

Reactions of Co-ordinated Ligands. Part 25.¹ The Synthesis of μ -Allene-dicarbonylbis(η^5 -indenyl)dirhodium and Protonation to Form a Bridged Cationic Vinyl Complex; Molecular Structures of μ -Allene-dicarbonylbis(η^5 -indenyl)dirhodium and Dicarbonyl-bis(η^5 -indenyl)- μ -(1-methylvinyl)-dirhodium(*Rh*—*Rh*) Tetrafluoroborate

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Reaction (60 °C) of tri- μ -carbonyl-tris(η^5 -indenyl)-*triangulo*-trirhodium with allene in toluene as solvent affords μ -allene-(dicarbonyl)bis(η^5 -indenyl)dirhodium. An X-ray crystallographic study was carried out on this complex. Crystals are triclinic, space group $P\bar{1}$, in a unit cell of dimensions $a = 12.148(5)$, $b = 10.682(5)$, $c = 9.620(5)$ Å, $\alpha = 115.84(3)$, $\beta = 121.09(4)$, $\gamma = 82.25(4)^\circ$, and $Z = 2$. The structure has been refined to R 0.024 (R' 0.026) for 5 027 unique reflections to $2\theta \leq 60.0^\circ$. The allene group bridges the metal atoms, which are not bonded [$Rh(1) \cdots Rh(2)$ 3.711(1) Å]. Reaction of this complex with $HBF_4 \cdot Et_2O$ affords in high yield the cationic species dicarbonylbis(η^5 -indenyl)- μ -(1-methylvinyl)-dirhodium tetrafluoroborate, which was identified by X-ray crystallography. Crystals are monoclinic, space group $P2_1/n$, in a unit cell of dimensions $a = 13.851(5)$, $b = 15.207(6)$, $c = 12.652(3)$ Å, $\beta = 110.62(2)^\circ$, and $Z = 4$. The structure has been refined to R 0.036 (R' 0.039) for 4 932 reflections at 240 K to $2\theta \leq 60^\circ$. Protonation has occurred at an end carbon atom of the allene to form $[Rh_2(\mu-CO)(CO)\{\mu-C(Me)=CH_2\}(\eta^5-C_9H_7)_2][BF_4]$ with a Rh—Rh bond length of 2.693(1) Å.

THERE is currently considerable interest in the reactions of organic molecules co-ordinated to two or more metal centres.² Although protonation of the mononuclear complex tetracarbonyl(tetramethylallene)iron has been shown³ to form a cationic η^3 -allylic complex *via* attack on the central carbon atom, mechanistic considerations suggested that an alternative reaction path might be followed with a system in which an allene molecule bridges two metal centres. At the start of this investigation there was one example of a dinuclear complex containing a bridging allene, the compound $[Rh_2(CO)_2(C_3H_4)(acac)_2]$ (*acac* = acetylacetonate),⁴ and during the course of our studies Group 6 complexes μ -allene-tetracarbonylbis(cyclopentadienyl)-molybdenum or -tungsten were reported.^{5,6} Rather than attempt to examine the protonation of these known molecules we chose to initially study the reaction of allene with tri- μ -carbonyl-tris(η^5 -indenyl)-*triangulo*-trirhodium⁷ in the belief that this would lead to a molecule containing a μ -allene system more suitable for protonation studies.

RESULTS AND DISCUSSION

An excess of allene was bubbled for 1 h through a solution (60 °C) of $[Rh_3(\mu-CO)_3(\eta^5-C_9H_7)_3]$ in toluene as solvent. The resulting clear yellow solution was filtered and chromatographed to afford (60% yield) a yellow crystalline complex (1), which on the basis of elemental analysis, mass spectroscopy, i.r., and n.m.r. spectroscopy was assigned the molecular formula $[Rh_2(CO)_2(C_3H_4)(\eta^5-C_9H_7)_2]$. However, it proved difficult to unequivocally establish the structure of this molecule on the basis of the complex temperature-dependent n.m.r. spectra, and therefore, a single crystal X-ray diffraction study was undertaken.

The molecular structure of (1) is shown in Figure 1, the

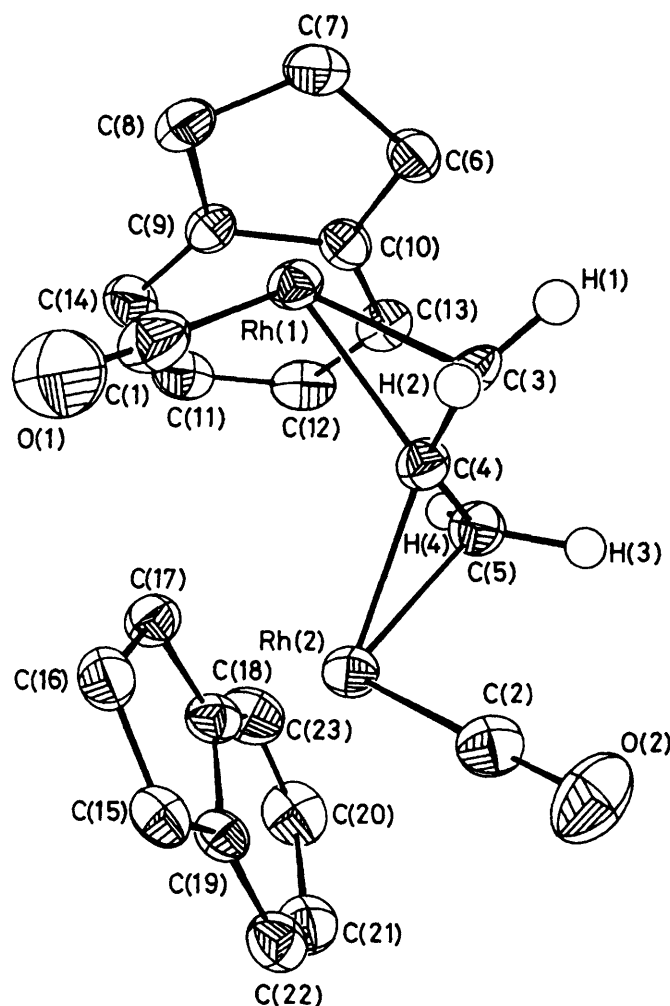


FIGURE 1 Molecular structure of $[Rh_2(CO)_2(C_3H_4)(\eta^5-C_9H_7)_2]$ (1) with 50% thermal ellipsoids for non-hydrogen atoms

positional parameters of the atoms, and the interatomic distances and angles being listed in Tables 1 and 2.

The X-ray diffraction analysis confirms the chemical identity of the crystals as $[\text{Rh}_2(\text{CO})_2(\text{C}_3\text{H}_4)(\eta^5\text{-C}_9\text{H}_7)_2]$. The allene group bridges the metal atoms, which are not bonded to one another $[\text{Rh}(1) \cdots \text{Rh}(2) \text{ } 3.711(1) \text{ \AA}]$.

TABLE 1

Final atomic positions (fractional co-ordinates) for $[\text{Rh}_2(\text{CO})_2(\text{C}_3\text{H}_4)(\eta^5\text{-C}_9\text{H}_7)_2]$ (1) *

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Rh(1)	0.289 3(1)	0.381 0(1)	0.124 2(1)
Rh(2)	0.219 4(1)	0.005 6(1)	−0.008 3(1)
O(1)	0.029 2(2)	0.362 3(3)	0.077 7(4)
O(2)	0.314 6(2)	−0.016 9(3)	0.303 4(3)
C(1)	0.126 4(3)	0.365 3(3)	0.087 0(4)
C(2)	0.277 1(2)	−0.037 1(3)	0.182 8(3)
C(3)	0.365 7(3)	0.304 7(3)	0.325 5(3)
C(4)	0.341 0(2)	0.197 0(2)	0.160 7(3)
C(5)	0.408 0(2)	0.096 4(2)	0.093 2(3)
C(6)	0.474 3(2)	0.479 9(2)	0.192 9(3)
C(7)	0.389 3(3)	0.584 0(2)	0.202 1(3)
C(8)	0.274 4(2)	0.540 0(2)	0.029 6(3)
C(9)	0.297 8(2)	0.417 4(2)	−0.095 9(3)
C(10)	0.422 2(2)	0.381 6(2)	0.007 5(3)
C(11)	0.274 7(3)	0.223 9(3)	−0.363 3(3)
C(12)	0.396 7(3)	0.190 9(3)	−0.263 2(4)
C(13)	0.471 8(2)	0.266 6(3)	−0.078 5(3)
C(14)	0.222 2(3)	0.335 4(3)	−0.282 4(3)
C(15)	0.021 2(2)	−0.106 8(3)	−0.201 9(3)
C(16)	0.017 7(2)	0.025 8(3)	−0.202 6(3)
C(17)	0.100 1(3)	0.033 3(3)	−0.264 0(3)
C(18)	0.139 1(2)	−0.105 3(2)	−0.329 1(3)
C(19)	0.090 6(2)	−0.192 3(2)	−0.289 9(3)
C(20)	0.225 0(3)	−0.300 3(3)	−0.470 4(4)
C(21)	0.178 6(3)	−0.387 4(3)	−0.430 1(4)
C(22)	0.113 9(2)	−0.334 1(3)	−0.338 1(3)
C(23)	0.208 0(3)	−0.161 1(3)	−0.418 7(4)
H(1)	0.324(4)	0.310(5)	0.360(6)
H(2)	0.450(5)	0.360(6)	0.421(6)
H(3)	0.420(3)	0.088(3)	−0.010(4)
H(4)	0.489(3)	0.068(4)	0.192(4)
H(5)	0.561	0.474	0.307
H(6)	0.409	0.683	0.317
H(7)	0.187	0.590	−0.003
H(8)	0.226	0.169	−0.508
H(9)	0.435	0.103	−0.328
H(10)	0.562	0.232	−0.003
H(11)	0.124	0.356	−0.357
H(12)	−0.017	−0.142	−0.144
H(13)	−0.037	0.107	−0.161
H(14)	0.133	0.124	−0.262
H(15)	0.272	−0.349	−0.548
H(16)	0.192	−0.497	−0.473
H(17)	0.094	−0.392	−0.284
H(18)	0.247	−0.094	−0.444

* Estimated standard deviations are in parentheses in Tables throughout this paper.

Each rhodium atom is co-ordinated to one pentahapto indenyl ligand, and a terminally bonded carbonyl group. The carbonyl groups on alternate metal atoms may be considered *gauche* to one another [the torsion angle $\text{C}(1)\text{--Rh}(1)\text{--Rh}(2)\text{--C}(2)$ is 92.7°]; this geometric relationship between the two rhodium centres is transferred through the bridging allene unit.

The bonding of the allene moiety to the metal atoms is similar to that reported for $[\text{Mo}_2(\text{CO})_4(\text{C}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)]$,⁶ $[\text{Rh}_2(\text{CO})_2(\text{C}_3\text{H}_4)(\text{acac})_2]$,⁴ and $[\text{Mn}_2(\text{CO})_3(\text{C}_3\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)_2]$.⁸ It is most usefully represented as two independent 'alkene'-metal bonds with a common carbon atom, C(4). The interplanar angle of 89.9° between the

planes defined by $\text{Rh}(2), \text{C}(4), \text{C}(5)$ and $\text{Rh}(1), \text{C}(3), \text{C}(4)$ demonstrates the metal interaction with the orthogonal π orbitals of the allene system. The carbon-carbon bond lengths in the allene group are significantly longer [$1.393(2) \text{ \AA}$] than those observed⁹ in unco-ordinated allene fragments ($1.29\text{--}1.36 \text{ \AA}$). This is a result of metal→ligand back-donation into the π^* orbitals of the unsaturated system, and parallels observations made for

TABLE 2

Interatomic distances (Å) and angles ($^\circ$) for complex (1)

(a) Distances

Rh(1)–Rh(2)	3.711(1)	Rh(2)–C(17)	2.253(2)
Rh(1)–C(1)	1.837(3)	Rh(2)–C(18)	2.428(2)
Rh(1)–C(3)	2.143(3)	Rh(2)–C(19)	2.403(2)
Rh(1)–C(4)	2.103(2)	C(1)–O(1)	1.141(3)
Rh(1)–C(6)	2.259(2)	C(2)–O(2)	1.145(3)
Rh(1)–C(7)	2.257(2)	C(3)–C(4)	1.393(3)
Rh(1)–C(8)	2.200(2)	C(4)–C(5)	1.393(3)
Rh(1)–C(9)	2.366(2)	C(3)–H(1)	0.72(5)
Rh(1)–C(10)	2.399(2)	C(3)–H(2)	0.98(5)
Rh(2)–C(2)	1.842(3)	C(5)–H(3)	1.04(3)
Rh(2)–C(4)	2.108(2)	C(5)–H(4)	1.08(3)
Rh(2)–C(5)	2.147(2)	C(6)–C(7)	1.417(3)
Rh(2)–C(15)	2.215(2)	C(7)–C(8)	1.424(3)
Rh(2)–C(16)	2.242(2)	C(8)–C(9)	1.459(3)
C(9)–C(10)	1.429(3)	C(17)–C(18)	1.455(3)
C(10)–C(6)	1.438(3)	C(18)–C(19)	1.426(3)
C(10)–C(13)	1.409(3)	C(19)–C(15)	1.455(3)
C(13)–C(12)	1.384(4)	C(18)–C(23)	1.400(3)
C(12)–C(11)	1.390(4)	C(23)–C(20)	1.371(4)
C(11)–C(14)	1.389(4)	C(20)–C(21)	1.419(4)
C(14)–C(9)	1.406(3)	C(21)–C(22)	1.373(4)
C(15)–C(16)	1.414(4)	C(22)–C(19)	1.414(3)
C(16)–C(17)	1.425(4)		

(b) Angles

Rh(1)–C(4)–Rh(2)	142.5(1)	C(13)–C(12)–C(11)	121.9(2)
C(1)–Rh(1)–C(3)	90.5(1)	C(12)–C(11)–C(14)	121.4(2)
C(1)–Rh(1)–C(4)	95.0(1)	C(11)–C(14)–C(9)	118.1(2)
C(3)–Rh(1)–C(4)	38.3(1)	C(14)–C(9)–C(10)	120.4(2)
C(2)–Rh(2)–C(4)	91.6(1)	C(15)–C(16)–C(17)	107.9(2)
C(2)–Rh(2)–C(5)	92.9(1)	C(16)–C(17)–C(18)	108.0(2)
C(4)–Rh(2)–C(5)	38.2(1)	C(17)–C(18)–C(19)	107.5(2)
Rh(1)–C(1)–O(1)	174.7(3)	C(18)–C(19)–C(15)	107.2(2)
Rh(1)–C(3)–C(4)	69.3(1)	C(19)–C(15)–C(16)	108.5(2)
Rh(1)–C(4)–C(3)	72.4(1)	C(18)–C(19)–C(22)	120.3(2)
Rh(2)–C(2)–O(2)	178.9(2)	C(19)–C(22)–C(21)	118.6(2)
Rh(2)–C(4)–C(5)	72.4(1)	C(22)–C(21)–C(20)	120.6(2)
Rh(2)–C(5)–C(4)	69.4(1)	C(21)–C(20)–C(23)	121.8(3)
C(3)–C(4)–C(5)	137.8(2)	C(20)–C(23)–C(18)	118.7(3)
C(6)–C(7)–C(8)	108.2(2)	C(23)–C(18)–C(19)	120.0(2)
C(7)–C(8)–C(9)	107.6(2)	C(4)–C(3)–H(1)	121.1(3.7)
C(8)–C(9)–C(10)	107.0(2)	C(4)–C(3)–H(2)	124.3(2.7)
C(9)–C(10)–C(6)	108.0(2)	H(1)–C(3)–H(2)	111.5(4.2)
C(10)–C(6)–C(7)	108.2(2)	C(4)–C(5)–H(3)	123.3(1.6)
C(9)–C(10)–C(13)	120.0(2)	C(4)–C(5)–H(4)	114.5(1.6)
C(10)–C(13)–C(12)	118.2(2)	H(3)–C(5)–H(4)	114.0(2.2)

co-ordinated alkenes (*e.g.* ref. 10). The three allenic carbons are no longer arranged in a linear manner as in the free allene, the angle $\text{C}(3)\text{--C}(4)\text{--C}(5)$ [$137.8(2)^\circ$] representing a partial loss of *sp* character for the central carbon atom on co-ordination. As expected, there is also back-bonding at the terminal carbon atoms such that C(4) is now displaced out of the plane defined by C(3), H(1), H(2) by 0.39 \AA , and out of the plane defined by C(5), H(3), H(4) by 0.64 \AA (see Table 3). The net effect of the orthogonal co-ordination of the allene group is to require it to lie partly across the metal-metal vector such that the dihedral angle between the planes defined by $\text{Rh}(1), \text{Rh}(2), \text{C}(4)$ and $\text{C}(3), \text{C}(4), \text{C}(5)$ is 55.5° (Table 3).

TABLE 3

Planes of best fit for complex (1)

Plane (1): C(6)—C(14) Indenyl ligand

$$8.205X + 0.617Y - 7.032Z = 6.7215$$

Atom	Deviations (Å) from plane
C(6)	-0.051
C(7)	0.084
C(8)	-0.025
C(9)	-0.007
C(10)	-0.022
C(11)	0.016
C(12)	0.029
C(13)	-0.001
C(14)	-0.023

Plane (2): C(15)—C(23) Indenyl ligand

$$5.301X - 0.807Y + 4.925Z = -0.826$$

C(15)	0.031
C(16)	-0.098
C(17)	0.030
C(18)	0.028
C(19)	0.034
C(20)	-0.055
C(21)	-0.032
C(22)	0.035
C(23)	0.028

Plane (3): Rh(1), C(3), C(4)

$$11.727X + 2.608Y - 3.462Z = 3.956$$

Plane (4): Rh(2), C(4), C(5)

$$-1.394X - 6.669Y + 8.555Z = -0.414$$

Plane (5): C(3), C(4), C(5)

$$6.823X + 9.315Y - 7.110Z = 3.019$$

Plane (6): Rh(1), Rh(2), C(1)

$$-1.721X - 2.749Y + 8.695Z = -0.465$$

Plane (7): Rh(1), Rh(2), C(2)

$$11.852X - 0.875Y - 3.774Z = 2.627$$

Plane (8): Rh(1), Rh(2), C(4)

$$-9.8591X - 1.1129Y + 8.3543Z = -2.2386$$

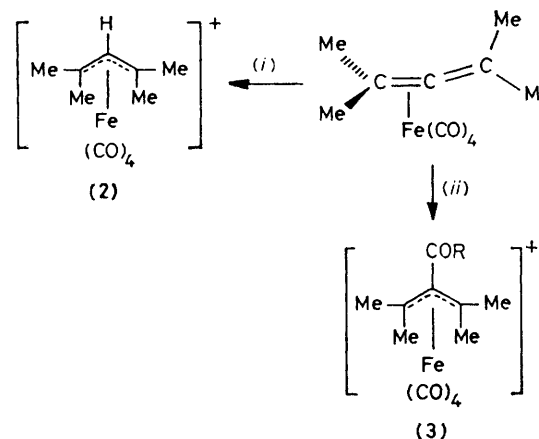
Angles (°) between planes

(1)–(2)	86.3	(3)–(5)	54.0
(1)–(3)	45.6	(3)–(6)	86.5
(1)–(4)	50.4	(3)–(7)	22.1
(1)–(5)	8.5	(3)–(8)	49.8
(1)–(6)	65.6	(4)–(5)	44.6
(1)–(7)	60.2	(4)–(6)	24.0
(1)–(8)	50.8	(4)–(7)	87.0
(2)–(3)	52.1	(4)–(8)	56.9
(2)–(4)	43.3	(5)–(6)	62.5
(2)–(5)	92.2	(5)–(7)	68.5
(2)–(6)	34.4	(5)–(8)	55.5
(2)–(7)	60.6	(6)–(7)	87.3
(2)–(8)	80.5	(6)–(8)	47.6
(3)–(4)	89.9	(7)–(8)	39.8

The geometries associated with the indenyl ligand are typical;^{11–17} the most significant deviation from planarity is the bending toward the metal of the carbon atoms furthest from the uncomplexed six-membered rings [C(7) and C(16)]. The metal atom is significantly closer to the three carbon atoms that are not part of the six-membered ring [Rh–C(average) 2.241(14) Å] than the two bridgehead carbon atoms [Rh–C(average) 2.399(18) Å].

As was noted in the introduction, tetracarbonyl-(tetramethylallene)iron rapidly reacts with HBF₄–acetic

anhydride or RCOCl–AlCl₃ (R = Me or Ph) to give tetracarbonyl(η³-allyl) cations (2) and (3) (Scheme 1), which on warming in acetone solution deprotonate forming tricarbonyl(1,3-diene)iron complexes.³

SCHEME 1 (i) HBF₄·(MeCO)₂O; (ii) RCOCl·AlCl₃

The availability of complex (1) containing Rh(CO)(η⁵-C₉H₇) fragments, which are isolobal with Fe(CO)₄, bonded to both alkenic groups of allene, therefore provided an opportunity to carry out a comparative study of the protonation reaction. Treatment of (1) with a molar equivalent of HBF₄–diethyl ether led to a rapid colour change and the formation of a red cationic species (4), which analysed as a 1 : 1 adduct. An X-ray diffraction study (see Tables 4–7) on a crystal of (4) obtained on slow crystallisation from methylene chloride–diethyl ether established the structure shown in Figures 2 and 3.

The crystal structure consists of the packing of discrete dinuclear molecules of formula [Rh₂(CO)₂(CH₃C=CH₂)(η⁵-C₉H₇)₂] together with BF₄ counter ions and disordered CH₂Cl₂ solvent molecules in the ratio 1 : 1 : 1. There are no significantly short intermolecular interactions.

The molecular geometry of the cation [Rh₂(CO)₂(CH₃C=CH₂)(η⁵-C₉H₇)₂]⁺ consists of two Rh(CO)(η⁵-C₉H₇) fragments linked by a metal–metal bond [2.693(1) Å] and bridged by a σ-bonded 1-methylvinyl group. The most useful formulation of this system regards the vinyl system as a substituted alkene side-bound to Rh(1), with the other metal atom Rh(2) a simple substituent at carbon atom C(1). The very small deviations of the atoms Rh(2), C(1), C(2), and C(3) from their plane of best fit (see Table 7) illustrates the sp² nature of C(1). The carbon–carbon double bond is lengthened from that of an uncomplexed alkene [C(1)–C(2) 1.402(8) Å]. Whilst in symmetrically bound alkenes there is a symmetric back-bending of the substituents on the carbon atoms, in this more strained species only one of the hydrogen atoms, H(1) at C(2), is deformed out-of-plane (0.34 Å, see Table 7) while the other hydrogen H(2) is not significantly affected (see Figure 3). The dihedral angle between the planes formed by atoms Rh(1), C(1), C(2) and Rh(2), C(1), C(2), C(3) is 111.7°

indicating that the rhodium atom lies considerably to one side of a normal from the plane defined by Rh(2), C(1), C(2), C(3) (see Figure 3). The imperfect orbital overlap that follows results in a slightly longer Rh(1)–C(2) distance, 2.223(5) Å, than is found (2.167 Å)¹⁰ in a normal alkene complex. The partial rehybridisation of C(2) towards sp^3 thus affects the substituent H(1) on the same side of the double bond considerably more than the remote hydrogen atom and this effect is

TABLE 4

Atomic positional parameters (fractional co-ordinates) for $[\text{Rh}_2(\text{CO})_2(\text{CH}_3\text{C}=\text{CH}_2)(\eta^5\text{-C}_9\text{H}_7)_2][\text{BF}_4]$ (4)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Rh(1)	0.163 47(2)	0.177 91(2)	0.087 05(3)
Rh(2)	0.348 45(2)	0.097 59(2)	0.151 09(2)
C(1)	0.311 0(4)	0.220 7(3)	0.189 2(4)
C(2)	0.252 1(4)	0.228 0(4)	0.259 0(5)
C(3)	0.356 7(5)	0.299 1(4)	0.155 0(6)
C(4)	0.183 3(4)	0.058 0(4)	0.129 8(4)
C(5)	0.380 2(4)	0.060 4(3)	0.304 2(4)
C(6)	−0.040 4(4)	0.277 5(5)	0.027 4(5)
C(7)	0.005 5(4)	0.294 2(5)	0.002 6(6)
C(8)	0.035 1(4)	0.151 5(4)	−0.071 5(5)
C(9)	0.094 3(3)	0.215 3(4)	−0.108 6(4)
C(10)	0.145 1(4)	0.211 2(4)	−0.187 0(4)
C(11)	0.195 7(4)	0.284 3(4)	−0.203 2(4)
C(12)	0.199 7(4)	0.361 2(4)	−0.141 6(5)
C(13)	0.150 7(4)	0.367 7(4)	−0.065 1(5)
C(14)	0.098 0(4)	0.294 4(4)	−0.046 6(4)
C(15)	0.491 9(3)	0.045 6(3)	0.140 5(4)
C(16)	0.471 1(3)	0.126 2(3)	0.079 5(4)
C(17)	0.374 3(3)	0.117 6(3)	−0.011 1(4)
C(18)	0.343 3(3)	0.026 0(3)	−0.011 0(4)
C(19)	0.258 0(4)	−0.019 6(3)	−0.091 9(4)
C(20)	0.248 3(4)	−0.106 7(4)	−0.071 5(5)
C(21)	0.317 5(5)	−0.150 1(3)	0.020 4(5)
C(22)	0.401 1(4)	−0.109 0(3)	0.097 0(4)
C(23)	0.414 2(3)	−0.018 3(3)	0.077 2(4)
O(1)	0.158 0(3)	−0.011 6(3)	0.139 4(4)
O(2)	0.403 8(3)	0.036 2(3)	0.392 9(3)
B(1)	0.163 1(5)	0.627 5(5)	0.866 7(6)
F(1)	0.076 4(3)	0.575 2(3)	0.855 2(3)
F(2)	0.215 3(4)	0.640 3(4)	0.977 9(4)
F(3)	0.126 5(4)	0.709 2(3)	0.820 1(5)
F(4)	0.219 1(4)	0.590 4(3)	0.810 5(5)
Cl(1)	−0.011 8(5)	0.155 0(5)	0.460 6(8)
Cl(2)	0.042 5(3)	0.023 1(6)	0.318 3(9)
Cl(3)	−0.021 9(4)	0.174 8(3)	0.387 6(7)
Cl(4)	0.006 3(3)	0.025 4(10)	0.306 2(11)
C(24)	0.037 3(10)	0.137 9(10)	0.355 9(12)
C(25)	0.044(2)	0.073 9(11)	0.439 2(14)
H(1)	0.246(4)	0.191(3)	0.307(4)
H(2)	0.230(4)	0.280(3)	0.276(4)
H(3)	0.349(5)	0.342(5)	0.178(6)
H(4)	0.374(4)	0.294(4)	0.112(5)
H(5)	0.417(4)	0.301(3)	0.198(4)

illustrated in Figure 3. These arguments are reinforced by a recent combined X-ray neutron diffraction study¹⁸ of the bridging vinyl complex $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{C}_2\text{H}_3)]$.

The metal–carbon bonds [Rh(1)–C(1) 2.099(4), Rh(2)–C(1) 2.046(4) Å] are short, resembling those found (average 2.105 Å) in the bridgehead carbon of the parent complex (1).

Each of the rhodium atoms in the molecule carries a carbonyl ligand. That attached at Rh(2) has a terminal geometry [Rh(2)–C(5) 1.915(5), C(5)–O(2) 1.115(6) Å, Rh(2)–C(5)–O(2) 175.8(5)°] while the other carbonyl ligand is semi-bridging [Rh(1)–C(4) 1.895(5), Rh(2)–C(4) 2.288(5), C(4)–O(1) 1.134(6) Å, Rh(1)–C(4)–O(1) =

155.4(4), Rh(2)–C(4)–O(1) 124.6(4)°]. With the positive charge localised at Rh(1), and counting the semi-bridging carbonyl as a two-electron donor to Rh(1), application of the 18-electron rule indicates that both metal atoms are saturated. The acceptor semi-bridging carbonyl group is presumably created to delocalise the positive charge.¹⁹

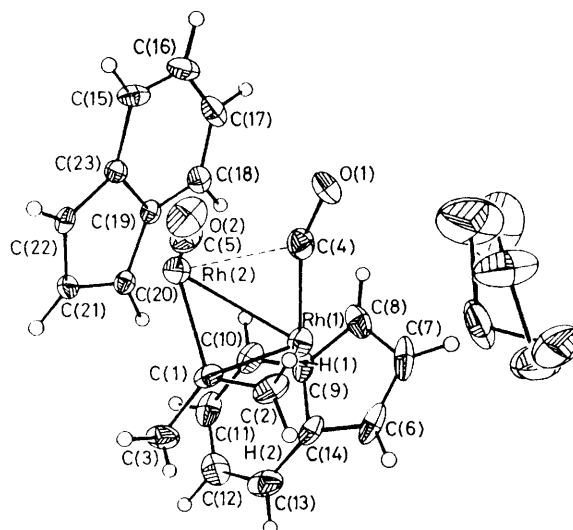


FIGURE 2 Molecular structure of $[\text{Rh}_2(\text{CO})_2(\text{CH}_3\text{C}=\text{CH}_2)(\eta^5\text{-C}_9\text{H}_7)_2][\text{BF}_4]$ (4) with 50% thermal ellipsoids (tetrafluoroborate anion omitted)

The η^5 -indenyl ligands complete the co-ordination spheres of the rhodium atoms and these are in a mutually *cis* orientation such that the angle between the planes is 50.8°. As with the parent compound the three terminal carbon atoms of the five-membered ring make considerably closer approaches (average 2.210 Å) to the rhodium atoms than the two bridgehead atoms (average 2.366 Å).

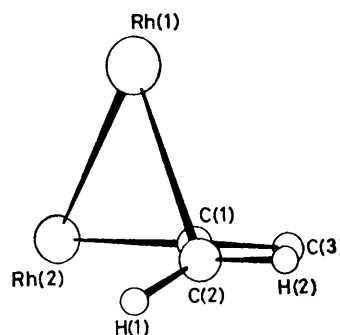
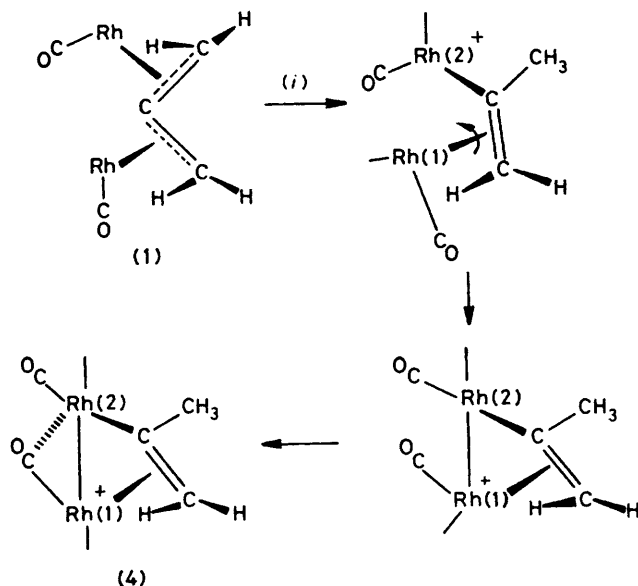


FIGURE 3 View along the alkene bond C(1)–C(2) of complex (4)

Reaction of (1) with $\text{CF}_3\text{CO}_2\text{D}$ resulted in the selective (^1H , ^{13}C , and ^2H n.m.r. spectra) incorporation of the deuterium into the methyl substituent of (4) indicating that the formation of the bridged vinyl cation does not involve a complex sequence of hydrogen-transfer reactions, and suggests that protonation occurs selectively on a terminal carbon atom of the bridged allene present in (1).

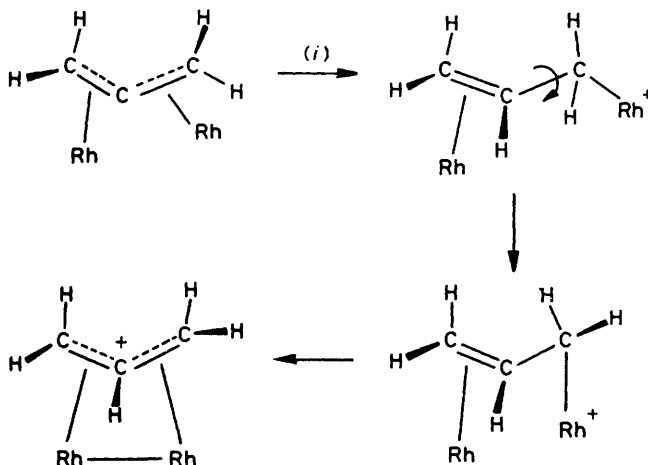
As is shown in Scheme 2, attack by a proton either *exo* or *endo* to the rhodium leads to the formation of a cationic species containing two rhodium centres with different oxidation states. The Rh(2) atom carrying a σ -vinyl substituent is in the oxidation state +3 and is a co-ordinatively unsaturated 16-electron centre. Intra-



SCHEME 2 (i) $\text{HBF}_4\text{-Et}_2\text{O}$; $\eta^5\text{-C}_9\text{H}_7$ ligands are omitted for clarity

molecular attack by the low-valent Rh(1) centre (oxidation state +1) on Rh(2) with concomitant rotation of the $\text{Rh}(\text{CO})(\eta^5\text{-C}_9\text{H}_7)$ fragment about an axis perpendicular to the C-C bond of the co-ordinated vinyl group then results in the formation of a metal-metal bond, and the transfer of the positive charge from Rh(2) to Rh(1). The charge is then delocalised by formation of an acceptor semi-bridging carbonyl system.

If electrophilic attack had occurred on the central carbon atom of the allene, as is observed with the mononuclear system, then as shown in Scheme 3 a



SCHEME 3 (i) $\text{HBF}_4\text{-Et}_2\text{O}$; C_9H_7 and CO ligands are omitted for clarity

bridged allyl system of the kind discovered by Werner and co-workers²⁰ would have been formed. There are no obvious pathways by which such a species could transform into a bridged σ -1-methylvinyl system, and we therefore conclude that co-ordination of an allene molecule to two adjacent metal centres results in a change in the reactivity pattern towards electrophiles.

TABLE 5

Bond lengths (Å) for complex (4)

Rh(1)-Rh(2)	2.693(1)	Rh(1)-C(1)	2.099(4)
Rh(1)-C(2)	2.223(5)	Rh(1)-C(4)	1.895(5)
Rh(1)-C(6)	2.205(5)	Rh(1)-C(7)	2.219(5)
Rh(1)-C(8)	2.199(4)	Rh(1)-C(9)	2.387(4)
Rh(1)-C(14)	2.396(5)	Rh(2)-C(1)	2.046(4)
Rh(2)-C(4)	2.288(5)	Rh(2)-C(5)	1.915(5)
Rh(2)-C(18)	2.356(4)	Rh(2)-C(17)	2.224(5)
Rh(2)-C(16)	2.230(5)	Rh(2)-C(15)	2.186(4)
Rh(2)-C(23)	2.326(4)	C(1)-C(2)	1.402(8)
C(1)-C(3)	1.484(8)	C(4)-O(1)	1.134(6)
C(5)-O(2)	1.115(6)	C(6)-C(7)	1.402(9)
C(6)-C(14)	1.451(8)	C(7)-C(8)	1.410(9)
C(8)-C(9)	1.450(8)	C(9)-C(10)	1.404(7)
C(9)-C(14)	1.428(7)	C(10)-C(11)	1.368(8)
C(11)-C(12)	1.395(8)	C(12)-C(13)	1.367(9)
C(14)-C(13)	1.396(7)	C(22)-C(21)	1.372(6)
C(21)-C(20)	1.387(6)	C(20)-C(19)	1.364(7)
C(18)-C(19)	1.415(5)	C(18)-C(17)	1.452(6)
C(18)-C(23)	1.413(5)	C(17)-C(16)	1.430(5)
C(16)-C(15)	1.422(6)	C(15)-C(23)	1.461(5)
C(23)-C(22)	1.424(6)	B(1)-F(1)	1.403(7)
B(1)-F(2)	1.350(7)	B(1)-F(3)	1.392(8)
B(1)-F(4)	1.347(9)		
C(24)-Cl(1)	1.71(2)	C(25)-Cl(3)	1.79(2)
C(24)-Cl(4)	1.82(2)	C(25)-Cl(2)	1.7(2)
C(2)-H(1)	0.85(6)	C(3)-H(4)	0.51(6)
C(2)-H(2)	0.90(5)	C(3)-H(5)	0.82(5)
C(3)-H(3)	0.74(9)		

TABLE 6

Interbond angles (°) for complex (4)

Rh(2)-Rh(1)-C(1)	48.6(1)	Rh(2)-Rh(1)-C(2)	73.9(1)
C(1)-Rh(1)-C(2)	37.7(2)	Rh(2)-Rh(1)-C(4)	56.7(1)
C(1)-Rh(1)-C(4)	96.4(2)	C(2)-Rh(1)-C(4)	94.4(2)
Rh(2)-Rh(1)-C(6)	162.4(2)	C(1)-Rh(1)-C(6)	117.7(2)
C(2)-Rh(1)-C(6)	101.1(2)	C(4)-Rh(1)-C(6)	140.9(2)
Rh(2)-Rh(1)-C(7)	157.9(2)	C(1)-Rh(1)-C(7)	153.5(2)
C(2)-Rh(1)-C(7)	124.0(2)	C(4)-Rh(1)-C(7)	105.5(2)
C(6)-Rh(1)-C(7)	37.0(2)	Rh(2)-Rh(1)-C(8)	124.7(2)
C(1)-Rh(1)-C(8)	156.5(2)	C(2)-Rh(1)-C(8)	161.1(2)
C(4)-Rh(1)-C(8)	94.3(2)	C(6)-Rh(1)-C(8)	62.2(2)
C(7)-Rh(1)-C(8)	37.2(2)	Rh(2)-Rh(1)-C(9)	114.3(1)
C(1)-Rh(1)-C(9)	120.8(2)	C(2)-Rh(1)-C(9)	144.6(2)
C(4)-Rh(1)-C(9)	119.3(2)	C(6)-Rh(1)-C(9)	60.2(2)
C(7)-Rh(1)-C(9)	60.2(2)	C(8)-Rh(1)-C(9)	36.6(2)
Rh(2)-Rh(1)-C(14)	129.1(1)	C(1)-Rh(1)-C(14)	104.4(2)
C(2)-Rh(1)-C(14)	112.2(2)	C(4)-Rh(1)-C(14)	153.4(2)
C(6)-Rh(1)-C(14)	36.5(2)	C(7)-Rh(1)-C(14)	60.3(2)
C(8)-Rh(1)-C(14)	60.5(2)	C(9)-Rh(1)-C(14)	34.8(2)
Rh(1)-Rh(2)-C(1)	50.4(1)	Rh(1)-Rh(2)-C(4)	43.8(1)
C(1)-Rh(2)-C(4)	86.7(2)	Rh(1)-Rh(2)-C(5)	107.1(1)
C(1)-Rh(2)-C(5)	91.1(2)	C(4)-Rh(2)-C(5)	84.6(2)
Rh(1)-Rh(2)-C(18)	102.4(1)	C(1)-Rh(2)-C(18)	134.8(2)
C(4)-Rh(2)-C(18)	93.4(2)	C(5)-Rh(2)-C(18)	134.0(2)
Rh(1)-Rh(2)-C(17)	96.1(1)	C(1)-Rh(2)-C(17)	103.2(2)
C(4)-Rh(2)-C(17)	114.0(2)	C(5)-Rh(2)-C(17)	156.8(2)
C(18)-Rh(2)-C(17)	36.8(1)	Rh(1)-Rh(2)-C(16)	124.7(1)
C(1)-Rh(2)-C(16)	102.1(2)	C(4)-Rh(2)-C(16)	151.2(2)
C(5)-Rh(2)-C(16)	122.1(2)	C(18)-Rh(2)-C(16)	60.8(1)
C(17)-Rh(2)-C(16)	37.5(1)	Rh(1)-Rh(2)-C(15)	159.2(1)
C(1)-Rh(2)-C(15)	131.1(2)	C(4)-Rh(2)-C(15)	142.2(2)
C(5)-Rh(2)-C(15)	93.7(2)	C(18)-Rh(2)-C(15)	61.2(1)
C(17)-Rh(2)-C(15)	63.1(1)	C(16)-Rh(2)-C(15)	37.6(2)
Rh(1)-Rh(2)-C(23)	133.5(1)	C(1)-Rh(2)-C(23)	163.0(2)
C(4)-Rh(2)-C(23)	105.7(2)	C(5)-Rh(2)-C(23)	101.5(2)

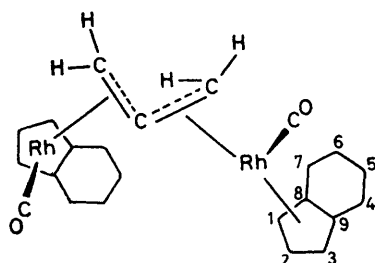
TABLE 6 (continued)

C(18)—Rh(2)—C(23)	35.1(1)	C(17)—Rh(2)—C(23)	61.3(2)
C(16)—Rh(2)—C(23)	61.5(2)	C(15)—Rh(2)—C(23)	37.6(1)
Rh(1)—C(1)—Rh(2)	81.0(1)	Rh(1)—C(1)—C(2)	75.9(3)
Rh(2)—C(1)—C(2)	118.2(3)	Rh(1)—C(1)—C(3)	119.5(3)
Rh(2)—C(1)—C(3)	119.8(4)	C(2)—C(1)—C(3)	121.5(5)
Rh(1)—C(2)—C(1)	66.4(2)	Rh(1)—C(4)—Rh(2)	79.5(2)
Rh(1)—C(4)—O(1)	155.4(4)	Rh(2)—C(4)—O(1)	124.6(4)
Rh(2)—C(5)—O(2)	175.8(5)	Rh(1)—C(6)—C(7)	72.0(3)
Rh(1)—C(6)—C(14)	78.9(3)	C(7)—C(6)—C(14)	109.0(5)
Rh(1)—C(7)—C(6)	71.0(3)	Rh(1)—C(7)—C(8)	70.6(3)
C(6)—C(7)—C(8)	108.0(6)	Rh(1)—C(8)—C(7)	72.2(3)
Rh(1)—C(8)—C(9)	78.8(2)	C(7)—C(8)—C(9)	108.1(5)
Rh(1)—C(9)—C(8)	64.6(2)	Rh(1)—C(9)—C(10)	127.1(3)
C(8)—C(9)—C(10)	132.9(5)	Rh(1)—C(9)—C(14)	72.9(2)
C(8)—C(9)—C(14)	107.5(4)	C(10)—C(9)—C(14)	119.6(5)
Cl(1)—C(24)—Cl(4)	107.5(9)	C(1)—C(3)—H(3)	118(7)
Cl(3)—C(25)—Cl(2)	102.6(9)	C(1)—C(3)—H(4)	103(7)
Rh(1)—C(2)—H(1)	108(3)	C(1)—C(3)—H(5)	106(4)
Rh(1)—C(2)—H(2)	115(3)	H(3)—C(3)—H(4)	121(9)
C(1)—C(2)—H(1)	128(4)	H(3)—C(3)—H(5)	88(6)
C(1)—C(2)—H(2)	123(4)	H(4)—C(3)—H(5)	122(8)
H(1)—C(2)—H(2)	107(5)		

EXPERIMENTAL

N.m.r. spectra (^1H and hydrogen-1 decoupled ^{13}C) were recorded on JEOL PFT, PS 100, and FX 90 Q spectrometers, with ^{13}C shifts relative to SiMe_4 (0.0 p.p.m.). Infrared spectra were obtained as Nujol mulls or in hexane solution on a Perkin-Elmer 457 spectrophotometer. Mass spectra were measured on an MS 902 spectrometer. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere, with solvents dried and distilled under nitrogen prior to use.

Reaction of Allene with Tri- μ -carbonyl-tris(η^5 -indenyl)-triangulo-trirrhodium.—An excess of allene (1 bubble per second) was passed through a solution of $[\text{Rh}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3]$ (0.40 g, 0.54 mmol) in toluene (100 cm^3) at 60 °C for 1 h. The solution changed from dark green to yellow. The volatile material was removed *in vacuo* and the residue dissolved in diethyl ether and chromatographed on an alumina packed column. Elution with hexane afforded $[\text{Rh}(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)]$, identified by ^1H n.m.r., i.r., and mass spectroscopy. Further elution with diethyl ether gave a yellow band which was recrystallised (–20 °C) from diethyl ether to afford yellow crystals of (1) (0.26 g, 60%) (Found: C, 51.7; H, 3.4. $\text{C}_{23}\text{H}_{18}\text{O}_2\text{Rh}_2$ requires C,



51.9; H, 3.4%); ν_{max} (hexane) at 2 003 cm^{-1} , ν_{max} (Nujol) at 3 040w, 3 020w, 1 970vs,br, 1 600w,br, 1 540w,br, 1 315m, 1 310m, 1 235w, 1 210m, 1 150w, 1 035m, 1 005w, 990m, 900w, 860w, 805s, 750s, 745s, 735w, and 600m cm^{-1} . The mass spectrum showed peaks at m/e 532 [P , 0.5%], 504 [$P - \text{CO}$, 5%], 436 [$(\text{RhC}_9\text{H}_7)_2$, 32%], 218 [RhC_9H_7 , 91%], and 115 [C_9H_7 , 100%]; ^1H n.m.r. ($[\text{C}_6\text{H}_6]$ toluene, –50 °C), τ 2.5–3.3 (complex, H^{4-7}), 4.1 [quartet, H^{1-3} , $J(\text{HH})$ 3], 4.45 (s, br H^{1-3}), 4.6 [d, H^{1-3} , $J(\text{HH})$ 3 Hz], 5.08 (s, br, H^{1-3}), 5.16 (s, br, H^{1-3}), 5.9 [s, br, H (allenic)],

6.65 [s, br, H (allenic)], 6.95 [s, br, H (allenic)], 7.5 [s, br, H (allenic)], and 8.1 [s, br, H (allenic)]; ^{13}C n.m.r. (CD_2Cl_2 , 30 °C), δ (p.p.m.) 124–118 (singlets, C^{4-9}), 100.2 (s, C^2), 99.9 (s, C^2), 95.9 (s, C^2), 82.2 (s, $\text{C}^{1,3}$), 78.6 (s, $\text{C}^{1,3}$), 77.4 (s, $\text{C}^{1,3}$), 76.1 (s, $\text{C}^{1,3}$), 30.1 [d, C (allenic), $J(\text{RhC})$ 12.2], 26.5 [d, C (allenic), $J(\text{RhC})$ 9.1], and 24.6 [d, C (allenic), $J(\text{RhC})$ 9.1 Hz].

Crystal Structure Determination of Complex (1).—The crystal chosen for intensity measurements ($0.45 \times 0.3 \times 0.3$ mm) was mounted on a Syntex P3 diffractometer according to methods described previously.²¹ Of 5 596 unique reflections measured in the range $2.9 \leq 2\theta \leq 60.0^\circ$, 5 027 were deemed observed according to the criterion $I \geq 2.5\sigma(I)$ and only these were used in the solution and refinement of the structure.

Crystal data. $\text{C}_{23}\text{H}_{18}\text{O}_2\text{Rh}_2$, $M = 531.8$, Triclinic, space group $P\bar{1}$, $a = 12.148(5)$, $b = 10.682(5)$, $c = 9.620(5)$ Å, $\alpha = 115.84(3)$, $\beta = 121.09(4)$, $\gamma = 82.25(4)^\circ$, $U = 955.5(8)$ Å³, $Z = 2$, $F(000) = 524$, $\text{Mo-K}\alpha$ X-radiation (graphite monochromator), $\lambda = 0.710$ 69 Å, $\mu(\text{Mo-K}\alpha) = 16.6$ cm^{-1} .

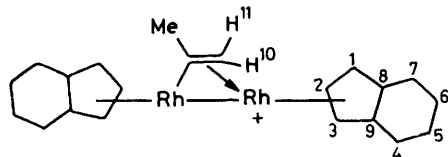
Structure solution and refinement. The structure was solved by conventional heavy-atom methods. All non-hydrogen atoms were refined freely with anisotropic thermal parameters using the program SHELX.²² The allene hydrogen atoms were located on the subsequent difference map and were allowed free refinement with isotropic thermal parameters. The indenyl hydrogens were also located but these were fixed to their respective carbon atoms such that $\text{C-H} = 1.08$ Å, and the C-H vertex bisects the C-C-C angle. The contribution of the reflections to the refinement was weighted according to the Scheme $w = 1.09/[\sigma^2(F) + 0.0001 F_o^2]$ so as to equate as closely as possible the sums of the variances $\sum w\Delta F^2$ for different classes of reflection.

The refinement converged at $R = 0.024$, $R' = 0.026$. The final difference electron-density map showed no peaks >0.7 or <-0.8 e Å⁻³. Atomic scattering factors for non-hydrogen atoms were those of ref. 23 with corrections for anomalous dispersion for rhodium from ref. 24. Scattering factors for hydrogen were from ref. 25. Absorption corrections were not applied due to the irregular shape of the crystal. All computational work was carried out at the South-Western Universities Computation Centre with the program 'SHELX-76'. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 23147 (58 pp).*

Reaction of Complex (1) with Tetrafluoroboric Acid.—Tetrafluoroboric acid-diethyl ether was added dropwise to a stirred solution (0 °C) of (1) (0.5 g, 0.94 mmol) in diethyl ether (60 cm^3) until the yellow colour disappeared, and precipitation was complete. The deep red precipitate was washed with diethyl ether and recrystallised (–20 °C) from methylene chloride-hexane to give red crystals of (4) (0.58 g, 100%) (Found: C, 43.9; H, 2.9. $\text{C}_{23}\text{H}_{19}\text{BF}_4\text{O}_2\text{Rh}_2$ requires C, 44.5; H, 3.0%); ν_{max} (CH_2Cl_2) at 2 025s, 1 908s, br cm^{-1} ; ^1H n.m.r. (CD_2Cl_2 , 30 °C), τ 2.17–2.78 (complex, 8 H, H^{4-7} , $\text{H}^{4'-7'}$), 3.03–5.31 (complex, br, 6 H, H^{1-3} , $\text{H}^{1'-3'}$), 6.10 (complex, 1 H, H^{11}), 7.47 (complex, 1 H, H^{10}), and 7.36 (s, 3 H, Me); ^{13}C n.m.r. (CD_2Cl_2 , 30 °C), δ (p.p.m.) 186.19 [d, CO, $J(\text{RhC})$ 83 Hz], 132.34–129.74 (3 s, C^{4-7}), 123.46–120.65 (4 s, $\text{C}^{4'-7'}$), 117.4 (s, $\text{C}^{8,9}$), 112.52 (s, $\text{C}^{8',9'}$), 109.92 (s, C^{11}), 103.31–83.92 (6 s, C^{1-3} , $\text{C}^{1'-3'}$), and 39.8 (s, Me).

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

Crystal Structure Determination of Complex (4).—A large irregular crystal ($0.4 \times 0.4 \times 0.4$ mm) was mounted on a Nicolet R3 diffractometer. The crystal was centred according to methods described earlier,²¹ cooled to 240 K, and recentred. Cell parameters were determined and the space group identified on the basis of systematic absences as $P2_1/n$.^{*} Intensity data were collected using graphite



monochromated Mo- K_α X-radiation and a variable scan speed. The intensities of two standard reflections were measured every 100 observations and revealed no significant crystal decay. 7 690 Independent intensity data were collected to $2\theta = 60^\circ$ of which 4 932 were retained for structure solution and refinement according to the criterion $I > 3.0\sigma(I)$.

Crystal data. $C_{24}H_{21}BCl_2F_4O_2Rh_2$, $M = 532.8$, Monoclinic, space group $P2_1/n$, $a = 13.851(5)$, $b = 15.207(6)$, $c = 12.652(3)$ Å, $\beta = 110.62(2)^\circ$, $U = 2 494.2(13)$ Å³, $Z = 4$, $F(000) = 1 384$, Mo- K_α X-radiation (graphite monochromator), $\lambda = 0.710 69$ Å, $\mu(\text{Mo-}K_\alpha) = 15.7$ cm⁻¹.

TABLE 7

Planes of best fit with deviations (Å) in square brackets for complex (4)

Plane (1): Rh(2), C(1), C(2), C(3)	
$7.656X - 0.425Y + 7.400Z = 3.733$	
[Rh(2) 0.012, C(1) -0.046, C(2) 0.017, C(3) 0.017, H(1) 0.342, H(2) -0.050]	
Plane (2): Rh(1), C(1), C(2)	
$-1.962X + 14.253Y - 3.141Z = 1.942$	
Plane (3): C(6)—C(14)	
$8.466X - 4.918Y + 5.830Z = -0.906$	
[C(6) 0.042, C(7) -0.082, C(8) 0.040, C(9) 0.012, C(10) 0.005, C(11) -0.021, C(12) -0.006, C(13) -0.007, C(14) 0.016]	
Plane (4): C(15)—C(23)	
$10.982X - 3.717Y - 10.143Z = 3.835$	
[C(15) -0.027, C(16) 0.063, C(17) -0.049, C(18) 0.001, C(19) 0.003, C(20) 0.014, C(21) 0.004, C(22) -0.008, C(23) -0.001]	

Angles ($^\circ$) between planes

(1)–(2)	111.7	(2)–(3)	128.3
(1)–(3)	18.5	(2)–(4)	99.4
(1)–(4)	91.1	(3)–(4)	80.8

Structure solution and refinement. Following Lorentz and polarisation corrections a Patterson map was calculated and the positions of the metal atoms determined from this. A subsequent difference-Fourier map with phases calculated from the positions of the metal atoms revealed the rest of the non-hydrogen atoms in the cation and the position of the tetrafluoroborate anion. At this point a difference map was calculated and a region of electron density appeared which would be best modelled as one methylene chloride molecule disordered between two sites. All non-hydrogen

* A few forbidden reflections were observed. The pattern of Patterson map vectors and the subsequent successful structure solution supported the choice of space group, however it is possible that the 'offending' reflections appeared as a result of Renninger effects.

atoms were with anisotropic thermal parameters. All hydrogen atoms save those of the solvent molecules were also found; those of the vinyl cation were allowed to refine freely with isotropic thermal parameters while those of the indenyl ligands were constrained to appropriate geometries (C–H 0.96 Å). The contribution of each reflection to the refinement process was weighted according to the scheme $w = 1/[\sigma^2(F) + 0.000 15 F^2]$ in order to reflect both random and systematic sources of error. The refinement converged at $R = 0.036$, $R' = 0.039$. Apart from one peak of about $1.3 \text{ e } \text{\AA}^{-3}$ in the vicinity of the disordered solvent molecule the largest peaks in the final difference map did not rise above $0.8 \text{ e } \text{\AA}^{-3}$.

Atomic scattering factors were as for complex (1).^{23–25} No absorption corrections were applied to the data [$\mu(\text{Mo-}K_\alpha) = 15.7 \text{ cm}^{-1}$]. All computations were performed on a DATA GENERAL ECLIPSE 5/230 using the SHELXTL system.²⁶ Observed and calculated structure factors are listed in the Supplementary Publication.

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