_1)$	$J(RH_2)$	$J(RhH_1)$	$J(RhH_2)$
(XXIV)	6·88	7·51	5·24	7·7—8·2	3·44	7·66	8·4	13·2	2·5	2·0
(XXV)	7·49	7·51	5·14	7·8—8·2		7·77	*c*	14·4	2·0	<1
(XXVI)	6·83	7·54	5·24	7·6—8·2	2·66 3·75	5·98	8·5	12·5	2·7	1·9
(XXVII)	7·23	7·52	8·26	7·7—8·2	3·72	7·64			2·3	2·0
(XXIX)	7·59	7·56	8·36	7·6—8·2		7·78			2·0	<1
(XXVIII)	6·96	7·83	8·38	7·7—8·2	2·74 3·99	5·98			2·7	2·2

[a] Measured at 28 °C in $CDCl_3$. [b] Broad methylene resonances were observed. [c] Not measurable due to coincidence of signals.

complexes (Table 4) were interpreted straightforwardly, and are consistent with structures containing equivalent



(XXX; M = Rh, R = H)
(XXXI; M = Rh, R = Me)
(XXXII; M = Ir, R = H)



(XXXIII)

asymmetrically bonded allyl ligands. It is of interest that the resonance due to the *anti*-proton H_3 of (XXXI) is downfield of the resonance due to the *syn*-proton H_4. Such a reversal of the usual pattern is also found in the

[12] M. Green, T. Kuc, and S. H. Taylor, *J. Chem. Soc.* (*A*), 1971, 2334.
[13] M. Green and T. A. Kuc, *J.C.S. Dalton*, 1972, 832.

spectrum of the acetylacetonate complex and the chloro-bridged dimer, suggesting that these three complexes have similar structure. This evidence coupled with the expectation that the *trans*-influence of the electronegative tropolonate ligand is less than that of the allyl ligand suggests that the direction of the asymmetry in the allyl ligand is as illustrated, with the more weakly bonded terminal allyl carbon atoms mutually *trans*.

TABLE 4

^{1}H N.m.r. data [a] for tropolonate complexes: chemical shifts as τ values, coupling constants in Hz

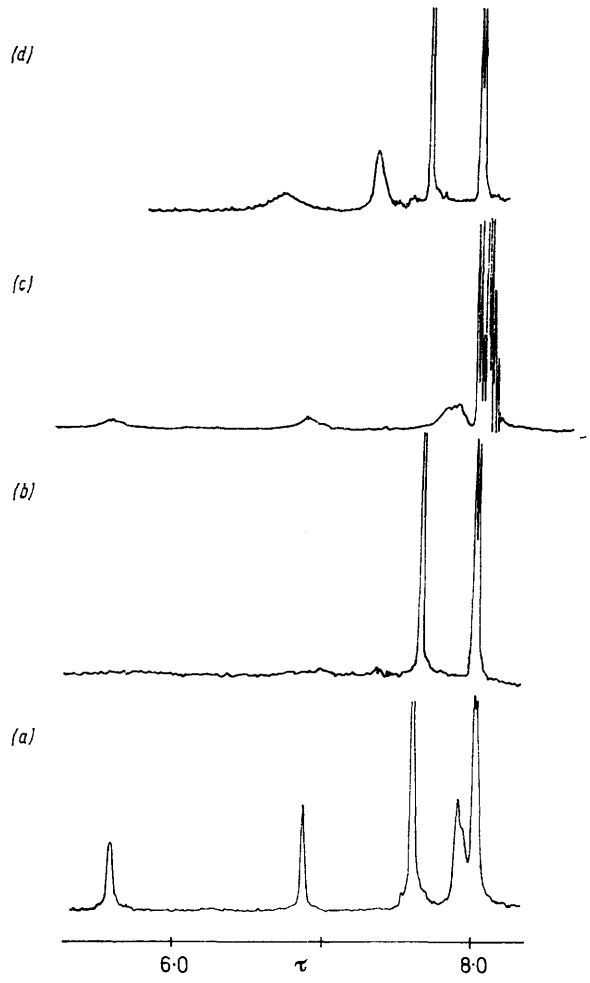
	Chemical shifts					Coupling constants					
Complex	τ_1	τ_4	τ_2	τ_3	τ_5	J_{15}	J_{45}	J_{25}	J_{35}	J_{14}	J_{34}
(XXX) [b]	5·45	7·5	7·5	8·06	5·26	7·0	6·0	11·0	10·4	<1	<1
(XXXI) [c]	5·69	7·85	7·64	7·74	8·03					1·8	<0·5
(XXXII) [d]	6·0	7·37	8·20	8·25	5·61	6·5	6·2	10·2	10·0	1·8	<1

[a] Measured in $CDCl_3$ solution; two tropolonate resonances are broad multiplets τ 2·6—3·3. [b] At −60 °C. [c] At 34 °C; J(RhMe) 1·9 Hz. [d] At 34 °C.

The ^{1}H spectrum of the pyridine-2-carboxylate complex (XXXIII) shows (see Experimental section) as expected ten signals for the methylallyl protons, as the methylallyl ligands are now non-equivalent. Double-irradiation experiments, at 25 °C, showed that the signals at τ 5·75, 7·94, and 7·80 and those at 5·96, 7·50, and 8·40 are due to protons within the same allyl ligands. The relative magnitudes of the coupling constants and the chemical shifts enabled the assignments to be made which are listed in the Experimental section. The signals due to the low-field *anti*-protons and the methyl groups could not be assigned to a particular allyl group. The nitrogen atom of the picolinate ligand should have a relatively strong *trans*-influence and thus the carbon atom of the allyl group, which is *trans* to nitrogen, will be more weakly bonded as illustrated. However, the asymmetry in the other allyl group would be expected to be in the reverse direction, as the *trans*-influence of the electronegative oxygen atom would be less than that of the allyl ligand. Since in the pyridine complexes $\tau_3 > \tau_4$ whilst $\tau_3 < \tau_4$ in the acac and tropolonate complexes, it is suggested that the protons H_1, H_3, and H_4 are attached to the methylallyl ligand (*a*) (see illustration), which is opposite the nitrogen donor, and the protons H_1', H_3', and H_4' are in ligand (*b*).

Dynamic Processes.—A study of the variable-temperature ^{1}H n.m.r. spectra of the complexes described has provided evidence for both *syn–anti* and left-to-right exchange processes. Since all the crystal-structure data available for π-allyl metal complexes has indicated that each π-allyl group is best regarded as occupying two co-ordination sites, in the following discussion of possible exchange mechanisms the complexes $[M(all)_2L_2]^+$ are treated as six-co-ordinate (distorted octahedral) species. The left-to-right exchange process referred to is a process in which the protons on each end of the allyl group exchange environments.

At room temperature, the ^{1}H n.m.r. spectrum of complex (VIII) in $CDCl_3$ showed sharp signals due to the methyl groups of the acetonitrile and allyl ligands but only two broad resonances at τ 6·68 and 7·29 for the other allyl protons (Figure). At −50 °C the spectrum showed the normal static spectrum, although the H_3 and H_4 signals are coincident (Table 1). Double-irradiation studies at −15 °C showed that there is an exchange process that averages the environments of the *syn*-protons (H_1 and H_4) and of the *anti*-protons (H_2 and H_3). The signal of the 2-methyl group was unchanged throughout the temperature range studied.



^{1}H N.m.r. spectra of the cation $[Rh(\pi\text{-}C_4H_7)_2(MeCN)_2]^+$: (*a*) in $CDCl_3$ at −50; (*b*) in $CDCl_3$ at 25; (*c*) in CD_3CN at 25; and (*d*) in $CDCl_3$ at 42 °C

It was also observed that the linewidths of the signals at −10 °C, were independent of the concentration of complex (VIII) in $CDCl_3$. Thus, the temperature dependence of this spectrum is caused by a rapid monomolecular left-to-right exchange process. When a small amount of CD_3CN was added to a solution of complex (VIII) in $CDCl_3$ the ^1H spectrum showed that free and co-ordinated acetonitrile exchange very readily. Moreover, the rate of the left-to-right exchange process, as shown by the line shape of the resonances, is retarded by the presence of free acetonitrile. This is illustrated by the spectrum [Figure (*c*)] of (VIII) in CD_3CN solution at 25 °C.

From these observations, and other evidence yet to be discussed, it seems probable that ligand dissociation plays a prominent part in the left-to-right exchange process. The ^1H spectrum of complex (XVIII), the π-C_3H_5 analogue of (VIII), showed a similar, but much slower, left-to-right exchange. At 34 °C the ^1H spectrum showed four very broad resonances due to the terminal π-allyl protons. The AM_2X_2 spectrum is not observed below 60 °C, and the complex decomposes at this temperature. Similar left-to-right exchange processes occur with the other cations, the rate being dependent on the nature of the ligand L. The variation of the linewidths of suitable resonances of some of the complexes have been used to calculate the reaction rates and activation parameters of the exchange reactions. The procedure used is detailed in the Experimental section. The values obtained (Table 5) and other data described below, show that at 25 °C the exchange rate decreases as L (L–L) varies in the series 2-picoline > MeCN > $NC(CH_2)_4CN$ ⩾ 3-picoline > pyridine > 4-picoline ~ diars > $P(OMe)_3$ ~ $P(OPr^i)_3$ > bipy > dppe ~ dpae ~ PMe_2Ph.

TABLE 5

Activation parameters for left-to-right exchange reactions of the cations $[Rh(all)_2L_2]^+$ ($CDCl_3$ solution)

Complex	Allyl group	Ligand L	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]
(VIII)	C_4H_7	MeCN	9·8 ± 0·5	54·4 ± 12·6
(IV)	C_4H_7	Pyridine	19·6 ± 0·6	50·2 ± 8·4
(XVIII)	C_3H_5	Pyridine	22·1 ± 0·5	62·8 ± 8·4
(V)	C_4H_7	2-Picoline	20·9 ± 1·3	150·6 ± 21·0
(XV)	C_3H_5	2-Picoline	23·2 ± 0·7	146·4 ± 12·6
(XI)	C_4H_7	½ diars [c]	19·7 ± 0·4	10·5 ± 6·3
(XI)	C_4H_7	½ diars [d]	20·7 ± 0·5	12·6 ± 6·3

[a] In kJ mol^{-1} [b] In J K^{-1} mol^{-1}; the variation of $\Delta S^{\ddagger}$ with temperature was not significant [c] Values determined from line shape of diars methyl resonance [d] Values determined from line shape of allyl protons

The temperature dependence of the spectrum of the diars complex (XI) showed that the averaging of the environments of the arsine methyl groups proceeds at a similar rate to that of the left-to-right exchange of the allyl protons; this is illustrated by the activation parameters (Table 5). Since the interconversion of the methyl groups can only occur if there is free rotation about the arene–arsenic bond, and this can only occur if there is rupture of the Rh–As bond, formation of a five-co-ordinate intermediate in the left-to-right exchange process is indicated.

At 25 °C, irradiation at the frequency of H_1 in the ^{31}P-decoupled ^1H n.m.r. spectrum of complex (I) showed that, not only is H_1 coupled to H_4, but also that H_4 and H_1 are exchanging as shown by the reduction of the intensity of the observed singlet resonance. Similar behaviour was observed for (II), but as this cation decomposed at a relatively low temperature (60 °C) it was not possible to determine whether the left-to-right exchange is accompanied by an exchange of the prochiral methyl groups of the $P(OPr^i)_3$ ligands.

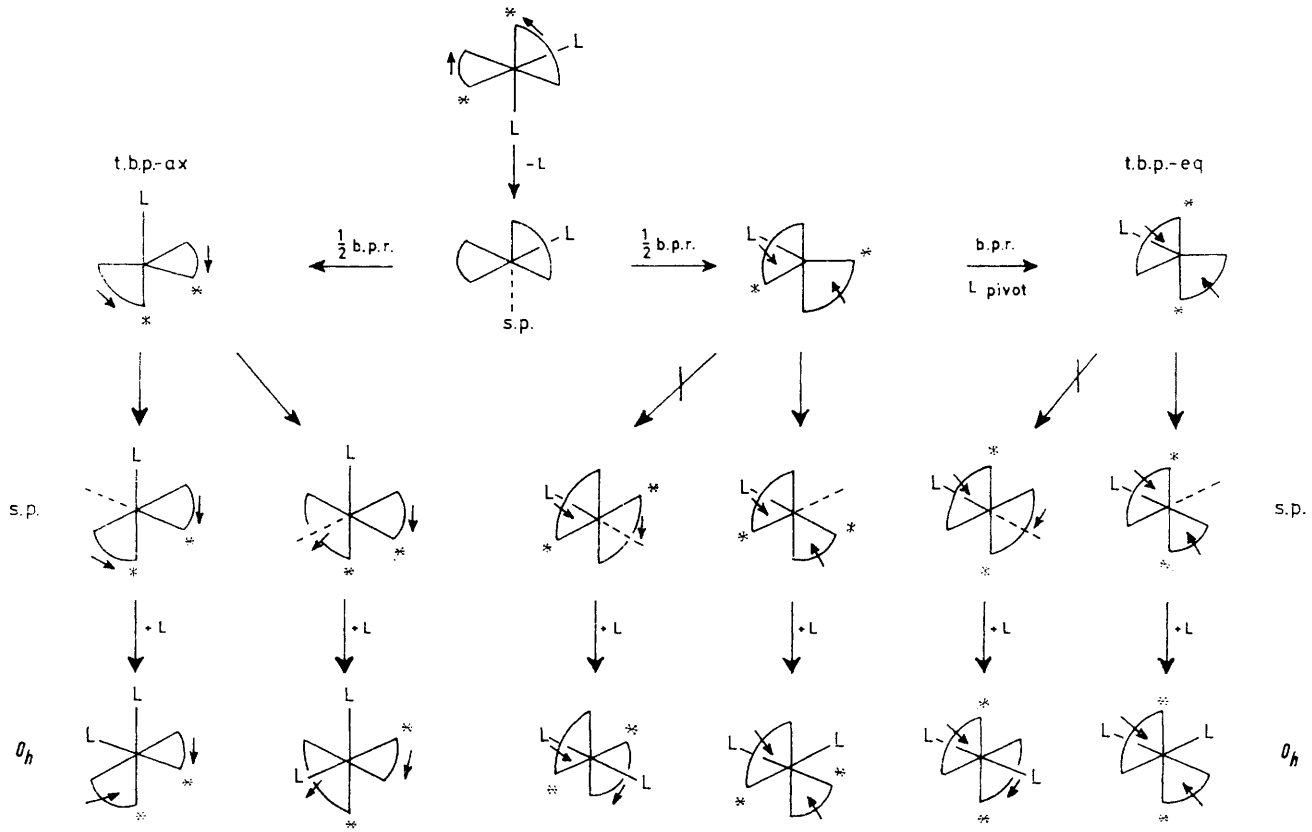
The spectra of the pyridine and methylpyridine complexes (IV)—(VII) and (XIV)—(XVII) also provided evidence for a dissociative process. Linewidth measurements showed that the left-to-right exchange rates for complexes (IV) and (XIV) are larger than those for (VII) and (XVII), as would be expected since 4-picoline is a better donor ligand than pyridine. However, the ^1H spectrum of complex (XV) exhibits an AM_2X_2 spectrum at 30 °C due to a very fast exchange reaction, and even though the sample contained free 2-picoline the spectrum of (V) showed fast left-to-right exchange at −5 °C. Inspection of molecular models indicates that if there is free rotation about the Rh–N bonds of complexes (V) and (XV) there will be considerable steric interaction between the two methyl groups of the 2-picoline ligands. Thus, it seems probable that the fast left-to-right exchange is caused by rapid dissociation of a 2-picoline ligand with relief of steric compression. This is consistent with the observed (Table 5) high positive entropy values $\Delta S^{\ddagger}$ for these two cations. A similar but smaller steric interaction between the 3-picoline ligands of complexes (VI) and (XVI) provides an explanation for the faster exchange rate of these cations. It was also found that the rate of the left-to-right exchange of $[Rh(\pi\text{-}C_4H_7)_2(py)_2]^+$ (IV) measured (34 °C) from the linewidth of the H_2 resonance, decreases as the solvent varies in the series $(CD_3)_2CO$ > $CDCl_3$ ⩾ pyridine. Since a solvent such as acetone would be expected to stabilise a five-co-ordinate intermediate, this is further evidence for a dissociative process.

As mentioned earlier evidence was also obtained for a *syn–anti*-exchange process. In the case of the cation (VIII), double irradiation of the ^1H n.m.r. signal at τ 7·29 due the *anti*-protons caused a significant decrease in the intensity of the signal at τ 6·68 due to the *syn*-protons. Similar effects were noted in the spectra of $CDCl_3$ solutions of complexes (V), (XV), and (XVIII). However, at the temperatures at which this exchange is sufficiently fast to be observable there was evidence of decomposition. Although the left-to-right exchange and decomposition are retarded by free ligand, double-irradiation studies on the spectra of complex (IV) in pyridine and (VIII) in CD_3CN show that the *syn–anti*-exchange process is, to a small extent, catalysed by free ligand.

This is to be expected if the *syn–anti*-exchange proceeds *via* formation of a σ-allyl intermediate.

In relating these observations to a detailed reaction path or paths for left-to-right exchange it is important to note that the relative configuration of the two allyl groups and the two ligands L is retained, and as discussed earlier this is assumed to be configuration established [8] by *X*-ray crystallography for the related ruthenium complex $[Ru(\pi\text{-}C_4H_7)_2P(OMe)_3]_2$.

The observations described require that there is a relatively low-energy path for isomerisation involving or more simply half of the Berry pseudo-rotation (b.p.r.) motion, rearrange into two possible t.b.p. isomers, there being two pairs of *trans*-ligands in the s.p. structure which can become the *trans*-axial pair in the t.b.p. structure. Each t.b.p. isomer thus formed can convert into three s.p. structures, there being three equatorial ligands which can serve as ' pivots.' The resultant new s.p. isomers can then recombine with the dissociated ligand L to reform the formally octahedral species. Examination of Scheme 2 shows that although left-to-right exchange can be achieved, the additional feature of the



SCHEME 2

dissociation of a ligand L from the cations $[M(all)_2L_2]^+$ (M = Rh or Ir), and it is probable that such a step nvolves initial formation of a square-pyramidal (s.p.) intermediate, where the apical ligand is the one initially *trans* to the leaving group.[14,15] In order for left-to-right exchange to occur the s.p. isomer must rearrange into a trigonal-bipyramidal (t.b.p.) isomer. As shown in Scheme 2 such an s.p. isomer can, *via* a ' reverse Berry ' * retention of the relative configuration of the π-allyl ligands (indicated by arrows) is only obtained if the t.b.p.–equatorial isomer undergoes a complete Berry pseudo-rotation (with L as a pivot) into an alternative t.b.p.–equatorial isomer before recombination with L. In explaining these experiments we believe that in the light of recent observations,[18–20] it is not necessary to

* Although analysis of the five-co-ordinate surface is possible in terms of the 'turnstile ' rotation [16] (t.r.), because recent calculations [16,17] with simple molecules suggest that the b.p.r. process is lower in energy than that of t.r., we have considered only a b.p.r. process in this paper.

[14] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, 1967, p. 249.

[15] J. E. Gordon and R. H. Holm, *J. Amer. Chem. Soc.*, 1970, **92**, 5319.

[16] P. Gillespie, P. Hoffman, H. Llusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolio, and I. Ugi, *Angew. Chem. Internat. Edn.*, 1971, **10**, 687.

[17] R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.

[18] D. L. Tibbetts and T. L. Brown, *J. Amer. Chem. Soc.*, 1970, **92**, 3031.

[19] J. W. Faller and M. J. Incorvia, *Inorg. Chem.*, 1968, **7**, 840.

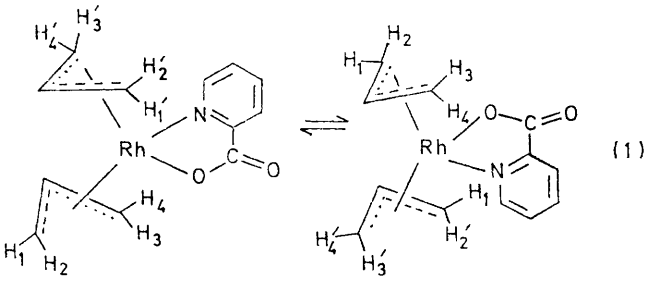
[20] K. Vrieze, H. C. Volger, and P. W. N. M van Leeuwen, *Inorg. Chim. Acta Rev.*, 1969, 109.

take into account the possibility of rotation of the π-allyl ligand about an axis through the metal and perpendicular to the plane of the allyl group.

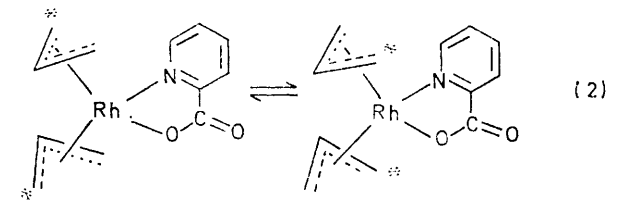
In a dissociative process of the kind shown in Scheme 2, the faster rate of left-to-right exchange for the 2-methylallyl complexes over their π-allyl analogues can be explained in terms of relief of steric compression on formation of a five-co-ordinate species. The variation of the rate with the nature of L is explicable in terms of the strength of the Rh–L bond. In comparing the rhodium with the analogous iridium species it is interesting that double-irradiation studies with complex (XXIII) $[Ir(\pi\text{-}C_3H_5)(MeCN)_2]^+$ showed the existence of left-to-right exchange at 55 °C, but there was insufficient variation in the linewidths of the resonances of this, or the other Ir^{III} species synthesised, below decomposition temperature to afford a quantitative comparison. However, double-irradiation studies clearly showed that the left-to-right exchange rate decreases as L varies in the series MeCN > 2-picoline > pyridine ≫ PPh_3, implying a similar dissociative process. It would be expected that the electrostatic effect of the increased effective nuclear change of Ir^{III} over Rh^{III} would play an important part in the strengthening of the M–L bond when L is a σ-donor and this would, consequently, retard the exchange rate. At higher temperature, and in the presence of free ligand, *syn–anti*-exchange as well as left-to-right exchange occurs. This may be explained by the straightforward formation of a σ-allyl five-co-ordinate intermediate, which, *via* processes similar to those outlined in Scheme 2, and in addition (π–σ) C–C rotation,[20] can lead to both kinds of exchange process.

It was of interest to compare the dynamic behaviour of the cationic species $[M(all)_2L_2]^+$ with that of the corresponding neutral complexes, *i.e.* the acetylacetonate, tropolonate, and pyridine-2-carboxylato-species. The known complexes $[Rh(\pi\text{-}C_3H_5)_2(acac)]$ and $[Rh(\pi\text{-}C_4H_7)_2(acac)]$ exhibit slow exchange reactions in solution. The ^1H n.m.r. spectrum of the 2-methylallyl complex, in PhCl, at 90 °C shows no significant line broadening, but double irradiation of the signal due to H_1 showed that saturation is transferred to the other three types of terminal proton and that *syn–syn*-exchange is slightly faster than *syn–anti*-exchange (by integration).

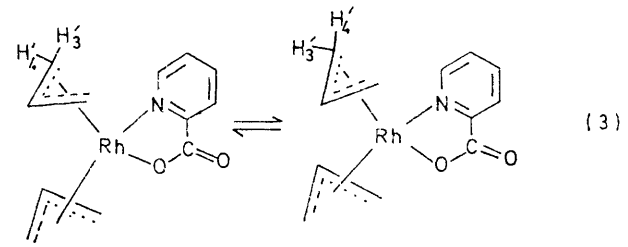
However, it proved more convenient to study the n.m.r. spectra of the related tropolonate complexes. At 30 °C ^1H resonances of the terminal allyl protons of complex (XXXI) are broad, and as the temperature is increased these lines broaden further until they disappear (60 °C). At 80 °C a very broad signal due to the X protons of an AX_4 system is observed. Further increases in the temperature decrease the linewidth until decomposition becomes rapid at 120 °C. The linewidths of the resonances, at 25 °C, were independent of the concentration of complex (XXXI), but increased as the solvent varied in the series $C_6H_6 < PhNO_2 < CDCl_3 < (CD_3)_2CO$. The corresponding exchange reactions of the analogous complexes (XXX) and (XXXII) are similar but slower, as in both of these complexes the fast-exchange limit is only reached at temperatures just below the decomposition temperature. Double-irradiation studies on the n.m.r. spectra of the iridium species (XXXII) at 45 °C showed that, for example, when H_1 is irradiated the decrease in intensity of H_4



N—O exchange: 1≡4′; 2≡3′; 3≡2′; and 4≡1′.



Left-to-right exchange: 1≡4; 2≡3; 1′≡4′; and 2′≡3′.



Syn-anti-exchange: 3′≡4′, *etc.*

SCHEME 3

is greater than the corresponding decrease for either H_2 or H_3. Similar effects were observed, for both (XXXI) and (XXX), indicating that *syn–syn* and *anti–anti*, *i.e.* left-to-right exchange, is faster than *syn–anti* exchange.

Further information on the nature of these exchange processes was obtained from a study of the ^1H n.m.r. spectrum of the pyridine-2-carboxylato-complex (XXXIII), in which three distinct exchange reactions could be discerned. At 90 °C, in $PhNO_2$ solution, the ^1H spectrum shows one methyl signal. As the chemical shifts of the allyl resonances are somewhat greater than

that of the two original methyl resonances, the averaged signals of the terminal protons are not observed and at higher temperatures decomposition occurs. However, at 55 °C, irradiation of the H_1' resonance produces decreases in intensity of all observable terminal proton resonances due to H_2', H_2, H_4, H_3, and H_3'. Irradiation at the frequency of the H_4' resonance, which is partially obscured by a methyl signal, decreases the intensity of the H_1 and H_1' resonances, while a similar saturation effect on H_3' was caused by irradiation at H_3. Thus, each terminal allyl proton is exchanging its environment with all other terminal proton environments and it seems that the rate of type (1) and (2) exchanges (Scheme 3), as measured from the integration of the irradiated spectrum, are both faster than type (3) *syn–anti*-exchange. As the directions of the bonding asymmetry in the non-equivalent π-allyl ligands are opposite, each normal N–O exchange (*via* dissociation) will also result in a left-to-right exchange (2). As *syn–anti*-exchange is relatively fast in these systems the rate-determining step for all types of exchange reaction observed is, almost certainly, formation of a σ-allyl intermediate, in which *syn–anti*-exchange, *via* rotation about a C–C single bond, or left-to-right exchange can occur.

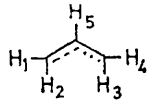
Thus, the experimental evidence described for both the cations $[M(all)_2L_2]^+$ and the neutral species $[M(all)_2(tpl)]$ or $[M(all)_2$picolinate] can be explained in terms of a dissociative process, there being no evidence for an intramolecular, *i.e.* twist, process of comparable energy.

EXPERIMENTAL

^{1}H n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer fitted with a calibrated variable-temperature accessory. More accurate temperature values were obtained by using an ethylene glycol (high temperatures) or methanol (low temperatures) internal reference. Chemical shifts are given in τ values, measured in p.p.m. (±0·02) from internal Me_4Si. Coupling constants are given in Hz (±0·2). Unless otherwise stated the solvent was $CDCl_3$. I.r. spectra were recorded using either Nujol mulls or in solution on a Perkin-Elmer 257 grating spectrophotometer. Mass-spectroscopic data were obtained using an A.E.I M.S9 spectrometer operating at 70 eV ionising potential; values of *m/e* given are those for the most abundant isotopes ^{35}Cl and ^{193}Ir. All reactions were carried out under an atmosphere of dry oxygen-free nitrogen.

Tetra(π-allyl)di-μ-chloro-dirhodium, di-μ-chloro-tetra(π-2-methylallyl)dirhodium, acetylacetonatobis(π-allyl)rhodium, and acetylacetonatobis(π-2-methylallyl)rhodium were prepared by published methods.[6] Tris(π-allyl)iridium was prepared by a modified version of the synthesis described by Chini *et al.*[7]

Preparations.—Tetra(π-allyl)di-μ-chloro-di-iridium. A solution of hydrogen chloride in diethyl ether was slowly added with stirring to a solution of tris(π-allyl)iridium (0·7 g, 2·2 mmol) in diethyl ether (10 cm^3) until no further precipitation of a yellow solid was observed. The precipitate was collected and washed with hexane to give yellow crystals of *tetra(π-allyl)di-μ-chloro-di-iridium* (0·55 g, 81%), m.p. 157 °C (decomp.) [Found: C, 23·4; H, 3·2; Cl, 11·5; *M*, 620 (mass spectrum). Calc. for $C_{12}H_{20}Cl_2Ir_2$: C, 23·3; H, 3·3; Cl, 11·5%; *M* 620]. $\nu_{max.}$ (Nujol) at 3 075w, 1 230m, 1 190w, 1 012w, 994m, 971m, 933m, 926s, 914s, and 730 cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 5·34 (1H, H_1, J_{14} 1·0 Hz), 5·46 (1H, H_5, J_{25} 5·0, J_{35} 10·0, J_{45} 8·5 Hz), 6·70 (1H, H_3, J_{34} 1·5, J_{35} 10·0 Hz), 7·54 (1H, H_2, J_{25} 5·0 Hz), and 8·58 (1H, H_4, J_{14} 1·0, J_{45} 8·5 Hz).



Cationic complexes. The procedures followed for the synthesis of the following complexes are similar, and representative details for each of the methods [(A), (B), (C), and (D)] are given.

Method (A): *Bis(acetonitrile)bis(2-methylallyl)rhodium tetrafluoroborate*, (VIII). Silver(I) tetrafluoroborate (0·12 g, 0·6 mmol) was added to a stirred solution of di-μ-chloro-tetra(2-methylallyl)dirhodium (0·15 g, 0·3 mmol) in dry tetrahydrofuran (40 cm^3). The precipitated silver(I) chloride was removed by filtration and the volume of the solvent reduced (10 cm^3) *in vacuo*. Acetonitrile (10 cm^3) was added to the yellow solution followed by diethyl ether (20 cm^3), which precipitated white *crystals* of (VIII) (0·19 g, 85%), m.p. 96—98 °C (Found: C, 37·7; H, 5·4. Calc. for $C_{12}H_{20}BF_4N_2Rh$: C, 37·7; H, 5·3%). $\nu_{max.}$ (Nujol) at 3 080w, 2 290m, 2 260m, 1 510w, 1 345w, 1 283w, 1 095vs, 1 055vs, 1 045vs, 966s, 945s, 855m, 841s, and 730 cm^{-1}.

Method (B): *Bis(2-methylallyl)bis(pyridine)rhodium tetrafluoroborate*, (IV). Sodium tetrafluoroborate (0·04 g, 0·35 mmol) in methanol (15 cm^3) was added to a stirred solution of di-μ-chloro-tetra(2-methylallyl)dirhodium (0·08 g, 0·15 mmol) in methylene chloride (5 cm^3) and pyridine (5 cm^3). After stirring at room temperature for 0·5 h the solvent was removed *in vacuo* and the yellow residue crystallised from methylene chloride–diethyl ether to give pale yellow *crystals* of (IV) (0·09 g, 67%), m.p. 94—95 °C (Found: C, 47·2; H, 5·3. Calc. for $C_{18}H_{24}BF_4N_2Rh$: C, 47·0; H, 5·3%). $\nu_{max.}$ (Nujol) at 1 605m, 1 335w, 1 281w, 1 219m, 1 156m, 1 095s, 1 055vs, 1 035s, 990sh, 975m, 943w, 920w, 840m, 825w, 760s, and 706s cm^{-1}.

Method (C): *(2,5-Dimethylhexa-1,5-diene)(hexamethylbenzene)rhodium tetrafluoroborate*, (XXIX). A solution of trityl tetrafluoroborate (0·084 g., 0·25 mmol) in methylene chloride (5 cm^3) was added to a solution of acetylacetonatobis(2-methylallyl)rhodium (0·078 g, 0·25 mmol) and hexamethylbenzene (excess, 5 mmol) in methylene chloride (3 cm^3). The reaction mixture was stirred for 0·5 h after which addition of diethyl ether (20 cm^3) precipitated a yellow solid. Recrystallisation from methylene chloride–diethyl ether afforded yellow *crystals* of (XXIX) (0·65 g., 56%), m.p. 135 °C (decomp.) (Found: C, 52·0; H, 7·0. $C_{20}H_{33}BF_4Rh$ requires C, 51·9; H, 7·0%). $\nu_{max.}$ (Nujol) at 1 470s, 1 342s, 1 312w, 1 285m, 1 220w, 1 208w, 1 045vs, 938m, 920w, 832w, 774s, and 728s cm^{-1}.

Method (D): *Bis(dimethylphenylphosphine)bis(2-methylallyl)rhodium tetrafluoroborate*, (III). Dimethylphenylphosphine (0·073 g, 0·6 mmol) was added to a stirred solution of bis(acetonitrile)bis(2-methylallyl)rhodium tetrafluoroborate (0·11 g, 0·28 mmol) in methylene chloride (5 cm^3). Addition of diethyl ether (20 cm^3) and crystallisation of the

resultant precipitate from methylene chloride–diethyl ether gave white *crystals* of (III) (0·103 g, 64%), m.p. 130—132 °C (decomp.) (Found: C, 49·8; 6·2. Calc. for $C_{24}H_{38}BF_4P_2Rh$: C, 50·0; H, 6·3%). $\nu_{max.}$ (Nujol) at 1 308w, 1 050vs, 1 027sh, 946s, 909, 836m, 760s, 746s, 737s, 708s, and 701s cm^{-1}.

The following complexes were similarly prepared. *Bis(2-methylallyl)bis(trimethylphosphite)rhodium tetrafluoroborate*, (I), by method (*B*); white crystals (58%), m.p. 98—99 °C (Found: C, 30·9; H, 6·0; P, 11·5. Calc. for $C_{14}H_{32}BF_4O_6PRh$: C, 30·6; H, 5·9; P, 11·6%). $\nu_{max.}$ (Nujol) at 3 080w, 1 345sh, 1 285w, 1 180s, 1 050vs, 850w, 815w, 790s, 775s, 745s, and 725s cm^{-1}. *Bis(2-methylallyl)bis(tri-isopropyl phosphite)rhodium tetrafluoroborate*, (II), by method (*A*); white crystals (84%), m.p. 104—105 °C (Found: C, 43·5; H, 7·9. Calc. for $C_{26}H_{56}BF_4O_6P_2Rh$: C, 43·5; H, 7·9%). $\nu_{max.}$ (Nujol) at 3 074w, 2 462s, 1 335m, 1 320w, 1 176s, 1 139s, 1 095s, 1 049vs, 970vs, 874s, 846m, 743s, and 733s cm^{-1}. *Bis(2-methylallyl)bis(2-picoline)rhodium tetrafluoroborate*, (V), by method (*A*); special precautions were taken including the use of specially dried, deoxygenated solvents. All manipulations were performed in an atmosphere of nitrogen at −78 °C, yellow crystals (52%). $\nu_{max.}$ (Nujol) at 1 610s, 1 563m, 1 475sh, 1 305m, 1 295m, 1 284w, 1 214w, 1 014s, 1 040vs, 976s, 938m, 846s, 800w, 768s, and 729m cm^{-1}. *Bis(2-methylallyl)bis(3-picoline)rhodium tetrafluoroborate*, (VI), by method (*A*); pale yellow crystals (70%), m.p. 94—96 °C (Found: C, 49·4; H, 5·9; N, 5·7. Calc. for $C_{20}H_{28}BF_4N_2Rh$: C, 49·4; H, 5·8; N, 5·8%). $\nu_{max.}$ (Nujol) at 1 602m, 1 583m, 1 285w, 1 245w, 1 208w, 1 149m, 1 094s, 1 045vs, 985sh, 951sh, 845m, 808s, and 714s cm^{-1}. *Bis(2-methylallyl)bis(4-picoline)rhodium tetrafluoroborate*, (VII), by method (*A*); pale yellow crystals (82%), m.p. 165—166 °C (Found: C, 49·5; H, 5·6. Calc. for $C_{20}H_{38}BF_4N_2Rh$: C, 49·4; H, 5·8%). $\nu_{max.}$ (Nujol) at 3 068w, 1 620s, 1 503w, 1 236m, 1 216s, 1 115sh, 1 045vs, 969m, 948w, 920m, 846m, 823s, and 727m cm^{-1}. [1,2-*Bis(diphenylphosphino)ethane*]*bis(2-methylallyl)rhodium tetrafluoroborate*, (IX), by method (*B*); pale yellow crystals (65%), m.p. 186—188 °C (Found: C, 58·1; H, 5·6. Calc. for $C_{34}H_{38}BF_4P_2Rh$: C, 58·4; H, 5·5%). $\nu_{max.}$ (Nujol) at 1 590w, 1 575w, 1 440s, 1 312w, 1 280w, 1 190m, 1 160m, 1 050vs, 870m, 844w, 811m, 757s, 745s, 698s, and 675 cm^{-1}. [1,2-*Bis(diphenylarsino)ethane*]*bis(2-methylallyl)rhodium tetrafluoroborate*, (X), by method (*A*); yellow crystals (83%), m.p. 203 °C (decomp.) (Found: C, 51·5; H, 4·7. Calc. for $C_{34}H_{38}As_2BF_4Rh$: C, 51·8; H, 4·8%). $\nu_{max.}$ (Nujol) at 1 579w, 1 560w, 1 478s, 1 434s, 1 307w, 1 282w, 1 269w, 1 187m, 1 156m, 1 090s, 1 045vs, 994sh, 950w, 837m, 759m, 743sh, 739s, and 969s cm^{-1}. *Benzene*[1,2-*bis(dimethylarsino)ethane*]*bis(2-methylallyl)rhodium tetrafluoroborate*, (XI), by method (*A*); white crystals (88%), m.p. 179—180 °C (Found: C, 36·7; H, 5·3. Calc. for $C_{18}H_{30}As_2BF_4Rh$: C, 36·9; H, 5·2%). $\nu_{max.}$ (Nujol) at 1 462s, 1 425s, 1 327w, 1 277m, 1 261s, 1 167w, 1 090s, 1 040vs, 911s, 874s, 837m, 761s, and 700w cm^{-1}. 2,2′-*Bipyridylbis(2-methylallyl)rhodium tetrafluoroborate*, (XII), by method (*B*); pale yellow crystals (59%), m.p. 125 °C (Found: C, 47·1; H, 4·9. Calc. for $C_{18}H_{22}BF_4N_2Rh$: C, 47·3; H, 4·9%). $\nu_{max.}$ (Nujol) at 1 598s, 1 582s, 1 409m, 1 317m, 1 246w, 1 227w, 1 148w, 1 095vs, 1 050vs, 1 018sh, 947w, 924w, 243s, 814m, 777s, 758s, and 735m cm^{-1}. (1,4-*Dicyanobutane*)*bis(2-methylallyl)rhodium tetrafluoroborate*, (XIII), by method (*A*); white crystals (76%), m.p. 165 °C (decomp.) (Found: C, 41·6; H, 5·3. Calc. for $C_{14}H_{22}BF_4N_2Rh$: C, 41·2; H, 5·4%). $\nu_{max.}$ (Nujol) at 2 284s, 1 274m, 1 045vs, 972m, 933s, 924s, 835s, and 733s cm^{-1}. *Bis(π-allyl)bis(pyridine)rhodium tetrafluoroborate*, (XIV), by method (*A*); pale yellow crystals (79%), m.p. 96—97 °C (Found: C, 44·3; H, 4·8; N, 6·3. Calc. for $C_{16}H_{20}BF_4N_2Rh$: C, 44·6; H, 4·7; N, 6·5%). $\nu_{max.}$ (Nujol) at 1 603s, 1 389w, 1 237m, 1 212m, 1 156m, 1 097s, 1 045vs, 1 010sh, 993sh, 970s, 948w, 763s, and 708s cm^{-1}. *Bis(π-allyl)bis(2-picoline)rhodium tetrafluoroborate*, (XV), by method (*A*); pale yellow crystals (68%), m.p. 89—90 °C (Found: C, 47·0; H, 5·3; N, 6·0. Calc. for $C_{18}H_{24}BF_4N_2Rh$: C, 47·1; H, 5·3; N, 6·1%). $\nu_{max.}$ (Nujol) 1 607s, 1 554m, 1 478sh, 1 303s, 1 285m, 1 247w, 1 211w, 1 154m, 1 092, 1 040s, 946sh, 800w, 765s, and 729s cm^{-1}. *Bis(π-allyl)bis(3-picoline)rhodium tetrafluoroborate*, (XVI), by method (*A*); pale yellow crystals (74%), m.p. 120—121 °C (Found: C, 47·2; H, 5·4. Calc. for $C_{18}H_{24}BF_4N_2Rh$: C, 47·1; H, 5·3%). $\nu_{max.}$ (Nujol) 1 605m, 1 583m, 1 238m, 1 206w, 1 190m, 1 096s, 1 050vs, 958m, 925w, 804s, and 712 cm^{-1}. *Bis(π-allyl)bis(4-picoline)rhodium tetrafluoroborate*, (XVII), by method (*A*); pale yellow crystals (84%), m.p. 165—166 °C (Found: C, 46·7; H, 5·3; N, 6·2. Calc. for $C_{18}H_{24}BF_4N_2Rh$: C, 47·1; H, 5·3; N, 6·1%). $\nu_{max.}$ (Nujol) at 1 619s, 1 290w, 1 213m, 1 091s, 1 050vs, 963sh, 943w, 924w, 809s, and 722s cm^{-1}. *Bis(acetonitrile)bis(π-allyl)rhodium tetrafluoroborate*, (XVIII), by method (*A*); white crystals (75%), m.p. 99—100 °C (Found: C, 33·7; H, 4·5; N, 8·0. Calc. for $C_{10}H_{16}BF_4N_2Rh$: C, 33·9; H, 4·6; N, 7·9%). $\nu_{max.}$ (Nujol) at 2 318m, 2 292m, 1 399m, 1 286m, 1 050vs, 980sh, 948s, 820w, 730sh, and 725s cm^{-1}. *Bis(π-allyl)*2,2′-*bipyridylrhodium tetrafluoroborate*, (XIX), by method (*B*); pale yellow crystals (62%), m.p. 150 °C (decomp.) (Found: C, 44·9; H, 4·5. Calc. for $C_{16}H_{18}BF_4N_2Rh$: C, 44·8; H, 4·3%). $\nu_{max.}$ (Nujol) at 1 602s, 1 575w, 1 313m, 1 283w, 1 240w, 1 163m, 1 090s, 1 045vs, 965sh, 932s, 762s, 744m, and 732s cm^{-1}. The iridium complexes were synthesised from tetra(allyl)di-μ-chloro-di-iridium using a method analogous to (*A*). *Bis(π-allyl)bis(triphenylphosphine)iridium tetrafluoroborate*, (XX), by method (*A*); white crystals (75%), m.p. 195—196 °C (Found: C, 56·5; H, 4·7; P, 7·0. Calc. for $C_{42}H_{30}BF_4IrP_2$: C, 56·8; H, 4·6; P, 7·0%). $\nu_{max.}$ (Nujol) at 1 586w, 1 572w, 1 435s, 1 312w, 1 238w, 1 186m, 1 162m, 1 096s, 1 058vs, 999m, 968m, 854w, 840w, 752s, 744s, 701s, and 694s cm^{-1}. *Bis(π-allyl)bis(pyridine)iridium tetrafluoroborate*, (XXI), by method (*A*); white crystals (74%), m.p. 115—116 °C (Found: C, 37·3; H, 4·2; N, 5·3. Calc. for $C_{16}H_{20}BF_4IrN_2$: C, 37·0; H, 3·9; N, 5·4%). $\nu_{max.}$ (Nujol) at 1 605s, 1 281w, 1 236m, 1 157m, 1 095s, 1 055vs, 990sh, 975m, 845w, 765s, and 704s cm^{-1}. *Bis(π-allyl)bis(2-picoline)iridium tetrafluoroborate*, (XXII), by method (*A*); pale yellow-brown crystals (69%), m.p. 125 °C (decomp.) (Found: C, 40·5; H, 4·4; N, 5·1. Calc. for $C_{18}H_{24}BF_4IrN_2$: C, 40·2; H, 4·5; N, 5·2%), $\nu_{max.}$ (Nujol) at 1 610s, 1 565m, 1 480sh, 1 303s, 1 249w, 1 248w, 1 205w, 1 177m, 1 095s, 1 055vs, 977sh, 960sh, 798w, 768s, and 729m cm^{-1}. *Bis(acetonitrile)bis(π-allyl)iridium tetrafluoroborate*, (XXIII), by method (*A*); white crystals (72%), m.p. 157 °C (decomp.) (Found: C, 27·0; H, 3·7; N, 6·2. Calc. for $C_{10}H_{16}BF_4IrN_2$: C, 27·0; H, 3·6; N, 6·6%). $\nu_{max.}$ (Nujol) at 2 313m, 2 292m, 1 420m, 1 287m, 1 098s, 1 058vs, 1 034m, 986m, 958s, and 730s cm^{-1}. (*Hexa*-1,5-*diene*)(*mesitylene*)*rhodium tetrafluoroborate*, (XXIV), by method (*C*); yellow crystals (54%), m.p. 150 °C (decomp.) (Found: C, 49·6; H, 6·3. Calc. for $C_{16}H_{18}BF_4Rh$: C, 49·7; H, 6·5%). $\nu_{max.}$ (Nujol) at 1 305w, 1 280w, 1 235w,

1 094s, 1 046vs, 1 030s, 972m, 919m, and 850m cm^{-1}. (*Hexa-1,5-diene*)(*hexamethylbenzene*)*rhodium tetrafluoroborate*, (XXV), by method (*A*); yellow crystals (67%), m.p. 140 °C (decomp.) (Found: C, 45·8; H, 5·8. Calc. for $C_{15}H_{22}BF_4Rh$: C, 45·8; H, 5·7%). $\nu_{max.}$ (Nujol) at 1 548w, 1 533m, 1 498w, 1 302m, 1 286w, 1 235s, 1 050vs, 991m, 950w, 926m, 919m, and 853s cm^{-1}. (1,2-*Dimethoxybenzene*)-(*hexa-1,5-diene*)*rhodium tetrafluoroborate*, (XXVI), by method (*A*); orange crystals (61%), m.p. 141 °C (decomp.) (Found: C, 41·7; H, 5·0. Calc. for $C_{14}H_{20}BF_4O_2Rh$: C, 41·4; H, 5·0%). $\nu_{max.}$ (Nujol) at 1 595m, 1 515m, 1 490s, 1 435s, 1 280s, 1 235s, 1 187w, 1 045vs, 1 001s, 955w, 932m, 753s, and 727m cm^{-1}. (2,5-*Dimethylhexa-1,5-diene*)(*mesitylene*)-*rhodium tetrafluoroborate*, (XXVII), by method (*A*); yellow crystals (68%), m.p. 155 °C (decomp.) (Found: C, 48·6; H, 6·0. Calc. for $C_{17}H_{26}BF_4Rh$: C, 48·5; H, 6·2%). $\nu_{max.}$ (Nujol) at 1 545m, 1 510w, 1 310m, 1 302m, 1 284w, 1 210w, 1 100s, 1 050vs, 987m, 976m, 932w, and 922m cm^{-1}. (2,5-*Dimethylhexa-1,5-diene*)(1,2-*dimethoxybenzene*)*rhodium tetrafluoroborate*, (XXVIII), by method (*C*); orange crystals (63%), m.p. 138 °C (decomp.) (Found: C, 43·4; N, 5·2. Calc. for $C_{16}H_{20}BF_4O_2Rh$: C, 43·7; H, 5·5%). $\nu_{max.}$ (Nujol) at 1 552m, 1 515w, 1 492s, 1 279s, 1 245m, 1 186w, 1 050vs, 945m, 823m, 772w, 752s, and 694w cm^{-1}.

Other allyl complexes. *Bis*(π-*allyl*)*tropolonatorhodium*, (XXX). A solution of potassium hydroxide (0·06 g, 1·2 mmol) in water (20 cm^3) was added with stirring to a solution of tropolone (0·123 g, 1·0 mmol) and tetra(allyl)-di-μ-chloro-dirhodium (0·22 g, 0·5 mmol) in diethyl ether (30 cm^3). After 2 h at room temperature the ether layer was collected and dried ($MgSO_4$). Removal of the solvent *in vacuo* followed by recrystallisation (−78 °C) of the residue from hexane afforded orange *crystals* of (XXX) (0·19 g, 62%), m.p. 111—112 °C [Found: C, 51·0; H, 4·9; *M* 306 (mass spectrometry). Calc. for $C_{13}H_{15}O_2Rh$: C, 50·9; H, 4·9%; *M* 306]. $\nu_{max.}$ (Nujol) at 1 541s, 1 495s, 1 421s, 1 401s, 1 346sh, 1 245w, 1 225sh, 1 219m, 968m, 951w, 924w, 888m, 871m, 735m, and 720s cm^{-1}.

The following complexes were prepared similarly. (2-*Methylallyl*)*tropolonatorhodium*, (XXXI), orange crystals (55%), m.p. 109—111 °C [Found: C, 54·1; H, 5·6; *M* 334 (mass spectrometry). Calc. for $C_{15}H_{19}O_2Rh$: C, 53·8; H, 5·7%; *M* 334]. $\nu_{max.}$ (Nujol) at 1 592s, 1 445s, 1 423s, 1 401s, 1 356s, 1 245w, 1 239w, 1 217m, 1 022w, 972w, 959w, 904m, 888w, 874w, 743m, 736m, and 721m cm^{-1}. *Bis*(π-*allyl*)*tropolonatoiridium*, (XXXII), orange crystals (58%), m.p. 95—96 °C [Found: C, 39·9; H, 4·0; *M* 396 (mass spectrometry). Calc. for $C_{13}H_{15}IrO_2$: C, 39·5; H, 3·8%; *M* 396]. $\nu_{max.}$ (Nujol) at 1 503s, 1 436s, 1 408m, 1 361s, 1 254w, 1 225m, 955w, 912sh, 906m, 742s and 726s cm^{-1}. 2-*Methylallyl*(*pyridine-2-carboxylato*)*rhodium*, (XXXIII). A solution of potassium hydroxide (0·06 g, 1·2 mmol) in water (10 cm^3) was added with stirring to a solution of pyridine-2-carboxylic acid (0·135 g, 1·1 mmol) and di-μ-chloro-tetra(2-methylallyl)dirhodium (0·25 g, 0·5 mmol) in methylene chloride (10 cm^3). After 4 h at room temperature the methylene chloride layer was separated, dried, and the solvent removed *in vacuo*. Recrystallisation (−30 °C) of the residue from methylene chloride–hexane gave pale yellow *crystals* of (XXXIII) (0·13 g, 37%), m.p. 121—122 °C [Found: C, 50·3; H, 5·2; N, 4·4; *M*, 335 (mass spectrometry). Calc. for $C_{14}H_{18}NO_2Rh$: C, 50·0; H, 5·4; N, 4·2%; *M* 335]. $\nu_{max.}$ (Nujol) at 1 585m, 1 548m, 1 460s, 1 384w, 1 356m, 1 259s, 1 185w, 1 157w, 1 097m, 1 043s, 1 016s, 959w, 903s, 857s, 749s, 703m, and 684s cm^{-1}. The ^1H n.m.r. spectrum ($CDCl_3$ at 25 °C) showed resonances at τ 5·75 (1H, H_1'), 5·96 (1H, H_1), 7·23 (1H, H_2'), 7·44 (1H, H_2), 7·50 (1H, H_4), 7·80 (1H, H_3'), 7·91 (1H, H_5'), 7·94 (1H, H_4'), 8·04 (1H, H_5), and 8·40 (1H, H_3) where $J_{14} = J_{1'4} = 2$, $J_{34} = J_{3'4'} = 0·5$, $J(RhH_{5'})$ 1·8, and $J(RhH_5) = 2·1$ Hz.

Kinetic Measurements.—The rates of the exchange reactions, in the slow-exchange limit,[21] were determined from line broadening of the exchanging protons. Decomposition of the complexes prevented studies of the rates in the fast-exchange limits. In the slow-exchange limit the rate constant, k, is given by $k = \pi(\omega - \omega_0)$, and the natural linewidths (ω_0) were taken from the value obtained from the limiting low-temperature spectra, as it was found that the linewidths of resonances due to static protons were not significantly dependent on temperature. Activation parameters (Table 5) were determined, from the values of k obtained, by the use of a least-squares fit computer program.

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[21] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' McGraw-Hill, 1959.