Synthesis and Characterisation of Disubstituted Di-μ-methylene-bis(η-pentamethylcyclopentadienyl)dirhodium(IV) Complexes; *X*-Ray Structure of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)_2]^{2+}$ †

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Reaction of either *cis*- or *trans*-$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ with HCl in pentane gave the *trans*-dichloro-complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2X_2]$ (4a; X = Cl), from which a variety of other complexes (4; X = Br, I, SCN, N_3, CN, or NCO) were made by metathesis. Reaction of (4a; X = Cl) with neutral ligands (L) in the presence of non-co-ordinating anions gave first the monocations, $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(L)Cl]^+$, and then the dications, $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2L_2]^{2+}$ (5; L = MeCN, CO, or H_2O). The *X*-ray crystal structure of (5b; L = CO) shows the *trans* configuration predicted on the basis of the ^1H n.m.r. spectra. Reaction of (5b) with methanol and base gave the bis(methoxycarbonyl) complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO_2Me)_2]$. *cis* Complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2X]^{n+}$ (X = O_2CMe or O_2CCF_3, *n* = 1; X = pyridazine or $Ph_2PCH_2PPh_2$, *n* = 2) were isolated and identified by their ^1H n.m.r. spectra which showed the diastereotopic methylene protons as two resonances, only one of which was coupled to the rhodiums. The nitrate complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(NO_3)_2]$ was found to exist as two isomers, one *trans* and the other *cis* with one bridging and one ionic nitrate, as shown by the n.m.r. spectra.

We have discussed, in previous papers, the syntheses and structural identification of the *cis*- and the *trans*-dimethyl-di-μ-methylene-bis[(η^5-pentamethylcyclopentadienyl)rhodium] complexes, (2) and (3), obtained by reaction of the tetrachlorodirhodium complex $[\{(C_5Me_5)Rh\}_2Cl_4]$ (1) with hexamethyldialuminium [1,2] or, less satisfactorily, with methyllithium.[1] We now report that both of the methyls can very easily be cleaved off the rhodiums by acid in the presence of a co-ordinating nucleophile to give the new series of complexes (4)—(10). Most surprisingly, in view of the ease with which Herrmann,[3] Shapley [4] and their co-workers have found acid to cleave μ-methylene-dirhodium bonds,‡ the di-μ-methylene-dirhodium framework in the complexes described here remains intact throughout a wide variety of transformations. It is, in fact rather difficult to break even though it is flexible and can easily move between the planar and the puckered geometries characteristic of the *trans* and the *cis* conformations with respect to the two C_5Me_5 rings. Preliminary Communications have appeared on part of this work [5] and also on some properties of cationic monomethyl complexes.[6]

A number of early experiments showed that the *cis*- and the *trans*-dimethyl-di-μ-methylene complexes reacted in identical fashion with acids. Since the *cis* isomer also isomerised to *trans* under conditions similar to those used in these reactions (Lewis acid catalysis), and since it was therefore rather harder to prepare in quantity of sufficient purity, most of the subsequent reactions were carried out with the *trans* complex (3).

Results and Discussion

trans-*Dihalogeno-di-μ-methylene and Related Complexes.*—Pentane solutions of both complexes (2) and (3) reacted readily with HCl gas (3 min at 20 °C); the colour changed from red to a deep purple and brown-red crystals of the dichloro-complex (4a) were obtained in 86% yield. The complex was characterised by microanalysis (Table 1), mass spectroscopy (which showed weak molecular ions at *m*/*e* 574 and 576 due to the species with $^{35}Cl_2$ and $^{35}Cl^{37}Cl$ respectively), i.r. spectroscopy (terminal Rh–Cl at 248 cm^{-1}), and n.m.r. spectroscopy. The ^1H n.m.r. spectrum showed just a singlet at δ 1.63 (due to C_5Me_5) and a triplet at 10.25 arising from the four equivalent μ-methylene hydrogens coupled to two equivalent rhodiums (J = 2.3 Hz). This pattern is quite characteristic of the centrosymmetric di-μ-methylene-dirhodium unit.[1,2] The ^1H n.m.r. spectrum of the complex in CD_2Cl_2 at −90 °C was the same as at +30 °C and showed no sign of any *cis* isomer.

The complex (4a) was stable to air and moisture both in the solid and in solution; it was sparingly soluble in pentane but freely soluble in methanol, benzene, or chloroform. Reaction of (3) with acetyl chloride also gave (4a).

When a methanol solution of the dichloro-complex (4a) was reacted with an excess of sodium bromide (or sodium iodide) in methanol the solution became purple (or blue-purple), and purple (or blue-purple) crystals of the dibromo, (4b) [or di-iodo, (4c)], complex were obtained in high yield. They showed bands due to terminal ν(Rh–Br) and ν(Rh–I) at 166 and 148 cm^{-1} respectively in the far-i.r. spectrum. Again their ^1H n.m.r. spectra showed the presence of C_5Me_5 and the low-field triplet characteristic of the centrosymmetric *trans*-di-μ-methylene complexes (Table 2). The mass spectrum of the iodide showed a very much stronger molecular ion than for (4a); this may be related to a greater bond strength of Rh–I than Rh–Cl.

Very analogous reactions occurred between the dichloro-complex (4a) and sodium azide, thiocyanate, cyanide, and cyanate to give the diazido, (4d), dithiocyanato, (4e), dicyano, (4f), and dicyanato, (4g), analogues. Again, all the properties, including the i.r. spectra and the low-field triplets in the ^1H n.m.r. spectra were consistent with their formulation as *trans* terminally disubstituted di-μ-methylene-dirhodium complexes. These conclusions were fully confirmed by two single-crystal *X*-ray analyses which showed both the molecules (4d) and (4e) to be centrosymmetric.[5] The thiocyanate in (4e) was S-bonded with an angle Rh–S–C of 104(1)°; the angle Rh–N–N in (4d) was 114(1)°.

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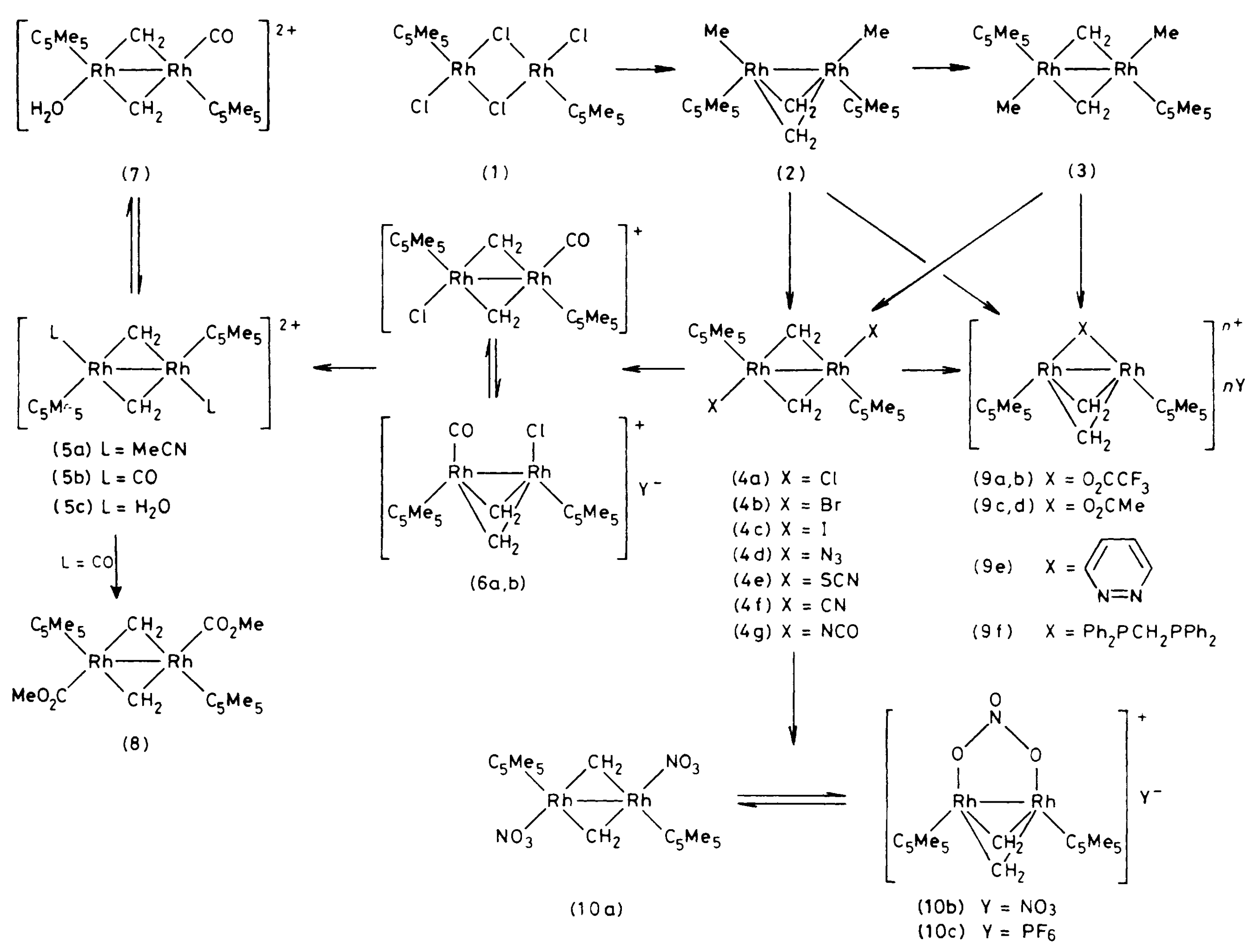
† Di-μ-methylene-bis[carbonyl(η-pentamethylcyclopentadienyl)-rhodium(IV)] dication.

Supplementary data available (No. SUP 23894, 20 pp.): H-atom co-ordinates, full bond lengths and angles, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: atm = 101 325 N m^{-2}.

‡ See also reviews on methylene-bridged complexes: W. A. Herrmann, *Pure Appl. Chem.*, 1982, **54**, 65; *Adv. Organomet. Chem.*, 1982, **20**, 159.



Cationic trans-*Di-μ-methylene Complexes.*—When the *trans* complex (3) was reacted with an excess of acid (*p*-toluenesulphonic acid was a convenient choice) in the presence of a ligand (L = acetonitrile) and potassium hexafluorophosphate (or sodium tetrafluoroborate), the dicationic *trans*-bis(acetonitrile)-di-μ-methylene-dirhodium complex (5a) was obtained. Again, analytical and spectroscopic data [in particular the low-field triplet in the ^1H n.m.r. spectrum at δ 10.31, J(Rh–H) = 1.5 Hz] fully support the structure shown.

Alternatively, such complexes could be made by reaction of the dichloro-complex (4a) with a suitable ligand in the presence of hexafluorophosphate or tetrafluoroborate. In most cases the replacement of Cl was stepwise giving first the monocationic monochloro-complex (6), which, under more drastic conditions, then gave (5). One interesting complex made in this way was the *trans* dicarbonyl (5b). Complex (4a) reacted readily with CO (3.5 atm, 20 min, 20 °C) in the presence of hexafluorophosphate (or tetrafluoroborate) in dichloromethane to give the chloro–carbonyl monocation (6) (see below). This complex reacted rapidly with CO under ambient conditions in acetone to give the dicarbonyl (5b), which showed one rather high-frequency ν(CO) in the i.r. spectrum (Table 1). The complex was insoluble in most solvents with which it did not react, but a solution of (5b) in nitromethane showed the characteristic triplet at δ 10.32. A slow reaction, giving first the monocarbonyl monoacetonitrile dication and then the bis(acetonitrile) dication (5a) (1d, 20 °C), was observed by n.m.r. spectroscopic monitoring of a solution of (5b) in acetonitrile (see below). This was reversed under CO (1 atm, 20 °C).

$$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)_2]^{2+} \overset{MeCN}{\rightleftharpoons} [\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)(MeCN)]^{2+} \overset{MeCN}{\rightleftharpoons} [\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(MeCN)_2]^{2+}$$

Similarly, on dissolving (5b) in water, reaction readily took place, with displacement of CO, to give, first the monoaqua–monocarbonyl and then, especially in the presence 30% of fluoroboric acid, the diaqua-dication (5c) [triplet at δ 10.13 (J = *ca.* 1 Hz) in the ^1H n.m.r. spectrum indicating a *trans* structure] (see below). Again, these reactions were reversed

$$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)_2]^{2+} \overset{H_2O}{\rightleftharpoons} [\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)(H_2O)]^{2+} \overset{H_2O}{\rightleftharpoons} [\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(H_2O)_2]^{2+}$$

under CO. A further, as yet uncharacterised compound was also formed during the reaction of (5b) with water.

This route to the *trans*-diaqua-complex (5c) is an alternative (albeit a much poorer one) to the method recently described in which the *cis*-μ-bicarbonato-complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}CO_3H)]BF_4$ was reacted with strong aqueous acid.[7]

Complex (5b) readily underwent nucleophilic attack by methanol, in the presence of sodium carbonate, to give the

Table 1.

	Complex	Yield	Microanalyses (%)			I.r. (cm^{-1})	
			C	H	Other		
(4a)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Cl_2]$ [a]	86	45.0 (45.9)	5.9 (6.0)	Cl, 12.8 (12.3)	Rh–Cl:	248
(4b)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Br_2]$ [b]	91	39.5 (39.8)	5.6 (5.2)	Br, 25.8 (24.1)	Rh–Br:	166
(4c)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2I_2]$ [c]	97	36.1 (34.9)	5.0 (4.5)	I, 32.9 (33.5)	Rh–I:	148
(4d)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(N_3)_2]$	93	46.3 (44.9)	6.3 (5.8)	N, 14.3 (14.8)	N_3:	2 000
(4e)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(SCN)_2]$ [d]	89	47.7 (46.5)	5.5 (5.7)	N, 4.8 (4.5)	SCN:	2 103
(4f)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CN)_2]$	83	52.4 (51.8)	6.3 (6.1)	N, 4.8 (5.0)	CN:	2 115
(4g)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(NCO)_2]$	78	49.1 (49.0)	5.9 (5.8)	N, 6.0 (4.8)	NCO:	2 190
(5a)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(MeCN)_2][PF_6]_2$	52	35.8 (35.6)	4.5 (4.6)	N, 3.8 (3.2)	CN: PF_6:	2 290, 2 315w 843, 879
(5b)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)_2][BF_4]_2$	67	39.5 (39.3)	4.9 (4.7)		CO: BF_4:	2 088 1 055
(5c)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(H_2O)_2][BF_4]_2$	58	37.9 (37.0)	5.5 (5.3)		H_2O: BF_4:	3 430, 1 625 1 050
(6a)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)Cl][PF_6]\cdot CH_2Cl_2$	84	36.3 (36.1)	4.6 (4.6)	Cl, 11.7 (13.3)	CO: PF_6:	2 072 840, 876
(6b)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)Cl][BF_4]$	93	42.1 (42.2)	5.2 (5.2)	Cl, 6.5 (5.4)	CO: BF_4:	2 070, 2 098 1 055
(7)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)(H_2O)][BF_4]_2\cdot 2H_2O$	20	36.4 (36.4)	4.7 (5.3)		CO: H_2O BF_4:	2 085, 2 102 3 360 1 080
(8)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO_2Me)_2]$ [e]	56	50.8 (50.2)	6.5 (6.5)		CO_2:	1 634, 1 645
(9a)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2CCF_3)][H(O_2CCF_3)_2]$	31	41.1 (39.8)	4.3 (4.2)		CO_2:	1 378, 1 460, 1 625, 1 780
(9b)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2CCF_3)][PF_6]$	82	39.3 (37.8)	4.1 (4.5)		CO_2: PF_6:	1 378, 1 460, 1 625 834
(9c)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2CMe)][H(O_2CMe)_2]$	47	48.9 (49.3)	6.2 (6.5)		CO_2:	1 375, 1 415, 1 530, 1 575, 1 731
(9d)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2CMe)][PF_6]$	63	39.7 (40.7)	5.2 (5.3)		CO_2: PF_6:	1 380, 1 460, 1 545 836
(9e)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(C_4H_4N_2)][PF_6]_2$	50	35.3 (35.7)	4.2 (4.4)	N, 5.4 (3.2)	CC, CN: PF_6:	1 585 840, 875
(9f)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(Ph_2PCH_2PPh_2)][PF_6]_2$	76	48.1 (47.9)	5.0 (4.8)		PF_6:	850
(10a,b)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(NO_3)_2]$	85	40.9 (42.1)	5.4 (5.5)	N, 4.0 (4.5)	NO_3:	1 266
(10c)	$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(NO_3)][PF_6]$	25	37.3 (37.2)	4.6 (4.8)	1.5 (2.0)	NO_3: PF_6:	1 234 840, 874

[a] Mass spectrum: $[M]^+$ 574 (relative intensity 4), 576 (6); $[M - C_2H_4]^+$ 564 (100), 548 (64), 550 (13). [b] Mass spectrum: $[M]^+$ not observed; $[M - C_2H_4]^+$ 634 (11), 636 (21), 638 (8). [c] Mass spectrum: $[M]^+$ 758 (60), $[M - CH_2]^+$ 744 (100), $[M - C_2H_4]^+$ 730 (87). [d] Mass spectrum $[M]^+$ not observed $[M - SCN]^+$ 562 (50). [e] Mass spectrum: $[M]^+$ 622 (weak).

neutral *trans*-bis(methoxycarbonyl) complex (8) [$\nu(CO_2)$ at 1 634 and 1 645 cm^{-1}; ^1H n.m.r., δ 8.95 (t, J = 1 Hz)]. Related reactions are well established.[8]

X-Ray Crystal Structure Determination of trans-$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)_2][BF_4]_2$ (5b).—A single-crystal *X*-ray diffraction study of complex (5b) showed the expected structure (Figure). The cation is centrosymmetric with the inversion centre in the middle of the planar di-μ-methylene-dirhodium ring. Each rhodium is η^5-bonded to one C_5Me_5 ring (perpendicular distance 1.88 Å) and σ-bonded to two methylene carbons (distances 2.060 Å) and one carbonyl (1.908 Å). The proximity of the metals to each other (2.659 Å) indicates the presence of some metal–metal bonding. A Rh–Rh bond is again required in this complex, which is diamagnetic, since otherwise a paramagnetic ground state for Rh^{IV}, d^5, would be predicted, unless the odd electrons were coupled.

This structure is similar to the skeleton of the *cis*-dimethyl complex (2) (Rh–Rh 2.620 Å),[2] and especially to those of the *trans*-diazido-di-μ-methylene and the *trans*-di-μ-methylene-bis(thiocyanato-*S*)dirhodium complexes, (4d) and (4e), which have also had their structures determined (Rh–Rh 2.635 and 2.657 Å respectively).[5] The structure of complex (5b) also shows the contrast between the various types of Rh–C σ bonds rather well: Rh–CH_2 2.060, Rh–CO 1.908, and Rh–C(methyl) 2.102 Å [from (2)]. The shortness of the Rh–CO is largely but not entirely accounted for by the smaller radius of the *sp* carbon compared to the sp^3 carbon of a methyl (difference 0.17 Å). The plane containing the rhodiums and the two carbonyls is very nearly perpendicular (92°) to the plane of the Rh_2C_2 ring.

Even though the dimetallacyclobutane (Rh_2C_2) ring in (5b) is planar while that in (2) is puckered (angles of fold, 28° about Rh–Rh and 32° about $CH_2 \cdots CH_2$),[2] the internal

Table 2. N.m.r. spectra [couplings (Hz) to Rh in square brackets, couplings to H in parentheses]

	^{1}H n.m.r. (δ/p.p.m.)			^{13}C n.m.r. (δ/p.p.m.)			
Complex	C_5Me_5	μ-CH_2	Other	C_5*Me*$_5$	*C*$_5$Me$_5$	CH_2	Other
(4a) [a]	1.63	10.25 t [2.3]					
(4b) [a]	1.66	10.27 t [2.1]					
(4c) [a]	1.81	10.53 t [2.0]					
(4d) [b]	1.70	9.72 t [1.7]					
(4e) [b]	1.72	9.60 t [2.2]					
(4f) [a]	1.87	9.23 t [1.6]					
(4g) [a]	1.68	10.02 t [1.8]					
(5a) [c]	1.80	10.31 t [1.5]	CH_3CN: 2.38	9.2	106.2	189.7 t [24]	MeCN: 3.0, 124.4
(5b) [c]	2.12	10.32 t [1.2]		10.0	114.0 d [2]	184.9 t [21]	
(5c) [d]	1.67	10.13		9.0	103.4 [2]	191.0 [21]	
cis-(6a) [e]	1.74 1.98	9.26 [1.4, 2.0] (2.0) 10.48 [0.8, 2.0] (2.0)		9.9 10.1	105.9 [5] 108.7 [4]	180.5 t [24]	CO: 185.2 d [79]
trans-(6a) [e]	1.73 2.00	10.10 [1.4, 2.8] (2.0) 10.24 [0, 2.0] (2.0)		9.2 10.5	106.4 [5] 110.5 [4]	184.4 dd [22, 24]	CO: 184.9 d [78]
(7) [d]	1.72 1.99	9.65 br 10.36 br		9.1 9.6	105.9 d [6] 110.4 d [4]	186.2 t [24]	
(8) [a]	1.69	8.95 t [1]	CO_2Me: 3.38	9.5	103.0	171.1 t [27]	CO_2Me: 52.1, 189.1 d [59]
(9d) [a]	1.70	8.99 d (1.8) 9.48 m	O_2CMe: 2.04				
(9b) [b]	1.73	9.07 d (0.4) 9.60 dt (0.4) [2.2]					
(9e) [f]	2.04	9.35 br 9.69 m	$C_4H_4N_2$: 8.04, 8.99 (2t, 4.0)				
(9f) [f]	1.74	9.52 m 9.98 m	$Ph_2PCH_2PPh_2$: 3.69 [t, J(P) = 11] 7.54 m	10.5	109.9 [2]	173.4 tt [J(P) = 6, J(Rh) = 24]	
(10a) [g]	1.77	9.5 br 10.1 t [2]					
(10b) [b]	1.73 1.65	9.27 br, 10.03 br, 10.40 br					
(10c) [b]	1.67	9.27 m, 10.05 t [2.5]					

[a] $CDCl_3$ at 30 °C. [b] CD_2Cl_2 at 30 °C. [c] CD_3NO_2 at 30 °C. [d] $D_2O + HBF_4$ at 35 °C. [e] $CDCl_3$ at 20 °C. [f] $(CD_3)_2CO$ at 30 °C. [g] CH_3OH at 36 °C.

angles at Rh (99.6°) and at carbon (80.4°) are very similar to those in (2) and in (4d) and (4e). The persistence of these features in a variety of complexes adds weight to the conclusion, from reactivity studies, that the $Rh_2(\mu\text{-}CH_2)_2$ ring possesses an unusual and unexpected stability.

cis-*Di-μ-methylene-dirhodium Complexes.*—In contrast to the complexes (4a)—(4e) which all have the *trans* configurations, reaction with potentially bidentate ligands in the presence of acids gave the *cis* complexes (9). The first examples of such complexes were obtained by reaction of (3) with carboxylic acids where the carboxylate acted as a bridging ligand thus forcing the molecule into the *cis* conformation. Thus, addition of trifluoroacetic acid to a solution of (3) in pentane caused a change in colour from red to brown; from the solution yellow-brown crystals could be obtained, the data for which were in best agreement with $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2\text{-}X]Y$ (9a), with X = O_2CCF_3 and Y is a hydrogen-bridged trifluoroacetate anion. For example, in the CO_2 region of the i.r. spectrum $\nu_{sym}(CO_2)$ were at 1 378 and 1 460 cm^{-1} and $\nu_{asym}(CO_2)$ were at 1 625 and 1 780 cm^{-1}, in agreement with literature values for bridging O_2CCF_3 ligands.[9] Reaction of this salt with hexafluorophosphate in acetone gave the salt (9b) (Y = PF_6). The acetate salts (9c) [Y = $H(O_2CMe)_2$] and (9d) (Y = PF_6) were obtained by similar means, and also by reaction of the *trans*-dichloro-complex (4a) with sodium acetate. This last reaction in particular shows how easily the change from *trans* to *cis* geometry can occur.

All these salts showed the common feature in the ^{1}H n.m.r. spectrum of a single C_5Me_5 resonance and two μ-methylene resonances, in the ratio of 30 : 2 : 2. The methylene-H resonance at higher field appeared as a doublet, coupling only to the lower field methylene hydrogen, which also coupled to the rhodiums. This behaviour has been analysed for the *cis*-dimethyl complex (2), where nuclear Overhauser enhancement measurements, combined with information about non-bonded distances from the *X*-ray structural analysis, allowed these two resonances to be ascribed to the diastereotopic axial and equatorial methylene hydrogens respectively.[2] In a variety of complexes the chemical shift separation between these two resonances is, with one exception, in the range 0.46—1.3 p.p.m. (Table 2) in the *cis* isomers and we propose this as a useful diagnostic test for the presence of this isomer (see below). The only complex we have so far observed to have a smaller chemical shift separation is the dicationic pyridazine complex (9e), but there may be some unusual steric constraints there owing to the smallness of the bite angle of that ligand.

The *cis*-μ-[bis(diphenylphosphino)methane] dication (9f) was prepared from the *trans*-bis(acetonitrile) dication (5a). The n.m.r. spectra were in full agreement with the proposed struc-

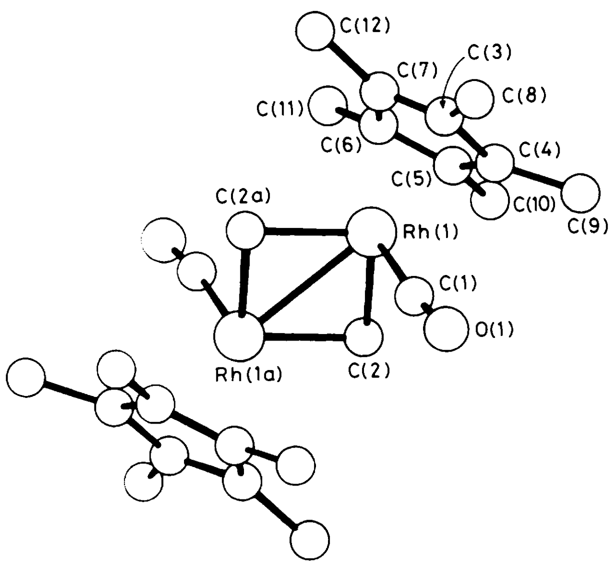


Figure. A view of the dicationic part of the complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)_2][BF_4]_2$ (5b)

Table 3. Important bond lengths (Å) and angles (°) for *trans*-$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)_2][BF_4]_2$ (5b)

Rh(1)–Rh(1a)	2.659(1)	Rh(1)–C(3)	2.202(6)
		Rh(1)–C(4)	2.208(6)
Rh(1)–C(1)	1.908(8)	Rh(1)–C(5)	2.258(7)
Rh(1)–C(2)	2.060(7)	Rh(1)–C(6)	2.233(6)
Rh(1)–C(2a)	2.061(6)	Rh(1)–C(7)	2.263(6)
		Rh(1)–C(av.)	2.234
C(1)–O(1)	1.116(10)		
C(2)–Rh(1)–C(2a)	99.6(2)	C(1)–Rh(1)–C(2a)	95.0(3)
Rh(1)–C(2)–Rh(1a)	80.4(2)	C(1)–Rh(1)–Rh(1a)	95.9(2)
C(1)–Rh(1)–C(2)	92.6(3)	Rh(1)–C(1)–O(1)	171.6(6)

ture, in particular the ^{31}P spectrum showed a ten-line pattern at δ 44.0 characteristic of an AA′XX′ spin system. Analysis [10] of the spectrum gave the following coupling constants: $J(P^1P^2) = 35.4$, $J(Rh^1P^1) = 159.1$, $J(Rh^2P^1) = 0.9$, $J(Rh^1\text{-}Rh^2) = 12.2$ Hz.

Another unusual complex is the dinitrate (10 a,b), obtained simply by addition of silver nitrate in acetonitrile to the dichloro-complex (4a). It is a remarkable feature of the stability of the dimetallacyclobutane ring that it binds so easily to oxy-ligands of this type; related carbonate and bicarbonate complexes have also been described.[7] The *cis* geometry for the dinitrate comes immediately from the observation of two methylene resonances in the ^1H n.m.r. spectrum in methanol; this suggests that one nitrate is a bridging, bidentate ligand and the other is ionic.

However, in less polar solvents the spectra were more complex and indicated the presence of two forms at low temperatures. Thus, in CD_2Cl_2 at −70 °C two sets of resonances are observed in the ratio 6 : 1, one [at δ 1.52 and 10.28 (t)] ascribed to the major, ' covalent ', *trans* isomer (10a), the other [at δ 1.68, 9.15 (d), and 9.96 (m)] to the minor, ionic, *cis* isomer (10b) ($Y = NO_3$). This proposal was confirmed by the preparation of the nitrate hexafluorophosphate salt (10c) ($Y = PF_6$), which in dichloromethane, even at 36 °C, showed the presence of only the *cis* ionic form [δ 1.67, 9.27 (m), and 10.05 (t)].

Asymmetrically Disubstituted Complexes $[\{C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2XY]^{n+}$ ($X = CO$, $Y = Cl$ *or* H_2O).—The complexes (6a,b) and (7) with different substituents on the two rhodiums, but with the dimetallacyclobutane ring intact, have been synthesised. In these cases the ^1H n.m.r. spectra are more complex since the *trans* isomers, having lost their centres of symmetry, now also give rise to two low-field resonances for their methylene protons. However, in general,* the difference in chemical shift between them is (as might be expected) significantly smaller than for the *cis* isomers (0.09—0.57 p.p.m.). This allows a guide for assigning structures to be proposed: chemical shift differences of 0.5 p.p.m. or less imply the presence of a *trans* isomer while differences greater than 0.5 p.p.m. suggest that the *cis* isomer is present.

Based upon this rule-of-thumb we can say that the chlorocarbonyl cation in (6) which shows two pairs of C_5Me_5 resonances (ratio 1 : 4.4 in $CDCl_3$ at 20 °C) and two pairs of resonances in the methylene region in the same ratio is composed of the *trans* and the *cis* isomers in the ratio 4.4 : 1. From the 400-MHz spectra all the methylene protons are found to have geminal coupling as well as coupling to the rhodiums. However, one of the couplings to rhodium is much less than the other (and, in other complexes, can even decrease to almost zero). This suggests, as we have proposed before,[2] that $^2J(Rh\text{–}H)$ is very sensitive to the relative positions of the nuclei, that is, to the bond angle Rh–C–H.

We have been able to deduce much less about the structure of the aqua–carbonyl dication (7) since the complex was only sufficiently soluble and stable for n.m.r. measurements in aqueous acid and this significantly limited the temperature range that could be examined. At ambient temperatures, however, both the ^1H and the ^{13}C spectra indicated the presence of only one (*trans*) isomer.

Conclusions

We have shown that a variety of complexes of the type $[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2XY]^{n+}$ can be prepared for a number of different types of ligand, in which X and Y may be identical or different and in which the complex bears a charge of 0, +1, or +2. In all of them the n.m.r. spectra show the presence of the dirhodacyclobutane ring and this has been confirmed by *X*-ray single-crystal structure determinations on some of them. The variety of interconversions that are possible without breaking this unit indicates a high and unexpected stability of the dirhodacyclobutane; although cleavage occurs readily with one-electron oxidisers,[11] it will withstand sulphuric acid at 20 °C down to pH 1.[7]

Experimental

Although the complexes here described are not significantly air-sensitive under normal conditions, they were usually handled under nitrogen. Yields, microanalyses (carried out by the University of Sheffield Microanalysis Unit), and i.r. spectra are in Table 1; n.m.r. spectra are collected in Table 2. (It may be noted that a few of the complexes have unexpectedly poor microanalyses. We suspect this to arise from difficulties in combustion since all the spectroscopic data agree with the proposed structures, several of which have also been confirmed by single-crystal *X*-ray structure determinations.) Typical synthetic procedures are detailed below.

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* Other complexes of this type have also been made: S. Okeya, N. J. Meanwell, B. F. Taylor, K. Isobe, A. Vázquez de Miguel, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, in the press.

$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Cl_2]$ (4a).—Hydrogen chloride gas was bubbled slowly through a red solution of either *cis*- or *trans*-$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Me_2]$ (2) or (3) (0.05 g, 0.1 mmol) dissolved in pentane (30 cm^3) (3 min at 20 °C). The colour of the solution immediately turned deep purple and brown-red crystals slowly began to precipitate; yield of (4a) after recrystallisation from benzene, 0.046 g (86%).

$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2Br_2]$ (4b).—A solution of sodium bromide (0.14 g, 1.4 mmol) in methanol (20 cm^3) was added to a brown-red solution of the dichloro-complex (4a) (0.04 g, 0.07 mmol) in methanol (40 cm^3). The solution was stirred (1 h at 20 °C) during which it turned purple; the solvent was then removed *in vacuo*. The residue was extracted with dichloromethane (60 cm^3) which gave red-purple crystals of (4b) (0.04 g, 91%) on evaporating the solution.

$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(\mu\text{-}O_2CMe)]Y$ [$Y = H(O_2CMe)_2$ (9c) *or* PF_6 (9d)].—Acetic acid (0.66 g, 11 mmol) was added to a solution of (2) or (3) (0.05 g, 0.1 mmol) in pentane (30 cm^3). The solution was stirred (30 h at 45 °C) during which time the colour changed slowly from red to brown and a brown oil was deposited. The solvent was evaporated and the brown oil dissolved in water (20 cm^3), which was extracted with dichloromethane (2 × 60 cm^3), the extract dried over anhydrous sodium carbonate, and then evaporated to dryness to yield (9c) as a somewhat sticky orange solid (0.03 g, 47%). Reaction of this solid (0.03 g, 0.004 mmol) with KPF_6 (0.1 g, 0.54 mmol) in acetone (30 cm^3) and normal work-up followed by crystallisation from dichloromethane–diethyl ether gave orange crystals of (9d) (0.02 g, 63%).

$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)Cl][PF_6]\cdot CH_2Cl_2$ (6a).—Potassium hexafluorophosphate (0.69 g, 3.75 mmol) was added to a solution of the dichloro-complex (4a) (1.0 g, 1.74 mmol) in dichloromethane (5 cm^3) in a Fisher-Porter tube and the mixture was stirred (20 min, 20 °C) under carbon monoxide (3.5 atm). The CO pressure was then released, the suspension was filtered, and diethyl ether (10 cm^3) was added slowly to the dark red filtrate to produce fine brown crystals of (6a) (1.17 g, 84%); the presence of dichloromethane of crystallisation was confirmed by analysis and the n.m.r. spectrum. The tetrafluoroborate (6b) was obtained analogously (93%).

$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO)_2][BF_4]_2$ (5b).—A solution of silver tetrafluoroborate (0.31 g, 1.6 mmol) in acetone (2 cm^3) was added to a solution of (6b) prepared above (0.49 g, 0.74 mmol). The precipitated silver chloride was filtered off and carbon monoxide was then bubbled into the red filtrate (20 °C, 1 atm, 2 min); orange-yellow crystals of (5b) (0.37 g, 67%) were precipitated which could be recrystallised from nitromethane–diethyl ether. The hexfluorophosphate salt could be obtained (67% yield) by an analogous reaction in the presence of excess KPF_6.

X-*Ray Structure Determination*.—A crystal (dimensions, 0.25 × 0.25 × 0.5 mm) of the bis(tetrafluoroborate) salt (5b) was selected from a batch grown as described above.

Crystal data. $[C_{24}H_{34}O_2Rh_2][BF_4]_2$, $M = 734.05$, orthorhombic, $a = 13.717(6)$, $b = 14.355(8)$, $c = 14.482(10)$ Å, $U = 2\,851$ Å^3, $Z = 4$, $D_c = 1.71$ g cm^{-3}, $F(000) = 1\,464$, space group *Pbca* (uniquely determined from absences), Mo-K_α radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu = 12.10$ cm^{-1}.

Unit-cell parameters were obtained from a least-squares fit of the setting angles of 25 well-centred reflections.

X-Ray reflection data in the range $3.5 \leqslant 2\theta \leqslant 55°$ were collected on a Nicolet R3M four-circle automatic diffractometer. 2 321 Independent reflections with $I \geqslant 3\sigma(I)$ were obtained and corrected for Lorentz and polarisation effects. An empirical absorption correction based on ψ-scans of six reflections (216 measurements) was also applied. The structure was solved by Patterson and difference-Fourier methods and refined by cascade blocked-matrix least squares with weights $w_i = 1/[\sigma^2(F_i) + 0.00247F_i^2]$ to an R value of 0.056. All the non-hydrogen atoms were refined with independent positional and vibrational parameters. Sufficient hydrogen atoms were observed in a low-angle difference map to define the torsion angles of the methyl groups. The hydrogen atoms were constrained each to ride on the adjacent heavy atom with idealised bond lengths and angles; the (isotropic) hydrogen thermal parameters were set at 1.2 times the $U_{eq.}$ values for their neighbours.

Table 4. Atomic co-ordinates (× 10^4) for (5b)

Atom	x	y	x
Rh(1)	751(1)	553(1)	188(1)
O(1)	668(4)	485(4)	2 268(4)
C(1)	632(4)	477(4)	1 498(6)
C(2)	694(4)	−872(5)	36(5)
C(3)	1 634(4)	1 834(4)	212(4)
C(4)	2 279(4)	1 034(5)	235(5)
C(5)	2 164(5)	569(4)	−612(5)
C(6)	1 449(5)	1 038(4)	−1 121(4)
C(7)	1 147(4)	1 845(4)	−625(4)
C(8)	1 612(7)	2 573(6)	958(6)
C(9)	3 018(6)	837(7)	950(7)
C(10)	2 775(7)	−229(6)	−927(8)
C(11)	1 181(8)	832(6)	−2 111(5)
C(12)	517(6)	2 593(5)	−976(7)
F(1)	4 349(12)	2 017(15)	2 958(13)
F(2)	3 599(15)	3 315(16)	2 373(12)
F(3)	2 783(12)	2 312(16)	3 112(16)
F(4)	3 846(17)	3 036(15)	4 017(12)
B(1)	3 671(6)	2 687(6)	3 143(7)
F(11)	2 845(25)	2 612(21)	−1 543(27)
F(12)	4 151(15)	1 801(18)	−1 312(12)
F(13)	4 106(36)	3 014(32)	−2 168(32)
F(14)	3 634(36)	1 646(35)	−2 283(24)

This was clear evidence for orientational disorder of the BF_4^- ion. The fluorines of the major component [62.3%, F(1)—F(4)] and those of the minor component [F(11)—F(14)] were treated as normal atoms with fractional population centred on a common boron atom (100%). Consequently the B–F distances, particularly for the minor component, are not very useful. A final difference-Fourier map showed no peak higher than 0.6 e Å^{-3} and none which could be interpreted as an atom. The final analysis of variance against sin θ and against $|F|$ showed no unusual features; the normal probability plot was satisfactory. The SHELXTL suite of crystallographic programs was used throughout.

Significant bond lengths and angles are collected in Table 3 and atomic co-ordinates in Table 4.

$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(CO_2Me)_2]$ (8).—Sodium carbonate (0.1 g, 1.0 mmol) was added to a solution of (5b) in methanol (0.8 cm^3), and the suspension stirred (20 °C, 30 min). A conventional work-up gave brown crystals of (8) (0.17 g, 56%).

$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(NO_3)_2]$ (10a,b).—A suspension of the dichloro-complex (4a) (0.28 g, 0.49 mmol) in methanol (10 cm^3) was stirred with silver nitrate (0.2 g, 1.18 mmol). The silver chloride was filtered off and the solvent removed *in vacuo*. Extraction of the residue with dichloromethane and crystallisation by addition of diethyl ether gave complex (10a,b) (0.26 g, 85%).

$[\{(C_5Me_5)Rh\}_2(\mu\text{-}CH_2)_2(C_4H_4N_2)][PF_6]_2$ (9e).—Pyridazine (0.03 cm^3) was added to a solution of the dichloro-complex (4a) (50 mg, 0.09 mmol) in dichloromethane (0.3 cm^3) containing KPF_6 (35 mg, 0.2 mmol). The suspension was stirred (1 h at 20 °C), then it was filtered, the filtrate evaporated to dryness and the residue crystallised from acetone–diethyl ether to give complex (9e) (38 mg, 50%).

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