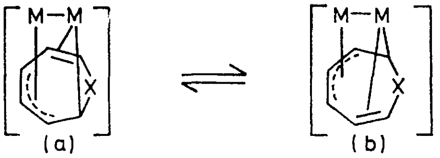
Dynamics and Reactivity of μ-(1-σ,5,6-η:2—4-η-Cycloheptadienyl)- and μ-(1-σ,5,6-η:2—4-η-Cyclo-octadienyl)-bis[(η-cyclopentadienyl)rhodium] (*Rh–Rh*)

By **John Evans, Brian F. G. Johnson, Jack Lewis,*** and **Robert Watt,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

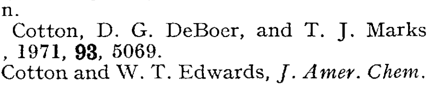
The title complexes, (I) and (II), have been prepared and characterised. Both adopt the 1-σ,5,6-η:2—4-η-structure in solution. High-temperature ^{1}H and ^{13}C n.m.r. spectra indicate that in each system there is an apparent mirror plane in the dienyl ring and that the two η-cyclopentadienyl ligands in each complex remain distinct. This is achieved by oscillation of the metal–metal axis with respect to the dienyl ring. When treated with strong acid both complexes (I) and (II) form cationic complexes containing bridging hydride ligands. For the cyclo-octadienyl complex, (I), this also causes a marked increase in the energy barrier to the oscillation; for (II) the bonding to the dienyl changes to the 1—3-η:4—6-η-type. Using CF_3CO_2D, the added deuteron is incorporated entirely in a methylene group in complex (I), and 50% so in (II). The displaced proton forms the bridging hydride ligand. The effect of the dienyl ligand on the metal–metal bond is considered and these systems are compared with corresponding bis(tricarbonyliron) systems.

We report the preparation and study of μ-(1-σ,5,6-η:2—4-η-cycloheptadienyl)- and μ-(1-σ,5,6-η:2,4-η-cyclo-octadienyl)-bis[(η-cyclopentadienyl)rhodium] (*Rh–Rh*); [(cp)Rh(μ-C_7H_8)Rh(cp)] (II) and [(cp)Rh(μ-C_8H_{10})Rh(cp)] (I) are analogues of bis(tricarbonyliron) and bis(tricarbonylruthenium) complexes which have received considerable attention [1] and have been recently reviewed.[2] The structure of the complex [$(OC)_3Fe(\mu$-$C_8H_{10})Fe(CO)_3$], (I),[3] has been shown to be asymmetric in the solid state.[4] However the room-temperature ^{1}H n.m.r. spectrum of this complex in solution indicates a plane of symmetry through the organic ligand.[3] By variable-temperature ^{1}H n.m.r. spectroscopy the bis(tricarbonyliron) complex was shown to adopt the same instantaneous structure in solution as in the solid state.[5,6] An oscillation between the two enantiometers (a) and (b) appeared to fit the experimental data.[4] In addition ^{13}C n.m.r. experiments [7] indicate that at room temperature carbonyl-site exchange occurs. In contrast, μ-(1—3-η:4—6-η-cycloheptadienyl)-bis(tricarbonyliron) (*Fe–Fe*), [$(OC)_3Fe(\mu$-$C_7H_8)Fe(CO)_3$] (III), possesses C_s symmetry in the solid state.[8] Structure (IIIa) was considered to be preferable to (IIIb) as a bonding description. Both ^{13}C [7] and ^{1}H n.m.r.[8] spectra support the view that this structure is maintained in solution. Two binuclear complexes of cyclo-octatetraene have been reported involving second-row transition metals; μ-(1-σ,5,6-η:2—4-η-cyclo-octatrienyl)-bis(tricarbonylruthenium) (*Ru–Ru*), (IV), has been shown by *X*-ray crystallography [9] and ^{1}H n.m.r. spectroscopy [10] to behave similarly to [I; M = $(OC)_3Fe$], whilst μ-(1,-2,5,6-η:3,4,7,8-η-cyclo-octatetraene)-, bis[(η-cyclopentadienyl)rhodium], (V),[11] adopts a totally different structure in which the cyclo-octatetraene group maintains a tub conformation thus allowing the two independent rhodium atoms their favoured chelating co-ordination.



(I) M = (cp)Rh or $(OC)_3Fe$ or M_2 = (cp)Rh(μ-H)-Rh(cp)$^+$, X = $CH_2{\cdot}CH_2$
(II) M = (cp)Rh, X = CH_2
(IV) M = $(OC)_3Ru$, X = CH:CH
(X) M = $(OC)_3Fe$, X = $CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH$
(XIa) M = $(OC)_3Fe$, X = $CH{\cdot}CH_2{\cdot}CH$
(XIIa) M = $(OC)_3Fe$, X = $CH{\cdot}O{\cdot}CH$

(III) M = $(OC)_3Fe$ or M_2 = (cp)Rh(μ-H)Rh(cp)$^+$, X = CH_2
(XIb) M = $(OC)_3Fe$, X = $CH{\cdot}CH_2{\cdot}CH$
(XIIb) M = $(OC)_3Fe$, X = $CH{\cdot}O{\cdot}CH$



(V)

---

[1] F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257.

[2] A. N. Nesmeyanov, M. I. Rybinkaya, and L. V. Kaganovich, *J. Organometallic Chem.*, 1973, **47**, 1.

[3] R. B. King, *Inorg. Chem.*, 1963, **2**, 807.

[4] F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 1969, **91**, 843.

[5] F. A. Cotton and T. J. Marks, *J. Organometallic Chem.*, 1969, **19**, 237.

[6] R. Aumann and B. Lohmann, *J. Organometallic Chem.*, 1972, **44**, C51.

[7] G. Deganello, *J. Organometallic Chem.*, 1973, **59**, 329 and refs. therein.

[8] F. A. Cotton, D. G. DeBoer, and T. J. Marks, *J. Amer. Chem. Soc.*, 1971, **93**, 5069.

[9] F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 1968, **90**, 5412.

[10] F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Amer. Chem. Soc.*, 1969, **91**, 6598.

[11] K. S. Brenner, E. O. Fischer, H. P. Fritz, and C. G. Kreiter, *Chem. Ber.*, 1963, **96**, 2632.

This structure is obviously not available to the dienyl complexes (I) and (II) [M = (cp)Rh]. They therefore are potential analogues of (I), (III), and (IV). If valence tautomerism occurs then the metal's nuclear spin should provide additional mechanistic information.

RESULTS

Preparation of Complexes.—Although obtainable in small amounts as a by-product in formation of (η-cyclo-octa-1,3,5-triene)(η-cyclopentadienyl)rhodium, (VI),[12] a more efficient synthetic route to complex [I; M = (cp)Rh] was required. Complex (VI) is recovered unchanged after being heated under reflux in n-nonane for 24 h, but does yield the dirhodium species on u.v. irradiation. The complexes (I) and (VI) are readily separated by fractional sublimation. In this way the complex $[(cp)Rh(\mu\text{-}C_8H_{10})Rh(cp)]$, (I), was obtained as air-stable, deep red, crystals. The reverse reaction takes place on treatment of (I) with excess of cyclo-octa-1,3,5-triene. Treatment of the product of the reaction between μ-dichloro-bis[bis(η-ethylene)rhodium] [13] and cycloheptatriene with thallium cyclopentadienide yielded (II) as the major product. Some $[(C_7H_8)Rh(cp)]$, (VII), was also formed and again the two were separable by fractional sublimation. Like (I), complex (II) is a deep red, crystalline, solid.

Properties.—*Complex* [I; M = (cp)Rh]. A comparison of the i.r. and u.v. spectra of (I) with those of (VI) indicated that the dirhodium complex does not possess an unco-ordinated olefinic bond but does exhibit at least one strong u.v. chromophore. This is presumed to be the σ–σ^* transition of the metal–metal bond. At room temperature the ^{1}H n.m.r. spectrum of complex (I) exhibited two sharp cp singlets and five other broad resonances. The spectrum was reversibly temperature dependent, the limiting low-temperature spectrum being obtained at −50 °C. By a combination of double-irradiation and subsequent ^{13}C n.m.r. experiments, this low-temperature spectrum was unambiguously assigned (Table 2) on the basis of the structure shown. Warming the solution to −26 °C caused coalescence of the signals due to H_2 and H_5 at τ 6·2 and broadening of the other signals of the protons of the eight-membered ring. Coalescence of protons H_3 and H_4 occurred at *ca*. −2 °C and of H_1 and H_6 at +3 ± 1 °C. As the temperature was raised, these signals sharpened, affording a limiting high-temperature spectrum at +65 °C (Table 2). No further change was observed up to + 95 °C. The cp singlets remained sharp and separate throughout.

This behaviour is entirely explicable in terms of complex (I) undergoing an oscillation in solution as depicted [(a) $\rightleftharpoons$ (b)] at a rate of the order of 10^3 s^{-1} at 30 °C. The free energy of activation of this oscillation was calculated at two different coalescence temperatures. For the coalescence of two singlets, $\Delta G^\ddagger$ can be estimated from equation (1),[14] where $\Delta\nu$ is the separation in Hz of the two resonances at the

$$\Delta G^\ddagger = -RT \ln (\pi h \Delta\nu / 2^{\frac{1}{2}} kT) \qquad (1)$$

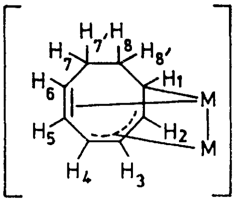
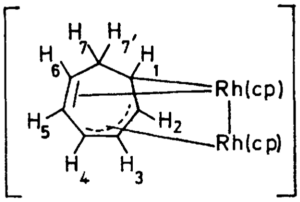
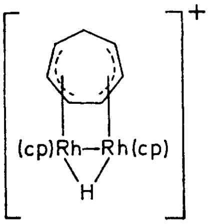
TABLE 1

Activation data for oscillation of complex (I)

Coalescence	T/K	$\Delta\nu$/Hz	Formula	$\Delta G_T^\ddagger$/ kcal mol^{-1}
H_3 and H_4	271	96	(2)	12·9
H_1 and H_6	276	148	(1)	12·9

TABLE 2

^{1}H N.m.r. data

Complex	Proton	Chemical shift, τ	Multiplicity
 (I) M = (cp)Rh in CDCl$_3$ at −50 °C	cp	4·87	s
	cp	4·96	s
	H_4	5·44	m
	H_6	5·9	m
	H_2, H_3, H_5	6·3	m
	H_1	7·40	m
	$H_{7'}$, H_8, $H_{8'}$	8·5	m
	H_7	9·43	m
(I) in $(CD_3)_2SO$ at 65 °C	cp	4·60	s
	cp	4·72	s
	H_3, H_4	5·85	m
	H_2, H_5	6·2	m
	H_1, H_6	6·6	m
	$H_{7'}$, $H_{8'}$	8·5	m
	H_7, H_8	8·75	m
(I) M_2 = (cp)Rh(μ-H)Rh(cp)$^+$ in CF_3CO_2H–$CDCl_3$ at 30 °C	cp	4·29	s
	cp	4·29	s
	H_4	4·65	m
	H_6	4·90	m
	H_2, H_3	5·53	m
	H_5	5·85	m
	H_1	7·07	m
	$H_{7'}$, H_8, $H_{8'}$	8·1	m
	H_7	8·7	m
	Rh_2–H	28·57	t (J 17·5 Hz)
 (II) in CDCl$_3$ at 30 °C	cp	4·67	s
	cp	4·73	s
	H_3, H_4	5·85	m
	H_2, H_5	6·25	m
	$H_{7'}$	7·45	m
	H_1, H_6, H_7	7·75	m
 (III) in CF_3CO_2H at 30 °C	cp	4·32	s
	2H	4·51	m
	4H	5·8	m
	methylenes	8·0	m
	Rh_2–H	24·1	t of doubled doublets (J_{RhH} 23·8, and 9·0 Hz)

---

[12] J. Evans, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 2668.

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

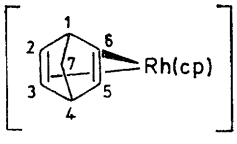
[14] A. Allerhand, H. S. Gutowsky, J. Jones, and R. P. Meiszer, *J. Amer. Chem. Soc.*, 1966, **88**, 3185.

low-temperature limit and T is the coalescence temperature. The use of this equation for the coalescence of multiplets has been discussed.[15,16] An error in $\Delta G^{\ddagger}$ of *ca.* 0·3 kcal mol^{-1} has been estimated if $\Delta\nu$ is much larger than the width of the multiplets at room temperature.[17,‡] For coalescence of the two resonances of an AB spin system a better formula is (2).[18] The estimates of $\Delta G^{\ddagger}$ obtained are displayed in Table 1.

$$\Delta G^{\ddagger} = -RT \ln [\pi \boldsymbol{h}(\nu^2 + 6J^2)^{\frac{1}{2}}/2^{\frac{1}{2}}\boldsymbol{k}T] \qquad (2)$$

TABLE 3

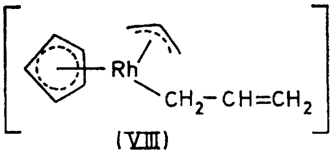
Proton-decoupled ^{13}C n.m.r. data *

Complex	Carbon	Chemical shift δ/p.p.m.	Multiplicity ($^1J_{Rh-C}$/Hz)
(I) M = (cp)Rh in −50 °C	cp	−87·0	d (2)
	cp	−83·1	d (4)
	C_3	−72·2	d (6)
	C_6	−62·5	d (15)
	C_5	−53·5	d (8)
	C_4	−49·5	d (10)
	C_2	−48·4	d (7)
	C_8	−45·3	s
	C_7	−24·2	s
	C_1	−17·9	d (19)
(I) in $(CD_3)_2SO$ at 145 °C	cp	−86·6	d (4)
	cp	−82·6	d (5)
	C_3, C_4	−60·2	d (8)
	C_2, C_5	−50·4	t (8) †
	C_1, C_6	−39·1	d (16)
	C_7, C_8	−34·3	s
(I) M_2 = (cp)Rh(μ-H)-Rh(cp)$^+$ in CF_3CO_2D-$CDCl_3$ at 35 °C	cp	−90·5	d (3)
	cp	−87·3	d (5)
	C_6	−75·1	d (10)
	C_3	−74·9	d (6)
	C_2, C_4, C_5	−63·2	d (8)
		−59·5	d (6)
		−56·6	d (9)
	C_8	−49·6	s
	C_1	−25·7	d (15)
	C_7	−23·3	s
(II) in CD_2Cl_2 at −74 °C	cp	−86·3	d (4)
	cp	−83·3	d (4)
	C_3	−67·5	d (7)
	C_5	−58·0	d (5)
	C_2	−51·7	d (9)
	C_4	−50·0	d (10)
	C_7	−39·3	d (3)
	C_6	−25·1	d (7)
	C_1	20·5	d (11)
(II) in $CDCl_3$ at 35 °C	cp	−86·2	d (4)
	cp	−82·9	d (4)
	C_3, C_4	−58·2	d (9)
	C_2, C_5	−54·7	t (7) †
	C_7	−39·3	d (5)
	C_1, C_6	−2·0	d (10)
(III) M_2 = (cp)Rh(μ-H)Rh(cp)$^+$ in CF_3CO_2H-$CDCl_3$ at 35 °C	cp	−87·0	s
	2C (A)	−69·3	t (7) †
	2C (B)	−67·0	t (9) †
	2C (C)	−56·9	t (3) †
	methylene	−33·6	s
	cp	−84·1	d (4)
	C_7	−57·0	d (8)
	C_1, C_4	−46·5	d (3)
	C_2, C_3, C_5, C_6	−27·8	d (10)

* For numbering of carbon atoms see formulae in Table 2.
† 'J' = $|J_{Rh_a-C} + J_{Rh_b-C}|$.

This dynamic behaviour was also studied by variable-temperature ^{13}C n.m.r. spectroscopy. The slow-exchange spectrum was obtained at −50 °C (Table 3) and supported the structural assignment. Selective double irradiation of the appropriate proton resonances was used to identify the signals due to C_1, C_6, C_7, and C_8. Two sets of signals remained: one at −72·2 and −49·5 p.p.m. corresponding to C_3 and C_4; and the other at −53·5 and −48·4 p.p.m. to C_2 and C_5. Generally the central carbon atom of a η-allyl group resonates at lower field than the two outer ones [19] so the resonance at −72·2 p.p.m. was assigned to C_3; C_2 and C_4 should exhibit similar chemical shifts, thus the signals at −49·5 and −48·4 p.p.m. were assigned to them, respectively. This then led to the assignment of the signal at −53·5 p.p.m. to C_5.

Rhodium–carbon couplings were observable on all carbon atoms directly bonded to the metal. Two-bond coupling constants were not detected in conditions which yielded a resolution of 1·25 Hz. Couplings to the cp ring carbon atoms were small but, contrary to a previous report,[20] were observable. The constant J_{Rh-C_6} (15 Hz) was similar to J_{Rh-C_1} (19 Hz), the latter being considered to be a rhodium–carbon σ-bond. The only other reported J_{Rh-C} for a σ-bonded sp^3 carbon atom is for (σ-allyl)(1—3-η-allyl)(η-cyclopentadienyl)rhodium, (VIII), and, at 26 Hz, is somewhat larger.[19]



(VIII)

^{13}C N.m.r. spectra were recorded for complex (I) at temperature intervals; signal broadening was observed at −20 °C but no accurate coalescence temperatures were obtained. At +95 °C the limiting fast-exchange spectrum was recorded (Table 3). Shifts and coupling constants of the averaged signals agreed well with those expected for this intramolecular oscillation. Doublets of averaged coupling were exhibited for the C_1,C_6 and C_3,C_4 resonances. A triplet, resolvable into a doubled doublet using a resolution-enhancement weighting function, was observed for the averaged C_2,C_5 signal with a total splitting of 8 Hz. These atoms are attached to each rhodium atom for half the time so the total splitting is: $(J_{Rh_a-C_2} + J_{Rh_b-C_5})/2$, *i.e.* 7·5 Hz. No further change was observed at 145 °C, there being no averaging of the cp resonances even at this temperature.

Complex (II). The molecular formula of complex (II) was established by normal analytical and spectroscopic techniques. At room temperature its ^{1}H n.m.r. spectrum

‡ 1 cal = 4·184 J.

[15] W. E. Stewart and T. H. Siddall, *Chem. Rev.*, 1970, **70**, 517.

[16] D. Kost, E. H. Carlson, and M. Raban, *Chem. Comm.*, 1971, 656.

[17] R. K. Harris and R. A. Spragg, *J. Chem. Soc.* (*B*), 1968, 684.

[18] R. J. Kurland, M. B. Rubin, and M. B. Wise, *J. Chem. Phys.*, 1964, **40**, 2426.

[19] B. E. Mann, R. Pietropaolo, and B. L. Shaw, *Chem. Comm.*, 1971, 790.

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

(Table 2) indicated an apparent plane of symmetry through the seven-membered ring but the two cp rings were inequivalent. This spectrum was markedly temperature dependent and even at −90 °C fluxional behaviour was sufficiently rapid to prevent observation of the limiting low-temperature spectrum. Due to the larger chemical-shift differences observed with the ^{13}C nucleus, it should be, in principle, possible for the slow-exchange ^{13}C spectrum of complex (II) to be attained at a higher temperature. Unfortunately the low solubility of the complex in CD_2Cl_2 below −90 °C mitigated against this. The best spectrum was obtained at −74 °C (Table 3). Slight broadening of the resonances C_{1-6} was still apparent so values of J_{Rh-C} were accurate to only *ca.* 3 Hz. Obviously, since a limiting low-temperature proton spectrum was not obtained, assignments from direct selective heteronuclear spin decoupling were impossible. At +35 °C the fast-exchange ^{13}C spectrum was observed (Table 3) and the resonances in this spectrum were so assigned. Hence the expected signals in the ' frozen-out ' spectrum were deduced from the high-temperature spectrum and the assignments made as for the spectra of complex (I).

Apparently complex (II) does not adopt the 1—3-η:4—6-η-structure of [III; M = $(CO)_3Fe$], its high-temperature spectra being entirely consistent with the (a) $\rightleftharpoons$ (b) type of tautomerism illustrated. The multiplicities of the proton-decoupled carbon resonances offered the clearest demonstration of this. However, the slow-exchange ^{13}C n.m.r. spectra of complexes (I) and (II) differed in several respects. In both complexes the η-allyl moieties were similar, but there were significant differences in the remainder of the dienyl rings. In complex (II) C_6 resonated considerably upfield of the equivalent carbon in (I) (−25·1 was opposed to −62·5 p.p.m.) and the difference between the two C_1 atoms [−17·9 p.p.m. in (I) and +20·5 p.p.m. in (II)] was also marked. Shifts of +23·5 and +28·9 p.p.m. have been reported for the methyl carbon atom σ-bonded to a transition metal in the complexes $[(cp)Fe(CO)_2Me]$ and $[(cp)W(CO)_3Me]$ respectively.[21] Alkyl substitution at the methyl carbon atom generally results in a downfield shift of *ca.* 40 p.p.m., *e.g.* −10·6 p.p.m. in $[IrCl_2(CO)(AsMe_2Ph)_2\{CH_2{\cdot}C(Me){:}CH_2\}]$,[22] so the shift of C_1 in complex (I) is more typical of a secondary carbon atom σ-bonded to a metal. Arguing simply on the basis of Pople's theory of carbon chemical shifts,[23] the higher chemical shifts of C_1 and C_6 in complex (II) compared to (I) could result from higher electron densities in these carbon atoms in (II). Alternatively, by analogy with discussion of metal hydride chemical shifts,[24] these atoms may simply be closer to the metal atom in complex (II) and molecular models support this possibility. The weighting of these two contributions to the shift changes is indeterminate. Finally there is rhodium coupling to the methylene carbon atom in complex (II); the significance of this is uncertain, but most frequently $^2J_{Rh-C-C}$ values are negligible, *e.g.* in (η-cyclo-octatetraene)-, (η-cyclo-octa-1,3,5-triene)- and (η-cyclohepta-1,3-diene)-(η-cyclopentadienyl)rhodium.[25] However (η-bicyclo[2.2.1]-hepta-2,5-diene)(η-cyclopentadienyl)rhodium, (IX), does provide an exception; its ^{13}C n.m.r. spectrum (Table 3) demonstrates rhodium coupling to all four types of carbon atoms, including the bridging methylene carbon.

A dependence of $^2J_{C-C-C}$ on the C–C–C bond angle has been suggested,[26] and a theoretical study has demonstrated an angular dependence for the related constant $^2J_{F-C-F}$.[27] It may be that the appropriate angles in complexes (II) and (IX) yield large values of $^2J_{Rh-C-C}$. Recently, large values of $^3J_{Pt-C}$ have been reported for the bridging carbon atom in (bicyclo[2.2.1]hepta-2,5-dienyl)platinum diketonates[28] and a directional through-space effect was suggested to explain this. However little is understood about coupling between nuclei heavier than the proton. Dependence of $^3J_{C-C-C-C}$ on dihedral angle has been noted experimentally[29] and calculations show that such an effect on $^3J_{F-C-C-F}$ is of a complicated nature.[27] For phosphorus compounds the disposition of the phosphorus lone-pair apparently effected the coupling $^2J_{P-H}$[30] and $^2J_{P-C}$.[31] So both bond angles and the metal's co-ordination stereochemistry may effect the couplings $^2J_{M-C}$, $^3J_{M-C}$, *etc.* Through-space decoupling has rarely been proven,[32] but possibly contributions from ' fragment coupling,' a better defined concept suggested for long-range fluorine–fluorine couplings,[27,33] may be significant when the metal–carbon distance is relatively small.

Protonation of complex [I; M = (cp)Rh]. The dirhodium complex possesses some nucleophilic character. An analytically pure salt $[(cp)Rh(\mu\text{-}C_8H_{10})(\mu\text{-}H)Rh(cp)]PF_6$ could not be obtained by addition of aqueous HPF_6 to a diethyl ether solution of (I), but, either by dissolving (I) in trifluoroacetic acid or by adding the acid to a solution of (I) in $CDCl_3$, a stable cationic species was observed spectroscopically. The best ^1H n.m.r. spectrum (Table 2) resulted from the latter technique. Double-irradiation experiments confirmed the structure of this cation. The chemical shift of the metal hydride proton (τ 28·57),[34] together with the multiplicity and coupling constant,[34] suggests that the proton bridges the metal atoms. The hydride proton is then part of an ABX spin system in which the X part reduces to a triplet,[35] due to the equality of J_{AX} and J_{BX}, so the bridge appears, therefore, to be symmetrical, but whether it is linear or bent cannot be determined. Protonation of complex (I) significantly increased the energy barrier to oscillation within the molecular framework so that the slow-exchange spectrum was observable at 30 °C.

Further information about the cation was obtained from its ^{13}C n.m.r. spectrum. This was recorded on a solution of complex (I) in 10% CF_3CO_2D in $CDCl_3$ at *ca.* 35 °C (Table 3). Assignments of the resonances due to C_6, C_7, and C_8 were

---

[21] L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Comm.*, 1971, 1078.

[22] L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Comm.*, 1971, 790.

[23] J. A. Pople, *Mol. Phys.*, 1963, **7**, 301.

[24] A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 2747, 4583.

[25] J. Evans and J. R. Norton, unpublished work.

[26] F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1972, **94**, 6021.

[27] K. Hirao, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, 1973, **95**, 31.

[28] R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1973, **60**, 427.

[29] J. L. Marshall and D. E. Miller, *J. Amer. Chem. Soc.*, 1973, **95**, 8305.

[30] J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, *Bull. Soc. chim. France*, 1969, 40.

[31] S. Sorensen, R. S. Hansen, and H. J. Jakobsen, *J. Amer. Chem. Soc.*, 1972, **94**, 5900.

[32] J. D. Kennedy, W. McFarlane, and D. S. Rycroft, *Inorg. Chem.*, 1973, **12**, 2742.

[33] K. Hirao, H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Amer. Chem. Soc.*, 1972, **94**, 4078.

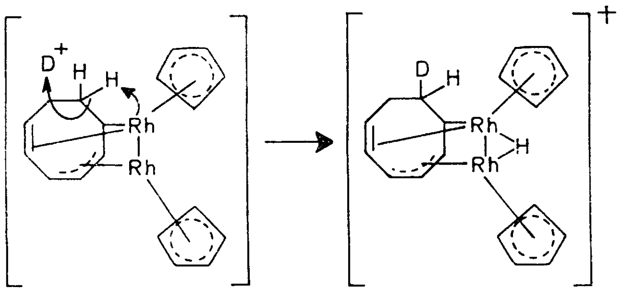
[34] (*a*) ' Transition Metal Hydrides,' ed. E. L. Muetterties, Marcel Dekker, 1971, and refs. therein; (*b*) A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 2517.

[35] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.

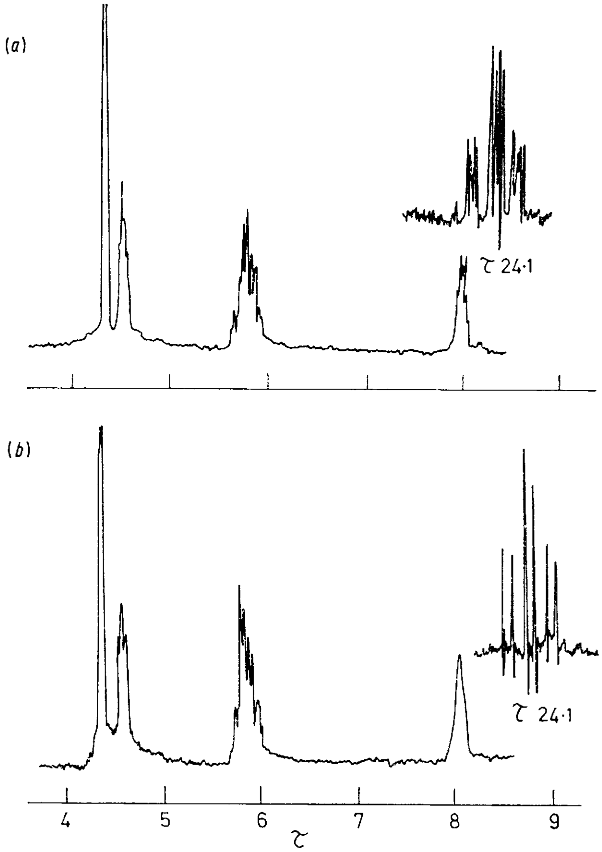
made on the basis of selective double-irradiation experiments; signals due to C_1 and C_3 were assigned on the evidence of their chemical shifts and coupling constants; the other three resonances due to the eight-membered ring were not individually assigned. Compared to the low-temperature spectrum of complex (I), all resonances except that of C_7 were moved downfield and rhodium–carbon coupling constants markedly reduced. Correlations between values of coupling constants and *s*-electron density have been made.[20] If the Fermi-contact term dominates, then a linear correlation between the two is possible as for protons, but since neither of the nuclei involved is a proton the corresponding conclusion would have to be established [36] and does not appear to be the case for fluorine–fluorine couplings.[33] The magnetic data do correlate however with the suggestion that the introduction of the hydride has reduced the electron density on the metal which is available to the octadienyl ligand.

When complex (I) was dissolved in CF_3CO_2D, the species $[(cp)Rh(\mu\text{-}C_8H_9D)(\mu\text{-}H)Rh(cp)]^+$ was formed. Surprisingly the ^1H n.m.r. spectrum of a solution of this cation still exhibited the metal hydride resonance. However, the integrated intensity of the resonance at τ 8·1 was reduced from 3H to 2H. Double-irradiation experiments indicated that the added deuterium atom resides on C_8. This evidence suggests that initial attack is on C_8 with β-hydrogen abstraction from C_8 to the metal atoms. The metal hydride proton did not exchange with the solvent deuterons at any detectable rate, as has been observed with other cationic species.[34b]

Protonation of complex (II). Like [I; M = (cp)Rh], complex (II) was also readily protonated. The cation $[(cp)Rh(\mu\text{-}C_7H_8)(\mu\text{-}H)Rh(cp)]^+$ was identified both in solutions of trifluoroacetic acid, and as its hexafluorophosphate salt. Its ^1H n.m.r. spectrum (Table 2), which was invariant between −90 and +35 °C, is shown in the Figure (*a*). Two features are noteworthy. First, there is an apparent plane of symmetry through the seven-membered ring which makes the two cp rings equivalent and thus probably the two rhodium atoms. Any accidental degeneracy of these two resonances was rendered statistically improbable by the degeneracy of their ^{13}C resonances (Table 3). Secondly, there is a complicated metal hydride resonance. It is basically that of a bridging hydride with proton–proton fine coupling, and is discussed below.



On this basis, the cation was considered to exhibit similar bonding as in complex [III; M = $(OC)_3Fe$].[8] Confirmation of the C_s symmetry of the system was obtained from its ^{13}C n.m.r. spectrum (Table 3). No rhodium coupling was observed to the methylene carbon C_7. However, resonances due to the three pairs of other atoms of the trienyl ring were triplets and were in accord with proton resonances obtained by selective double irradiation. Each particular carbon atom adopts the X part of an AA′X spin system. Since $\nu_0\sigma_{AB}$ is zero, the two rhodium atoms being equivalent, the two central lines of the doubled doublet of the ABX system converge to yield the observed triplet provided that $J_{AX} \simeq J_{A'X}$.[35] The splitting between the outer peaks of the triplet is the sum of the two coupling constants $J_{Rh_a-C} + J_{Rh_b-C}$. The relative sizes of the two J values could not be obtained from the spectrum.



^1H N.m.r. spectra of the complex $[(cp)Rh(\mu\text{-}C_7H_8)(\mu\text{-}H)Rh(cp)]^+$ in (*a*) CF_3CO_2H, (*b*) CF_3CO_2D

As stated above, the crystal structure of complex [III; M = $(OC)_3Fe$] has been determined.[8] Each metal atom was considered, ' to a zeroth approximation,' to be bonded to an individual η-allyl group, although some electron coupling between the two such groups was expected. There seemingly is such coupling in the cation $[(cp)Rh(\mu\text{-}C_7H_8)(\mu\text{-}H)Rh(cp)]^+$, so the question arises whether structure (a) (1—3-η:4—6-η-) or (b) (1—6-η-) is the better approximation. Some attempt was made to determine this on the basis of magnetic data, without conclusion.[37]

The mechanism of protonation was investigated using CF_3CO_2D. A ^1H n.m.r. spectrum of complex (II) in this solvent is shown in the Figure (*b*). The metal hydride resonance was still detected, but at half its normal intensity, and the relative intensity of the methylene proton was now

---

[36] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[37] J. Evans, Ph.D. Thesis, University of Cambridge, 1973.

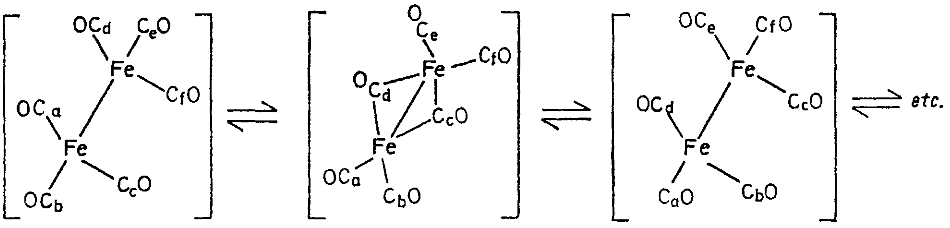
1·5. A ^{13}C n.m.r. spectrum of a solution of complex (II) in CF$_3$CO$_2$D–CDCl$_3$ (*i.e.* that of hydrido-complex) confirmed the one to one deuterium incorporation on the metal atoms and on C$_7$. This resulted in the expected superimposition of two C$_7$ signals, a singlet and 1 : 1 : 1 triplet from ^{13}C–^{2}H coupling. However the value of $^1J_{^{13}\mathrm{C}-^2\mathrm{H}}$ was small (10 Hz).

The change in fine structure of all the metal hydride resonance merits some explanation. In CF$_3$CO$_2$H, each peak in the triplet, caused by rhodium coupling, was further split into four lines, of outer and inner splittings of 9 and 3 Hz respectively. In CF$_3$CO$_2$D, the two inner lines were absent, still leaving the outer splitting at 9 Hz. The former spectral fragment is the X part of an ABX spin system,[38] the A and B components being the two methylene protons on C$_7$. But in CF$_3$CO$_2$D, for those molecules possessing a bridging hydride as opposed to deuteride, the B proton on C$_7$ is isotopically substituted leaving an AX system where J_{AX} 9 Hz. Hence J_{BX} is zero.[38] The splitting of the two central lines can be used to show that J_{AB} is *ca.* 5·8 Hz. Obviously, since the other 50% of the incorporated deuterium forms the bridging deuteride, the X component could not be observed by ^{1}H n.m.r. spectroscopy. Though 9 Hz is large for $^4J_{\mathrm{H-H}}$, it is not without precedent.[39]

So protonation of complex (II) causes rotation of the metal–metal axis with respect to the seven-membered ring by almost 90°; the six methine groups, puckered in (II), become planar in the cation. Further complication to the reaction mechanism is evident by the two alternative sites of solvent proton (deuteron) incorporation.

DISCUSSION

This work poses two general questions about complexes of this type, namely whether the structure adopted is 1—σ,5,6-η:2—4-η or 1—3-η:4—6-η and, if the former is adopted, what factors determine the rate of oscillation in the fluxional systems. As pointed out by Cotton *et al.*,[8] both the two bonding forms are similar energetically and small structural features may determine the form actually adopted. A consideration of one of these for the iron complexes, namely the metal–metal distance, does allow some conclusions. It is apparent that this bond length is largely constrained by the requirements of the organic ligand. In complex [III; M = (OC)$_3$Fe], the two central atoms of the η-allyl groups are 3·135 Å apart, dictating the Fe–Fe distance to increase from an approximate norm of 2·77 to 2·866 Å.[8] By an inspection of molecular models, if a bis(η-allyl) structure were maintained in an eight-membered ring the equivalent two carbon atoms would be separated by *ca.* 3·4 Å. This would in turn require a still greater Fe–Fe distance of over 3·0 Å, which would be exceptionally large. It therefore seems probable that the 1—σ-5,6-η:2—4-η-structure will be greatly favoured for eight-membered rings, especially since the puckered form appears to be a preferred conformation. Indeed this is the structure known to be adopted by the complexes [I; M = (OC)$_3$Fe],[4–6] [(OC)$_3$Fe(μ-C$_{10}$H$_{12}$)Fe(CO)$_3$] (X),[40] [(OC)$_3$Fe(μ-C$_{12}$H$_{12}$)Fe(CO)$_3$],[41] and (IV).[9,10] The bis(η-allyl) structure has been proposed for the complexes [(OC)$_3$Fe(μ-C$_9$H$_{10}$)Fe(CO)$_3$] (XI), and [(OC)$_3$Fe(μ-C$_8$H$_8$O)Fe(CO)$_3$] (XII),[42] in solution,[8,43,44] largely because of the invariance of the ^{1}H n.m.r. spectra down to *ca.* −90 °C. However, such evidence is not conclusive as the work on complex (X) [40,45] serves to illustrate. Only following the determination of the crystal structure of this complex was the correct structure in solution identified.[40] Similarly complex (XI) has been shown to adopt the unsymmetrical 1—σ,5,6-η:2—4-η-structure in the crystal.[46] Evidence obtained to support the suggestion that this complex changes structure on dissolution [43] is not yet entirely convincing.



It is not clear why the two cycloheptadienyl complexes (II) and [III; M = (OC)$_3$Fe] should adopt different structures. Models indicate a preferred M–M distance of *ca.* 2·6 Å for the 1—σ-5,6-η:2—4-η-structure. This is apparently compatible with the rhodium–rhodium bond in complex (II). Formation of bridging metal hydrides tends to lengthen metal–metal distances, other factors being equal,[34,47] and, as the ligand constrains this distance in structural forms (II) and (III), it may be rationalised that the structure changes to the symmetrical 1—3-η:4—6-η-form in the cation [(cp)Rh(μ-C$_7$H$_8$)(μ-H)Rh(cp)]$^+$ to accommodate the larger metal–metal distance allowed in that form.

---

[38] T. Schaefer, *Canad. J. Chem.*, 1962, **40**, 1678.

[39] S. Sternhell, *Quart. Rev.*, 1969, **6**, 236.

[40] F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometallic Chem.*, 1973, **50**, 227.

[41] H. W. Witlock, jun., and H. Stucki, *J. Amer. Chem. Soc.*, 1972, **94**, 8594.

[42] H. Matz and G. Deganello, *J. Organometallic Chem.*, 1971, **27**, 383.

[43] G. Deganello, H. Maltz, and J. Kozarich, *J. Organometallic Chem.*, 1973, **60**, 323.

[44] E. J. Reardon, jun., and M. Brookhart, *J. Amer. Chem. Soc.*, 1973, **95**, 4311.

[45] F. A. Cotton and G. Deganello, *J. Organometallic Chem.*, 1972, **38**, 147; *J. Amer. Chem. Soc.*, 1972, **94**, 2142.

[46] J. Takats, unpublished work cited in ref. 43.

[47] H. D. Kaesz, *Chem. in Britain*, 1973, **9**, 344.

Due to the inequivalence of the cp rings over the temperature range examined, evidently complexes (I) and (II) only undergo one type of tautomerism involving an oscillation during which the two metal atoms do not switch ends of the organic ring. At least one other process must be available to the corresponding bis(tricarbonyliron) system as all carbonyl groups become equivalent. If any comparison between the two systems is meaningful, and one assumes that the metal atoms do not switch ends of the organic ring in the iron system, scrambling of the carbonyl groups may be achieved by a process similar to that postulated for the complex $[(cp)(OC)_2Fe{-}Fe(CO)_2(cp)]$.[48]

Conformational effects seem to be important in determining the size of the energy barrier to oscillation. For the cyclo-octadienyl ligand in complexes [I; M = (cp)Rh or $(OC)_3Fe$] this is particularly large. These two complexes also indicate that the rearrangement of the bonding at the metal atoms in forming the transition state appears to have a marked effect on the barrier size.

EXPERIMENTAL

Reactions were carried out under an atmosphere of pure dry dinitrogen. M.p.s were measured in open capillary tubes on a Gallenkamp apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer using polystyrene film as calibrant. U.v.–visible spectra were recorded on a Pye Unicam SP 800 spectrometer. Mass spectra were obtained on an A.E.I. MS 12 spectrometer. Elemental analyses were determined by the microanalytical department of this laboratory. ^1H N.m.r. spectra were recorded on Perkin-Elmer R12B and Varian Associates HA100 and XL100 spectrometers. Methanol and ethylene glycol temperature standards were employed. ^{13}C N.m.r. spectra were recorded on a Varian Associates XL100-15 spectrometer, employing solvent deuterium lock. Shifts were measured in p.p.m. from tetramethylsilane. Proton decoupling with broad-band double irradiation was employed.

Cyclo-octa-1,3,5-triene,[49] thallium cyclopentadienide,[50] μ-dichloro-bis[bis(η-ethylene)rhodium],[13] and (η-cyclo-octa-1,3,5-triene)(η-cyclopentadienyl)rhodium [12] were all prepared by published procedures.

μ-(1-σ,5,6-η:2—4-η-*Cyclo-octadienyl*)-bis[(η-*cyclopentadienyl*)*rhodium*], (I).—A solution of the complex $[(C_8H_{10})Rh(cp)]$ (VI) (3·1 g) in benzene (120 cm^3) was irradiated by a high-pressure mercury lamp at room temperature for 30 h. The solvent was removed and the residue dried *in vacuo*. Unchanged complex (VI) (2·5 g) was sublimed out of the residue at 60 °C and 0·05 Torr. The *product* was subsequently obtained by sublimation at 140 °C and 0·05 Torr as deep red crystals (364 mg), m.p. 144 °C (Found: C, 49·25; H, 4·45. Calc. for $C_{18}H_{20}Rh_2$: C, 48·9; H, 4·55%). Mass spectrum: P^+, 442 (corresponds to $C_{18}H_{20}{}^{103}Rh_2$). The i.r. spectrum showed no unco-ordinated double bonds. U.v. spectrum: 520 (440); 447 (12 400); 300(sh) (13 000); and 233 nm (ε 29 000 mol^{-1} cm^2).

Action of Cyclo-octa-1,3,5-*triene on Complex* (I).—Complex (I) (50 mg) and cyclo-octa-1,3,5-triene (0·2 cm^3) were heated under reflux in toluene (5 cm^3) for 20 h. The solvent was removed to give a red crystalline solid which was dried *in vacuo*. The ^1H n.m.r. spectrum of this solid in $CDCl_3$ solution indicated that complex (VI) was the major product. Complexes (I) and (VI) were separated as above.

μ-(1-σ,5,6-η-*Cycloheptadienyl*)-bis[(η-*cyclopentadienyl*)-*rhodium*], (II).—μ-Dichloro-bis[bis(η-ethylene)rhodium] (2·6 g) was suspended in dry diethyl ether (13 cm^3) at room temperature and cyclohepta-1,3,5-triene (2 cm^3) added. Vigorous effervescence occurred and the mixture was stirred for 30 min. The resulting solid (2·9 g) was isolated by filtration, washed with diethyl ether, and dried *in vacuo*. It was then added to a thallium cyclopentadienide (4·0 g) and benzene (25 cm^3) and the resulting mixture was stirred, light being excluded, for 18 h. The mixture was then filtered and the residue washed with benzene. Removal of the solvent from the combined filtrate and washings yielded a red crystalline solid, which was then dried *in vacuo* for 1 h after which the complex $[(C_7H_8)Rh(cp)]$, (VII) (192 mg), was sublimed out at 70 °C and 0·05 Torr. Sublimation of the residue at 130 °C and 0·05 Torr yielded the *product* as a dark red crystalline solid (*ca*. 1 g) (Found: C, 47·7; H, 4·2. Calc. for $C_{17}H_{18}Rh_2$: C, 47·65; H, 4·20%). Mass spectrum: P^+, 428 (corresponds to $C_{17}H_{18}{}^{103}Rh_2$). U.v. spectrum: 548 (sh) (300); 347 (10 000); 298 (14 000); 235 (22 000), and 225 nm (ε 18 000 mol^{-1} cm^2).

We thank the S.R.C. for financial support (to J. E. and R. W.) and Johnson, Matthey and Co. Ltd. for a generous loan of rhodium trichloride.

[4/410 *Received*, 1*st March*, 1974]

---

[48] R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, 1973, **95**, 6589.

[49] W. O. Jones, *J. Chem. Soc.*, 1954, 1808.

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