Crystal and Molecular Structure of Di-μ-chloro-tetrakis-(4-methylpenta-1,3-diene)dirhodium(I)

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Crystals of the title compound are monoclinic, space group $I2/a$ with cell dimensions, a = 15·247(12), b = 12·103(11), c = 14·848(14) Å, β = 104·6(1)°, Z = 4. The intensities of 1473 independent reflections above background were collected by counter methods and refined to R 0·043. The dimeric molecule has imposed C_2 symmetry. The environment of each metal atom is approximately square planar, the co-ordination plane being defined by two bridging chlorine atoms and the mid-point of the less substituted C=C double bonds of two 1,3-diolefins. The two co-ordination planes intersect at 115·8° and there is a weak Rh · · · Rh interaction [3·090(3) Å]. Rh–Cl bond distances are 2·410(3) and 2·402(3) Å. The co-ordinated C=C bonds are not symmetric with respect to the co-ordination plane, probably because of steric effects; Rh–C distances are 2·120(9) and 2·161(9) in ligand (A), and 2·121(11) and 2·165(9) Å in ligand (B).

MONO-OLEFIN complexes of rhodium(I) are well characterised. However, published work on rhodium(I) complexes of acyclic conjugated dienes is sparse and fragmentary. In the course of an investigation of rhodium-promoted isomerisation reactions of substituted butadienes we have prepared a large number of new complexes in which, in most cases, the diene is co-ordinated to the metal in the expected manner *via* both double bonds (bidentate co-ordination). An X-ray analysis of chloro-bis-(π-butadiene)rhodium(I) has been described [1] and we have recently reported the structure of two π-cyclopentadienyl(diene)rhodium(I) complexes (diene = 2,3-dichloro- and 2,3-dimethyl-butadiene).[2]

Among the new compounds prepared were a few which, from analytical data and ^{1}H n.m.r. and i.r. spectra, were considered to contain diene linked to the metal *via* only one of the double bonds (unidentate co-ordination).[3] Compounds containing unidentate 1,3-diene are uncommon and, in the case of rhodium, unknown. An example is butadienetetracarbonyliron(0); however, this is unstable, losing carbon monoxide to give the tricarbonyl derivative wherein the diene is chelated.[4] While unidentate 1,3-diene is rarely found in isolable compounds, we believe it may occur widely in reaction intermediates. We have previously suggested the intermediacy of such species in the reactions of certain conjugated dienes [3] with $Fe(CO)_5$ and more recently have obtained evidence for their involvement in the isomerisation of the same group of dienes when co-ordinated to rhodium(II).[5] This paper describes the results of a single-crystal X-ray investigation of di-μ-chloro-tetrakis-(4-methylpenta-1,3-diene)dirhodium(I).

EXPERIMENTAL

Preparation of the Complex.—4-Methylpenta-1,3-diene (1 ml, 8 mmol) was added to a suspension of μ-dichlorotetraethylenedirhodium(I) (390 mg, 1 mmol) in diethyl ether (30 ml) and heated under reflux for 5 min. The red filtrate was concentrated to 5—10 ml and was set aside to give red crystals which were recrystallised (80%) from pentane–diethyl ether (1 : 1, v/v), m.p. 118—120 °C.

The product was characterised by i.r. and ^{1}H n.m.r. spectra and by elemental analysis (Found: C, 47·5; H, 6·7; Cl, 11·7%. $C_{24}H_{40}Cl_2Rh_2$ requires C, 47·5; H, 6·6; Cl, 11·7%).

Crystal Data.—$C_{24}H_{40}Cl_2Rh_2$, M = 604·34, Monoclinic, a = 15·247(12), b = 12·103(11), c = 14·848(14) Å, β = 104·6(1)°, U = 2652·0 Å^3, D_c = 1·52, Z = 4, D_m = 1·53(2), $F(000)$ = 1232. Space group $I2/a$, non-standard setting of $C2/c$ (C^6_{2h}, No. 15) from systematic absences: hkl, $h + k + l = 2n + 1$, and $h0l$, $h = 2n + 1$. Mo-K_α radiation, λ = 0·7107 Å, μ = 14·3 cm^{-1}. Equivalent positions: $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, z; -x, y, \frac{1}{2} - z)$.

A crystal with dimensions 0·13 × 0·13 × 0·13 mm was mounted with the (110) planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus used to measure diffraction intensities and cell dimensions. The apparatus was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. A molybdenum tube was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken from plots of background as a function of 2θ. Several standard

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

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

[3] S. M. Nelson and M. Sloan, *J.C.S. Chem. Comm.*, 1972, 745.

[4] H. Murdoch and E. Weiss, *Helv. Chim. Acta*, 1962, **45**, 1156.

[5] M. G. B. Drew, S. M. Nelson, and M. Sloan, to be published.

reflections were measured during the course of the experiment but no significant change in intensities was found. 2292 Independent reflections were measured with $2\theta < 50°$.

TABLE 1

Final positional co-ordinates, and thermal parameters, with estimated standard deviations in parentheses

	x	y	z	U/Å^2 $\times 10^2$
Rh	0·60407(4)	0·48180(5)	0·28817(4)	a
Cl	0·51112(14)	0·56181(18)	0·14773(14)	a
C(1A)	0·6881(6)	0·4719(9)	0·4254(6)	a
C(2A)	0·6545(6)	0·3663(8)	0·4002(6)	a
C(3A)	0·5799(7)	0·3157(8)	0·4304(6)	a
C(4A)	0·5528(6)	0·2115(7)	0·4216(6)	a
C(5A)	0·5946(10)	0·1260(10)	0·3760(11)	a
C(6A)	0·4751(8)	0·1742(10)	0·4561(8)	a
C(1B)	0·6642(6)	0·3804(8)	0·2037(7)	a
C(2B)	0·7260(6)	0·4636(8)	0·2399(7)	a
C(3B)	0·7408(6)	0·5581(8)	0·1854(6)	a
C(4B)	0·8073(6)	0·6319(8)	0·2077(7)	a
C(5B)	0·8789(7)	0·6294(10)	0·2996(9)	a
C(6B)	0·8163(7)	0·7204(9)	0·1412(8)	a
H(1A,1)	0·653(5)	0·524(6)	0·452(6)	5(2)
H(1A,2)	0·763(8)	0·493(8)	0·413(9)	9(3)
H(2A)	0·687(5)	0·301(7)	0·372(5)	6(2)
H(3A)	0·539(9)	0·360(10)	0·451(8)	12(4)
H(1B,1)	0·630(6)	0·390(7)	0·143(6)	6(3)
H(1B,2)	0·671(6)	0·305(8)	0·238(6)	7(3)
H(2B)	0·768(7)	0·438(7)	0·290(6)	6(3)
H(3B)	0·696(6)	0·580(7)	0·123(6)	7(3)
H(5A,1) [b]	0·653	0·149	0·351	
H(5A,2)	0·618	0·057	0·426	
H(5A,3)	0·545	0·091	0·318	
H(6A,1)	0·445	0·239	0·488	
H(6A,2)	0·425	0·143	0·397	
H(6A,3)	0·498	0·110	0·505	
H(5B,1)	0·873	0·565	0·350	
H(5B,2)	0·944	0·621	0·288	
H(5B,3)	0·875	0·707	0·336	
H(6B,1)	0·766	0·724	0·075	
H(6B,2)	0·813	0·800	0·175	
H(6B,3)	0·882	0·714	0·127	

[a] Anisotropic thermal parameters given in Table 2. [b] Positional parameters for this and following atoms were fixed. Thermal parameters were kept equivalent to those of the appropriate carbon atom.

TABLE 2

Anisotropic thermal parameters ($\times 10^3$) with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	43·5(3)	49·5(3)	50·5(3)	−03·0(3)	18·2(2)	−01·0(3)
Cl	56(1)	60(1)	57(1)	−02(1)	26(1)	09(1)
C(1A)	61(5)	89(7)	50(5)	−02(5)	10(4)	−03(5)
C(2A)	60(5)	74(6)	54(5)	10(4)	15(4)	11(4)
C(3A)	71(6)	69(6)	67(6)	12(5)	31(5)	20(4)
C(4A)	76(6)	60(6)	70(6)	06(4)	23(5)	04(4)
C(5A)	123(11)	81(8)	167(5)	02(7)	60(10)	−24(8)
C(6A)	95(8)	83(7)	104(8)	−14(6)	35(6)	21(6)
C(1B)	55(5)	60(5)	69(6)	04(4)	26(5)	−10(4)
C(2B)	45(4)	71(6)	68(5)	02(4)	24(4)	07(4)
C(3B)	56(5)	78(6)	61(5)	−05(4)	29(4)	−10(4)
C(4B)	48(5)	75(6)	90(6)	−17(4)	37(5)	−17(5)
C(5B)	61(5)	103(9)	121(9)	−11(5)	27(6)	−14(7)
C(6B)	94(8)	82(7)	96(8)	−26(6)	58(7)	−15(6)

Neither absorption nor extinction corrections were made. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0{\cdot}03I)^2]^{\frac{1}{2}}$, where I is the intensity and E the background of the reflection. 1473 Reflections with $I > 2\sigma(I)$ were used in the subsequent refinement.

Structure Determination.—The structure was determined from Patterson and Fourier syntheses and refined by full-matrix least-squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_o < 72$ and $\sqrt{w} = 72/F_o$ for $F_o > 72$. Calculations were made on an ATLAS computer at S.R.C., Chilton, Berkshire, with the programs described in ref. 6. Atomic scattering factors for rhodium, chlorine, and carbon were taken from ref. 7 and those for hydrogen from ref. 8. Corrections for

TABLE 3

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Rh–Rh$^{\mathrm{I}}$	3·090(3)		
Rh–Cl	2·410(3)	Rh–Cl$^{\mathrm{I}}$	2·402(3)

	Ligand (A)	Ligand (B)
Rh–C(0)	2·024	2·027
Rh–C(1)	2·120(9)	2·121(11)
Rh–C(2)	2·161(9)	2·165(10)
C(1)–C(2)	1·392(14)	1·391(12)
C(2)–C(3)	1·458(15)	1·451(14)
C(3)–C(4)	1·323(13)	1·330(13)
C(4)–C(5)	1·467(18)	1·518(14)
C(4)–C(6)	1·475(17)	1·485(15)
C(1)–H(1,1)	0·97(9)	0·93(8)
C(1)–H(1,2)	1·22(12)	1·04(10)
C(2)–H(2)	1·07(9)	0·90(8)
C(3)–H(3)	0·93(14)	1·05(9)

(*b*) Angles

Rh–Cl–Rh$^{\mathrm{I}}$	79·90(7)	C(1A)–Rh–C(1B)	106·8(4)
Cl–Rh–Cl$^{\mathrm{I}}$	81·45(7)	C(2A)–Rh–C(2B)	91·2(4)
C(0)–Rh–C(0)	93·4		

	Ligand (A)	Ligand (B)
Rh–C(0)–C(1)	88·2	88·1
Rh–C(0)–C(2)	91·8	91·9
Cl–Rh–C(0)	173·8	92·8
Cl–Rh–C(1)	159·4(3)	88·2(2)
Cl–Rh–C(2)	160·7(2)	97·0(2)
Cl$^{\mathrm{I}}$–Rh–C(0)	92·4	174·2
Cl$^{\mathrm{I}}$–Rh–C(1)	88·1(3)	159·3(2)
Cl$^{\mathrm{I}}$–Rh–C(2)	96·3(3)	161·2(2)
C(1)–Rh–C(2) [a]	87·2(4)	87·6(4)
C(1)–Rh–C(2)	37·9(4)	37·9(4)
Rh–C(1)–C(2)	72·6(5)	72·8(6)
Rh–C(1)–H(1,1)	95(4)	107(6)
Rh–C(1)–H(1,2)	102(5)	104(6)
C(2)–C(1)–H(1,1)	120(5)	116(5)
C(2)–C(1)–H(1,2)	116(5)	118(5)
H(1,1)–C(1)–H(1,2)	124(7)	123(7)
Rh–C(2)–C(1)	69·4(5)	69·3(6)
Rh–C(2)–C(3)	110·7(6)	111·8(6)
Rh–C(2)–H(2)	106(4)	105(7)
C(1)–C(2)–C(3)	124·5(9)	122·6(8)
C(1)–C(2)–H(2)	127(5)	110(6)
C(3)–C(2)–H(2)	107(5)	124(6)
C(2)–C(3)–C(4)	128·2(1)	127·3(8)
C(2)–C(3)–H(3)	120(8)	123(5)
C(4)–C(3)–H(3)	111(8)	109(5)
C(3)–C(4)–C(5)	123·8(11)	122·8(9)
C(3)–C(4)–C(6)	121·1(10)	120·7(8)
C(5)–C(4)–C(6)	115·1(10)	116·5(8)

[a] C(1), C(2) in different ligands.

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[6] J. C. Baldwin, R. C. Chastain, D. F. High, F. A. Kundell, and J. M. Stewart, 'X-ray '67,' System of Programs, revised July 1970, University of Maryland Technical Report, 67 58, 1967.

[7] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

the real and imaginary parts of the anomalous dispersion for rhodium and chlorine were also taken from ref. 7. The anisotropic thermal parameter is defined as $\exp(-2\pi^2\sum_i\sum_j U_{ij}h_ih_j)$ $i,j = 1$—3. The isotropic thermal parameter is defined as $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. Rhodium, chlorine, and carbon atoms were refined anisotropically to R 0·055 for the 1473 observed reflections. A difference-Fourier map was then calculated and the positions of the 20 hydrogen atoms located; their positions were idealised at 1·075 Å from the carbon atoms to which they were attached in trigonal or tetrahedral positions. The parameters of the eight non-methyl hydrogen atoms were allowed to refine but parameters of the remaining 12 hydrogen atoms were kept fixed. The final R was 0·043. The 819 zero reflections gave no large discrepancies. Difference-Fourier syntheses showed no significant peaks. In the final cycle of refinement no shift was $>0·05\sigma$. The final list of co-ordinates and thermal parameters are given in Tables 1 and 2. Table 3 lists the bond distances and angles. The final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20709 (7 pp.).*

TABLE 4

All intramolecular distances (Å) $<3·0$ Å, together with a few selected contacts above this distance. All contacts involving atoms on the same ligand are ignored, as are those involving the postulated methyl hydrogen atoms

Rh ··· H(1A,1)	2·41(8)	Rh ··· C(3A)	3·00
Rh ··· H(1A,2)	2·66(10)	Rh ··· C(3B)	3·02
Rh ··· H(1B,1)	2·55(10)	C(1A) ··· C(1B)	3·40
Rh ··· H(1B,2)	2·57(10)	C(1A) ··· C(2B)	2·95
Cl ··· C(3B)	3·40	C(2A) ··· C(2B)	3·09
Cl ··· H(3B)	2·94(10)	C(1B) ··· C(2A)	2·96
Cl ··· H(1B,1)	2·77(9)	C(1B) ··· H(2A)	2·61
Cl^{I} ··· C(3A)	3·37	C(1A) ··· H(2B)	2·63
Cl^{I} ··· H(3A)	2·86(12)	C(2A) ··· H(1B,2)	2·60
Cl^{I} ··· H(1A,1)	2·61(7)	C(2B) ··· H(1A,2)	2·51
		C(2B) ··· H(2A)	2·94
H(1A,2) ··· H(2B)	1·96(14)	C(2A) ··· H(2B)	2·80
H(1B,2) ··· H(2A)	1·95(12)		
H(2A) ··· H(2B)	2·55(14)	C(1B) ··· C(3A^{I})	3·84
		C(1B) ··· C(4A^{I})	3·94
		C(1B) ··· H(3A^{I})	3·37

Superscripts are defined in the footnote to Table 5.

DISCUSSION

The molecule is shown in Figure 1, together with the atomic numbering scheme. Carbon atoms in the two diolefinic ligands, (A) and (B), are numbered C(nA) and C(nB) with $n = 1$—6, and hydrogen atoms bonded to these carbon atoms are numbered H(nA,m) or H(nB,m) with $m = 1$—3. The molecule has crystallographically imposed C_2 symmetry, the four molecules in the unit cell enveloping the two-fold axes at $x = 0, \frac{1}{2}$ and $z = 1/4, 3/4$. The $RhCl_2Rh$ bridge is non-planar, the angle of intersection between the two $RhCl_2$ segments being 115·8°. This is precisely the same angle of intersection as found for the corresponding ethylene complex $[Rh(C_2H_4)_2Cl]_2$,[9] and is similar to those found for other chlorine-bridged rhodium(I) complexes, *e.g.* $[Rh(CO)_2Cl]_2$,[10] $Rh_2[P(OPh)_3](C_8H_{12})Cl_2$,[11] and the tetranuclear mixed Rh^{I}–Rh^{III} complex $[Rh_2(CO)(EtC_2Et)_2Cl_2]_2$,[12] *viz.* 124, 122·6, and 115·6°. The 1,5-cyclo-octadiene complex, $[Rh(C_8H_{12})Cl]_2$ is exceptional, however, in having a planar $RhCl_2Rh$ bridge with Rh ··· Rh 3·50 Å.[13] In the present molecule, the Rh ··· Rh distance is 3·090(3) Å, a value comparable with those found in most other structures containing folding bridges and is consistent with a weak metal–metal interaction. Shorter metal–metal bonds (2·618—2·796 Å) are observed in the metal and in a range of compounds including the carbonyl-bridged rhodium(0) complex $[Rh(PPh_3)_2CO]_2$.[14]

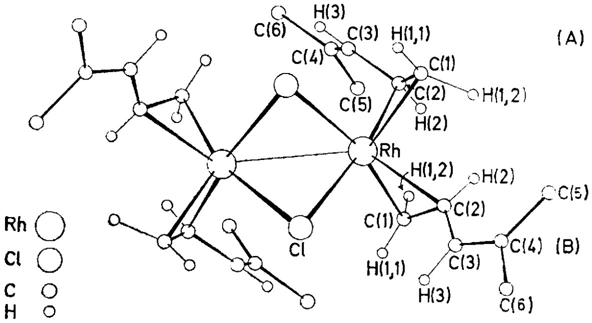

FIGURE 1 A view of the molecule projected down the two-fold axis

The Rh–Cl bond lengths are equivalent: 2·410(3) and 2·402(3) Å and similar to those in bent bridges [2·33, 2·38,[10] 2·39,[11] and 2·35 Å (ref. 9)], and also to terminal Rh–Cl bond lengths in molecules such as $Rh(C_2F_4)(PPh_3)_2Cl$ (2·374 Å), $Rh(PPh_3)_3Cl$ (2·370 Å),[15] and $Rh(PPh_3)_2(CS)Cl$ (2·386 Å).[16] In the planar $RhCl_2Rh$ bridge Rh–Cl is 2·38 Å.[13]

Although 4-methylpenta-1,3-diene can act as a bidentate ligand, having both double bonds co-ordinated, as in *e.g.* π-cyclopentadienyl-(4-methylpenta-1,3-diene)-rhodium(I),[5] in the present molecule each rhodium atom is bonded to only one olefinic group [C(1)–C(2)] of two ligands. Possible explanations as to why the conjugated diene should exhibit unidentate rather than bidentate behaviour in the present molecule are given in ref. 5. The environment of each rhodium atom is shown in Figure 2 which is a projection of half the dimer on the plane of the three atoms Rh, Cl, and Cl^{I}. In both diolefins (A) and (B), the mid-point of

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* For details, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. Items less than 10 pp. are sent as full-sized copies.

[9] Quoted in ref. 12.

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the C(1)–C(2) bond, designated C(0), is almost coplanar (mean deviation 0·025 Å) with the atoms Rh, Cl, and Cl^{I}. Thus, the rhodium atom can be considered four-co-ordinate [bonded to Cl, Cl^{I}, C(0A) and C(0B)] with a square-planar environment. Of the angles subtended by pairs of adjacent atoms, the $Cl–Rh–Cl^{I}$ angle is less [81·45(7)°] than, while the other three are greater than, 90°. The dienes are approximately planar and perpendicular to the Rh ··· C(0) vectors (however, *vide infra*).

In previously investigated square-planar rhodium(I) complexes containing co-ordinated ethylene, namely $Rh(C_2H_4)_2(C_5H_7O_2)$, $Rh(C_2H_4)(C_2F_4)(C_5H_7O_2)$,[17] and $Rh(C_2H_4)(C_2F_4)(C_5H_5)$,[18] the Rh–C bond lengths are equivalent and the C–C bond is approximately perpendicular to the co-ordination square plane. This geometry also occurs in complexes of symmetrically substituted ethylenes such as cyclo-octa-1,5-diene [11,13] and appears to be the most stable configuration for mono-olefin complexes. In the present molecule, however, the co-ordinated C–C bonds are twisted in two directions and the Rh–C bond lengths are significantly different.

First, the C–C bond is rotated about C(0) to bring C(1) closer to the metal atom than C(2), the angles Rh–C(0)–C(1) and Rh–C(0)–C(2) being equivalent in the two ligands at 88·1 and 91·9°, respectively. Consequently, the Rh–C(1) bonds are shorter than the Rh–C(2) bonds.* Thus, Rh–C(1A) is 2·120(9), Rh–C(1B) 2·121(11), Rh–C(2A) 2·161(9), and Rh–C(2B) 2·165(10) Å. The reason for this distortion is probably steric in origin in that thereby the H(2) atoms are pulled away from the H(1,2) atoms, increasing the contacts to 1·96(14) for H(1A,2) ··· H(2B) and 1·95(12) Å for H(1B,2) ··· H(2A), distances still well below the sum of van der Waals' radii (2·40 Å).

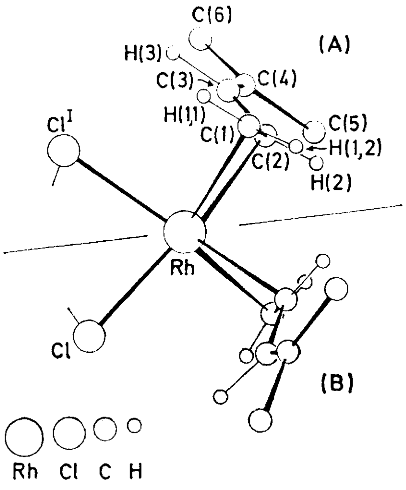

FIGURE 2 The asymmetric unit, showing the square planar co-ordination of the rhodium atom. A projection of the half-dimer on the Rh, Cl, Cl^{I} plane. The line represents an approximate C_2 axis (see text)

Secondly, the C(1)–C(2) bonds are further twisted about C(0) in a direction which is approximately perpendicular to the Rh–C(0) vectors to decrease the C(0A)–Rh–C(0B)–C(2B) and C(0B)–Rh–C(0A)–C(2A) dihedral angles from 90° (the expected value in a symmetric arrangement) to 77·9 and 77·2°. The reason for this rotation can be deduced from inspection of the intramolecular contacts (Table 4). The short H(2) ··· H(1,2) contacts mentioned earlier ensure that the C(3) atoms are *trans* to H(1,2) in both ligands. However, if the dihedral angles C(0)–Rh–C(0)–C(2) were 90°, each pair of C(3), H(3) atoms would be very close to one of the bridging chlorine atoms [Cl for ligand (B), and Cl^{I} for ligand (A)]. The rotation of *ca.* 13° in the dihedral angle increases the Cl ··· H(3) distances so that they are comparable with the Cl ··· H(1,1) contacts. Thus, Cl ··· H(3B) 2·94(10), Cl ··· H(1B,1) 2·77(9), Cl^{I} ··· H(3A) 2·86(12), and Cl^{I} ··· H(1A,1) 2·61(7) Å. Both ligands must rotate by roughly the same amount otherwise the H(1,2) ··· H(2) contacts are decreased.

TABLE 5

Intermolecular distances < 4·0 Å *

C(6B) ··· Rh^{II}	3·86	C(4B) ··· $C(5A^{III})$	3·80
C(6B) ··· $C(1A^{II})$	3·85	C(3A) ··· Cl^{IV}	3·93
C(6B) ··· $C(4B^{II})$	3·73	C(2A) ··· $C(6B^{IV})$	3·76
C(6B) ··· $C(5B^{II})$	3·77	C(1A) ··· $C(3B^{IV})$	3·76
C(2B) ··· $C(5A^{III})$	3·74	C(6B) ··· Cl^{V}	3·96
C(3B) ··· $C(5A^{III})$	3·64	C(5B) ··· $C(6A^{V})$	3·79

* Roman numerals as superscripts refer to an atom in the following equivalent positions relative to the reference molecule (Table 1) at *x*, *y*, *z*:

I $1 - x, y, \frac{1}{2} - z$
II $1\frac{1}{2} - x, 1\frac{1}{2} - y, \frac{1}{2} - z$
III $1\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$
IV $\frac{1}{2} + x, 1\frac{1}{2} - y, z$
V $1\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$

The rotations of the C(1)–C(2) bonds do not appear to weaken the rhodium–olefin bond significantly as the mean Rh–C distance (2·14 Å) is comparable with those found in related compounds containing rhodium–ethylene bonds: 2·19(1) (ref. 17) and 2·167(2) Å,[18] and rhodium–1,5-cyclo-octadiene bonds 2·10(2) (ref. 11) and 2·12(3) Å.[13]

The C(1)–C(2) bonds are equivalent [1·392(14) and 1·391(13) Å] and may be compared with values of 1·358(9),[18] 1·41(3),[19] 1·42(2),[11] and 1·44(7) Å [13] found for co-ordinated double bonds in related systems. Variations in magnitude have been attributed to differing *trans*-effects of the counter ligands involved. As expected the un-co-ordinated C(3)–C(4) bonds of the present molecule are considerably shorter [1·323(13) and 1·330(13) Å] and closer in value to that in ethylene [1·337(2) Å].[19]

In discussions of the nature of metal–olefin bonds,

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* Where a statement is applicable to equivalent atoms in both ligands, A and B are omitted from the atom numbers.

[17] J. A. Evans and D. R. Russell, *Chem. Comm.*, 1971, 197.

[18] L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.* 1972, **94**, 3779.

[19] L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, jun., *J. Chem. Phys.*, 1965, **42**, 2683.

particular significance attaches to the degree to which olefin substituents are bent back out of the plane containing the olefin bond and which is perpendicular to the co-ordination plane of the metal. It appears to be generally accepted that in most metal–ethylene bonds the olefin–metal σ-bonding and metal–olefin π-bonding make approximately equal contributions.[20,21] Electronegative substituents such as fluorine enhance the latter at the expense of the former leading to an approach to a ' tetrahedral ' geometry for the olefinic carbon atoms, the limit of which is a ' metallocyclopropane ' bonding model.[18] Crystallographic studies have shown that in Rh–C_2F_4 bonds, the fluorine atoms are bent back by 0·44 in $Rh(C_2F_4)(PPh_3)_2Cl$,[15] and by 0·49 Å in $Rh(C_2H_4)(C_2F_4)(C_5H_5)$; [18] yet in Rh–$C_2H_4$ bonds the bending back of the hydrogen atoms is much less, 0·18 Å in the latter molecule.[18]

TABLE 6

Equations of least-squares planes in the form $Ax + By + Cz = D$, where x,y,z are the crystallographic fractional co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets

	A	*B*	*C*	*D*
Plane (1): Rh, Cl^I, Cl	7·58	10·26	0·82	9·76
[C(0A) −0·03, C(0B) 0·02, C(1A) 0·65, C(1B) −0·65, C(2A) −0·71, C(2B) 0·70]				
Plane (2): C(1A)—(6A)	6 21	−3·10	11·07	7·44
[C(1A) 0·08, C(2A) −0·08, C(3A) −0·05, C(4A) 0·01, C(5A) 0·03, C(6A) 0·02, H(1A,1) −0·01, H(1A,2) 0·34, H(2A) 0·01, H(3A) −0·21]				
Plane (3): C(1B)—(6B)	11·22	−6·70	−8·35	3·11
[C(1B) 0·09, C(2B) −0·07, C(3B) −0·08, C(4B) −0·02, C(5)B 0·03, C(6B) 0·05, H(1B,1) 0·16, H(1B,2) 0·40, H(2B) 0·15, H(3B) −0·22]				
Plane (4): Rh, C(1A), C(2A)	13·87	−2·35	−8·66	4·75
Plane (5): Rh, C(1B), C(2B)	3·15	−6·95	10·60	1·61
Plane (6): * C(1A), C(2A)	1·02	−4·19	12·84	4·21
[Rh −2·02, C(0A) 0·00, C(3A) 0·24, C(4A) 0·46, C(5A) 0·46, C(6A) 0·68, H(1A,1) −0·06, H(1A,2) 0·09, H(2A) 0·08, H(3A) 0·12]				
Plane (7): * C(1B), C(2B)	−13·82	4·61	6·94	−6·02
[Rh −2·02, C(0B) 0·00, C(3B) 0·28, C(4B) 0·52, C(5B) 0·48, C(6B) 0·87, H(1A,1) 0·15, H(1A,2) 0·10, H(2B) 0·12, H(3B) 0·25]				

* Planes (6) and (7) are further defined by being perpendicular to planes (4) and (5) respectively (see text).

Angles (°) between planes:

(1)–(2)	81·1	(1)–(3)	79·6	(1)–(4)	77·3
(1)–(5)	76·3	(4)–(5)	89·4	(2)–(4)	84·3
(3)–(5)	80·7				

In the present molecule the C(1)–C(2) bonds are not perpendicular to the co-ordination square plane and therefore we have defined planes [(6) and (7), Table 6] which contain atoms C(1) and C(2) and are perpendicular to the Rh,C(1),C(2) planes [(4) and (5), Table 6]. Distances from planes (6) and (7) are therefore a measure of the extent to which the olefin substituents are bent back. Of the six hydrogen atoms, the mean distance from a plane is 0·08 Å (a positive distance represents the side of the plane opposite to the rhodium atom). In view of the standard deviations of the hydrogen positional parameters this is not significant. The C(3) atoms are bent back significantly (mean 0·26 Å) in both ligands. As C(3) is almost coplanar with atoms C(4)—(6) (mean deviation 0·01 Å) this results in these last three atoms being displaced further from planes (6) and (7) by 0·46—0·87 Å, thereby increasing the intramolecular contacts across the two-fold axis. Thus, the appreciable displacement of C(3) from planes (6) and (7) may be largely a result of relief of steric strain. There is no evidence therefore that the relative importance of σ- and π-bonding contributions in this compound is any different from that in rhodium–ethylene bonds.*

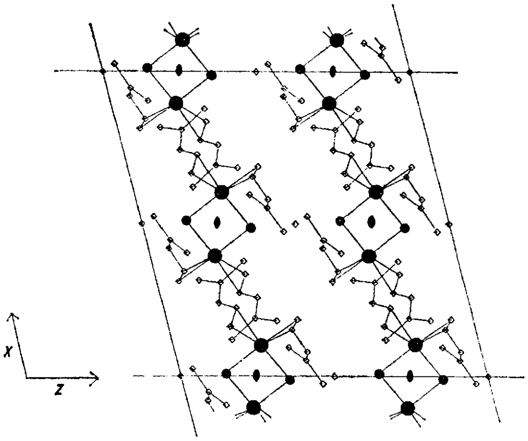

FIGURE 3 The unit cell in the *b* projection

The remaining dimensions of the two ligands are quickly considered. Least-squares planes calculated for the six carbon atoms in each ligand (Table 6) show that the maximum deviation of a carbon atom is only 0·09 Å. These planes intersect the Rh, C(1), C(2) planes at angles of 84·3° (A) and 80·7° (B). The dimensions of both ligands are similar. The C(2)–C(3) bonds are 1·458(13) and 1·452(14) Å as expected for C–C single bonds in =C–C= environments which the C(4)–C(5) and C(4)–C(6) bonds (mean 1·487 Å) are typical for C–C single bonds in =C–C environments.[22] The C–H bond lengths are all within 2σ of the expected values.

The Rh–C(2)–C(3) angles (mean 111°) are larger than the Rh–C(1)–H and Rh–C(2)–H angles (mean 103°)

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* We have calculated values of α and β following the convention of J. K. Stalick and J. A. Ibers (*J. Amer. Chem. Soc.*, 1970, **92**, 5333); α is the angle between the normal to the plane containing atoms C(1), H(1,1), and H(1,2) and the normal to the plane containing atoms C(2), H(2), and C(3); β is the angle between plane (6) [or (7)] and the normals to the planes containing atoms C(1), H(1,1), and H(1,2), or atoms C(2), H(2), and C(3). In the present molecule these angles are α: 15, 36° and β: 74, 64, 85, and 70° (for 1A, 2A, 1B, and 2B respectively). These values are comparable with those found for Rh–C_2H_4 bonds, a full set of which are given in ref. 18.

[20] M. J. S. Dewar, *Bull. Chem. Soc. Japan*, 1951, **18**, 279.

[21] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.

[22] *Chem. Soc. Special Publ.*, No. 11, 1958.

giving further indication that the C(3) atom is bent back from the C(1)–C(2) bond by a larger amount than are the hydrogen atoms. C–C–C Angles tend to be larger than C–C–H and H–C–H angles; mean values of C(1)–C(2)–C(3) and C(2)–C(3)–C(4) in the two ligands are 123·5 and 127·5° respectively.

Of the angles subtended at C(4) by pairs of carbon atoms, the C(5)–C(4)–C(6) angles are significantly the smallest by *ca.* 5°, due, presumably, to ligand–ligand repulsions between the C(5) and C(6) atoms and the remainder of the diene. The C–C–H angles are not sufficiently accurate to merit detailed discussion although all are within 2σ of expected values.

The two diolefin ligand have approximately the same configuration, with the minor differences which have been noted. There is therefore an approximate two-fold axis running through half the dimer (Figure 2) from the rhodium atom through the mid-point of the C(0A) ··· C(0B) vector. The minor configurational differences that do exist are presumably dictated by intra- and inter-molecular interactions. The shortest contacts are given in Table 5. The only C ··· C^{I} contacts of note, across the two-fold axis, are C(1B) ··· C($3A^{I}$) (3·84 Å) and C(1B) ··· C($4A^{I}$) (3·94 Å), but as these distances are comparable with the shortest intermolecular C–C contacts they are not particularly significant. The packing diagram of the molecules is shown in Figure 3 in the *b* projection.

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