Reactions of Co-ordinated Ligands. Part 26.[1] The Reaction of Ethylene and Acetylene with Tri-μ-carbonyl-tris(η^5-indenyl)-*triangulo*-trirhodium; the Formation and Molecular Structure of the Bridged Vinylalkylidene Complex $[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta^5\text{-}C_9H_7)_2]$,† and its Protolysis to Form a Bridged Cationic Vinyl Complex

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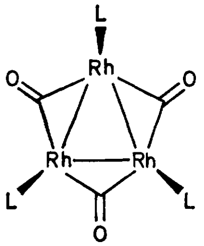
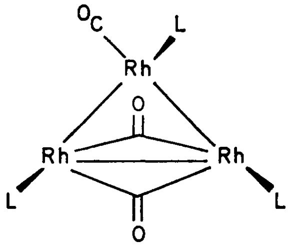
The complex $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ decarbonylates in refluxing heptane to form $[Rh_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]$. Reaction of the Rh_3 cluster with ethylene affords a high yield of $[Rh(CO)(C_2H_4)(\eta^5\text{-}C_9H_7)]$, which reforms the Rh_3 cluster in solution. Treatment (60 °C, toluene) of $[Rh(CO)(C_2H_4)(\eta^5\text{-}C_9H_7)]$ with acetylene affords as the major product the bridged vinylalkylidene complex $[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta^5\text{-}C_9H_7)_2]$. An *X*-ray crystallographic study has been carried out on this complex. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell of dimensions $a = 13.482(3)$, $b = 9.568(3)$, $c = 14.801(6)$ Å, and $\beta = 100.69(3)°$. The structure has been refined to R 0.021 (R' 0.021) for 2 999 unique reflections to $2\theta \leqslant 50°$ (Mo-K_α, *X*-radiation). The μ-C=CH$_2$ group symmetrically bridges two $Rh(CO)(\eta^5\text{-}C_9H_7)$ fragments linked by a Rh–Rh bond [Rh(1)–Rh(2)2.691(1) Å]. A minor product in this reaction is obtained in higher yield by treating acetylene with $[Rh_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]$, and is characterised as a complex containing two $Rh(\eta^5\text{-}C_9H_7)$ units linked by a μ-pentadien-3-one fragment. Reaction of this complex with carbon monoxide or heating affords the cyclopentadienone complex, $[Rh(\eta^4\text{-}C_4H_4CO)(\eta^5\text{-}C_9H_7)]$. Reaction of $[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta^5\text{-}C_9H_7)_2]$ with $HBF_4\text{–}Et_2O$ gives $[Rh_2(\mu\text{-}CH{=}CH_2)(\mu\text{-}CO)(CO)(\eta^5\text{-}C_9H_7)_2][BF_4]$, there being no evidence for the formation of a bridged alkylidyne complex.

THE photolysis of $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ affords two isomers of $[Rh_3(CO)_3(\eta\text{-}C_5H_5)_3]$, which have been shown by *X*-ray crystallography to have the illustrated structures (A) and (B).[2,3] More recently[4] it has been found that reaction of $[Rh(CO)_2(\eta\text{-}C_5H_5)]$ with Me_3NO in benzene affords the trinuclear complex (A) together with smaller amounts of $[Rh_2(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$, and an isomer of $[Rh_4(CO)_4(\eta\text{-}C_5H_5)_4]$. Irradiation of (A) results in its transformation into isomer (B), which on thermolysis reverts to (A).[5] Aside from a study of the reactions of the dimer with trimethyl phosphite[6] and *N*-methylnitrosourea,[7,8] the reactions of these molecules have not been explored.



(A) L = η-C_5H_5

(1) L = η^5-C_9H_7



(B) L = η-C_5H_5

In investigating the chemistry of the more reactive η^5-indenyl system we observed that dicarbonyl(η^5-indenyl)-rhodium decarbonylates in refluxing heptane to give tri-μ-carbonyl-tris(η^5-indenyl)-*triangulo*-trirhodium.[9] Here we report a study of the reaction of this Rh_3 cluster with ethylene and acetylene.

RESULTS AND DISCUSSION

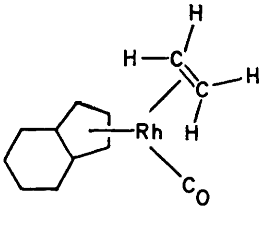
A refluxing solution of $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ in heptane deposits (24 h) in good yield (86%) dark green crystals of complex (1), which on the basis of elemental analysis, mass spectroscopy, i.r. and n.m.r. spectroscopy is formulated as $[Rh_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]$ isostructural with the C_{3v} isomer (A). The ^{13}C n.m.r. spectrum of (1) prepared from $[Rh(^{13}CO)_2(\eta^5\text{-}C_9H_7)]$ showed in the room-temperature spectrum a triplet centred at 223.0 p.p.m. [J(RhC) 50.4 Hz] due to the bridging carbonyl carbon consistent with the illustrated static structure. This contrasts with the report[4] that the corresponding room-temperature spectrum of the cyclopentadienyl analogue (A) appears as a quartet [J(RhC) 32 Hz] centred at 232.5 p.p.m., and that only on cooling to −65 °C is a triplet [232.5 p.p.m., J(RhC) 49 Hz] observed. Thus, there is an interesting difference in activation energy for the carbonyl site-exchange process for the η-C_5H_5 and η^5-C_9H_7 complexes.

The reaction leading to the formation of (1) is selective, there being no evidence for the formation of other Rh_3 isomers or Rh_4 clusters. When the thermal reaction was monitored by i.r. spectroscopy there was evidence for the build up, and then gradual disappearance, of bands assignable to $[Rh_2(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2]$, and it is suggested that the immediate precursor of the Rh_3 cluster (1) is the unsaturated species $[Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}C_9H_7)_2]$ formed by thermolysis of the tricarbonyl. Capture of this unsaturated Rh_2 species by a $Rh(CO)(\eta^5\text{-}C_9H_7)$ fragment would then be expected[10,11] to give the C_s isomer $[Rh_3(\mu\text{-}CO)_2(CO)(\eta^5\text{-}C_9H_7)_3]$, which in refluxing heptane would rearrange to the thermodynamically more stable C_{3v} isomer (1).

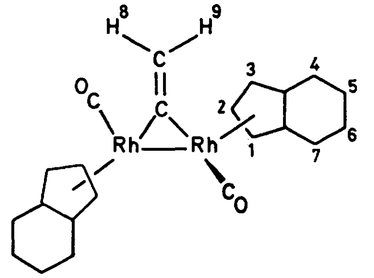
Reaction of (1) with ethylene in a Fischer–Porter

† μ-Vinylidene-bis[carbonyl(1–5-η-indenyl)rhodium] (*Rh–Rh*).

vessel (80 °C, 2 atm *) affords in high yield (90%) the yellow crystalline complex carbonyl(ethylene)(η^5-indenyl)rhodium (2), which showed a single terminal carbonyl band in the i.r. at 1 985 cm^{-1}. The room-temperature ^{1}H n.m.r. spectrum of (2) was consistent with rapid rotation on the n.m.r. time scale of both the indenyl ligand and the co-ordinated ethylene. At −90 °C the ethylene-proton signal was broad; however, the resonance due to the η^5-C_9H_7 ligand remained sharp as a 4 : 2 : 1 pattern suggesting a lower barrier to rotation of the indenyl ligand compared with rotation of the ethylene. Although stable in the solid state, solutions of (2) at room temperature gradually formed the Rh_3 cluster (1), presumably *via* dissociative loss of ethylene, suggesting that (2) was a potential source of a Rh(CO)(η^5-C_9H_7) fragment.



(2)



(3)

In order to explore this possibility, the reaction of (2) with acetylene was examined. Reactions at 60 °C afforded as the principal product (50% yield) a red crystalline complex (3), which on the basis of analysis, mass spectroscopy, and the appearance of one terminal carbonyl band in the i.r. spectrum could be formulated either as $[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta^5\text{-}C_9H_7)_2]$ or as $[Rh_2\{\mu\text{-}(\sigma\text{-}HC_2H)\}(CO)_2(\eta^5\text{-}C_9H_7)_2]$. Examination of the ^{1}H and ^{13}C n.m.r. spectra did not allow a firm decision between these two isomeric structures, and therefore a single-crystal *X*-ray diffraction study was undertaken.

The positional parameters of the atoms and interatomic distances and angles are listed in Tables 1 and 2 for the molecular structure as illustrated in the Figure. Tables of thermal parameters and planes of best fit are listed in Supplementary Publication No. SUP 23161 (20 pp.).†

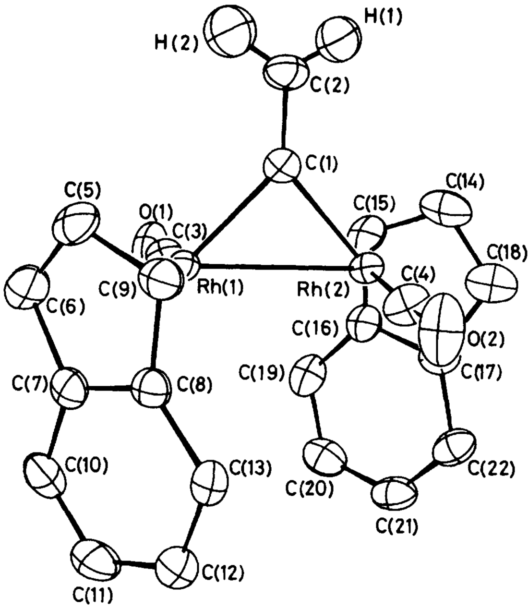
The *X*-ray diffraction analysis establishes the chemical identity of (3) as a bridged vinylalkylidene complex, in which the carbonyl ligands on alternate metal atoms have a *trans* configuration with a torsional angle C(3)–Rh(1)–Rh(2)–C(4) of 169.7°. Similarly, the η^5-indenyl ligands on either metal atom are near parallel with an interplanar angle of only 9.3°. The μ-(C=CH_2) ligand symmetrically bridges the Rh–Rh bond.

Several singly bridged dirhodium species of the type $[Rh_2X(CO)_2(\eta^5\text{-}C_5H_5)_2]$ have been previously investi-

TABLE 1

Atomic positions (fractional co-ordinates) for complex (3) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Rh(1)	0.742 5(1)	0.366 1(1)	0.266 2(1)
Rh(2)	0.661 7(1)	0.579 9(1)	0.347 3(1)
C(1)	0.641 7(2)	0.512 2(3)	0.218 1(2)
C(2)	0.587 7(3)	0.545 9(4)	0.138 5(3)
C(3)	0.849 9(3)	0.481 5(4)	0.254 7(2)
C(4)	0.567 5(3)	0.459 1(4)	0.379 9(2)
C(5)	0.688 4(3)	0.174 7(4)	0.186 7(2)
C(6)	0.791 6(3)	0.159 1(4)	0.222 1(2)
C(7)	0.804 2(3)	0.139 9(3)	0.321 2(2)
C(8)	0.707 7(3)	0.154 4(3)	0.344 8(2)
C(9)	0.636 0(3)	0.185 1(4)	0.259 9(2)
C(10)	0.889 6(3)	0.110 0(4)	0.389 6(3)
C(11)	0.875 2(3)	0.092 6(4)	0.477 7(3)
C(12)	0.779 8(3)	0.106 9(4)	0.501 7(2)
C(13)	0.696 3(3)	0.139 5(4)	0.437 3(2)
C(14)	0.653 7(3)	0.811 3(4)	0.336 9(3)
C(15)	0.752 0(3)	0.770 3(4)	0.329 6(2)
C(16)	0.803 9(3)	0.722 3(4)	0.419 5(2)
C(17)	0.730 3(3)	0.721 2(4)	0.477 6(2)
C(18)	0.636 4(3)	0.771 8(4)	0.424 8(3)
C(19)	0.903 1(3)	0.679 9(4)	0.453 4(3)
C(20)	0.928 2(3)	0.641 0(4)	0.543 8(3)
C(21)	0.856 2(3)	0.638 1(4)	0.601 5(3)
C(22)	0.758 7(3)	0.675 1(4)	0.569 9(2)
O(1)	0.917 0(2)	0.549 1(3)	0.243 4(2)
O(2)	0.505 9(2)	0.390 4(3)	0.400 5(2)
H(1)	0.541(3)	0.609(4)	0.132(3)
H(2)	0.596(3)	0.501(4)	0.083(3)
H(3)	0.657	0.170	0.114
H(4)	0.854	0.165	0.186
H(5)	0.559	0.221	0.255
H(6)	0.963	0.104	0.371
H(7)	0.940	0.070	0.531
H(8)	0.769	0.080	0.570
H(9)	0.628	0.166	0.462
H(10)	0.604	0.869	0.284
H(11)	0.792	0.788	0.274
H(12)	0.565	0.772	0.449
H(13)	0.957	0.695	0.409
H(14)	0.005	0.610	0.569
H(15)	0.882	0.614	0.673
H(16)	0.704	0.661	0.614



Structure of the complex $[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta^5\text{-}C_9H_7)_2]$ (3), showing 50% probability ellipsoids of thermal vibration

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* Throughout this paper: 1 atm = 101 325 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 2

Interatomic distances (Å) and bond angles (°) for complex (3) with estimated standard deviations in parentheses

(*a*) Distances

Rh(1)–Rh(2)	2.691(1)		
Rh(1)–C(3)	1.850(4)	Rh(2)–C(4)	1.843(4)
C(3)–O(1)	1.147(4)	C(4)–O(2)	1.142(4)
Rh(1)–C(5)	2.216(3)	Rh(2)–C(14)	2.207(4)
Rh(1)–C(6)	2.214(3)	Rh(2)–C(15)	2.224(4)
Rh(1)–C(7)	2.393(3)	Rh(2)–C(16)	2.427(3)
Rh(1)–C(8)	2.413(3)	Rh(2)–C(17)	2.391(3)
Rh(1)–C(9)	2.231(3)	Rh(2)–C(18)	2.215(4)
C(5)–C(6)	1.401(6)	C(14)–C(15)	1.405(6)
C(6)–C(7)	1.455(5)	C(15)–C(16)	1.457(3)
C(7)–C(8)	1.416(5)	C(16)–C(17)	1.428(5)
C(8)–C(9)	1.466(4)	C(17)–C(18)	1.442(5)
C(9)–C(5)	1.401(5)	C(18)–C(14)	1.413(5)
C(7)–C(10)	1.414(5)	C(16)–C(19)	1.398(5)
C(10)–C(11)	1.363(5)	C(19)–C(20)	1.369(5)
C(11)–C(12)	1.404(5)	C(20)–C(21)	1.407(6)
C(12)–C(13)	1.369(5)	C(21)–C(22)	1.357(5)
C(13)–C(8)	1.414(3)	C(22)–C(17)	1.418(5)
Rh(1)–C(1)	1.982(3)	Rh(2)–C(1)	1.988(3)
C(1)–C(2)	1.304(5)		
C(2)–H(1)	0.86(4)		
C(2)–H(2)	0.95(4)		

(*b*) Angles

C(3)–Rh(1)–C(1)	92.7(1)	C(4)–Rh(2)–C(1)	94.2(1)
C(3)–Rh(1)–Rh(2)	88.9(1)	C(4)–Rh(2)–Rh(1)	90.1(1)
C(1)–Rh(1)–Rh(2)	47.4(1)	C(1)–Rh(2)–Rh(1)	47.2(1)
Rh(1)–C(1)–Rh(2)	85.4(1)		
Rh(1)–C(1)–C(2)	136.7(3)	Rh(2)–C(1)–C(2)	137.9(3)
C(1)–C(2)–H(1)	123.4(2.4)	C(1)–C(2)–H(2)	122.5(2.2)
H(1)–C(2)–H(2)	114.1(3.2)		
Rh(1)–C(3)–C(1)	176.3(3)	Rh(2)–C(4)–O(2)	176.3(3)
C(5)–C(6)–C(7)	108.2(3)	C(14)–C(15)–C(16)	108.5(3)
C(6)–C(7)–C(8)	107.2(3)	C(15)–C(16)–C(17)	106.4(3)
C(7)–C(8)–C(9)	107.3(3)	C(16)–C(17)–C(18)	108.0(3)
C(8)–C(9)–C(5)	107.6(3)	C(17)–C(18)–C(14)	108.0(4)
C(9)–C(5)–C(6)	109.0(3)	C(18)–C(14)–C(15)	108.4(3)
C(6)–C(7)–C(10)	132.4(4)	C(15)–C(16)–C(19)	133.1(4)
C(10)–C(7)–C(8)	120.4(2)	C(19)–C(16)–C(17)	120.5(3)
C(7)–C(10)–C(11)	117.9(3)	C(16)–C(19)–C(20)	118.3(4)
C(10)–C(11)–C(12)	122.1(3)	C(19)–C(20)–C(21)	121.7(4)
C(11)–C(12)–C(13)	121.2(3)	C(20)–C(21)–C(22)	121.3(4)
C(12)–C(13)–C(8)	118.4(3)	C(21)–C(22)–C(17)	118.8(4)
C(13)–C(8)–C(9)	132.8(3)	C(22)–C(17)–C(18)	132.7(4)
C(13)–C(8)–C(7)	120.0(3)	C(22)–C(17)–C(16)	119.3(3)

gated. Where X = CO [12] a Rh–Rh bond length of 2.681(2) Å was observed, where X = $C_2(CF_3)_2$ [13] a bond of 2.682(1) Å was found, and where X = CH_2 [14] a Rh–Rh distance of 2.664 9(4) Å was recorded. Thus, a Rh–Rh bond distance of 2.691(1) Å for complex (**3**) is consistent with this overall picture.

The most interesting feature of the molecule is the bridging $C{=}CH_2$ ligand, and four previous examples * of complexes containing this ligand have been reported.[15–18] In (**3**) the bridge is symmetric, as has been found in the other systems, and although there is a range of bond lengths for the vinylidene (C=C) bond it would appear that the C–C bond length for unsubstituted vinylalkylidene complexes is somewhat shorter than in the substituted molecules (see Table 3), the bond lengths of which are comparable to those found in the free substituted ethylenes, tetraphenylethylene (1.356 Å) [19] and tetracyanoethylene (1.355 Å).[20]

The atoms Rh(1), Rh(2), C(1), and C(2) are essentially coplanar with a small rotation of 7° about the C–C bond displacing the hydrogen atoms above and below the plane. Such rotations are common to all previously observed μ-C=CRR′ complexes, and there seems no reason to doubt the existence of such a rotation in complex (**3**) as the positional integrity of the hydrogen atoms is established by the reasonable values of their other interactions. The vinylidene hydrogen atoms have no short non-bonded contacts with other atoms, so there is no apparent steric reason for this rotation. One can only conclude that this twisting deformation serves to improve the orbital overlap between the vinylidene moiety and the metal orbitals. Hofmann [21] has recently performed molecular-orbital calculations on the complex $[Rh_2(\mu\text{-}CH_2)(CO)_2(\eta^5\text{-}C_5H_5)_2]$, and concluded that the three highest occupied molecular orbitals are (*i*) the unperturbed π_{xy} orbital of the dirhodium fragment, (*ii*) a bonding linear combination of the Rh_2 π_{xy}^* orbital and the p orbital of the CH_2 units, and (*iii*) a bonding linear combination of the Rh–Rh σ bond and the CH_2 σ orbital. He suggested that this bonding description can be applied to cases where the $Rh(CO)(C_5H_5)$ fragment is replaced by other isolobal units, and the CH_2 by other bridges. Such a model can, therefore, be extended to complex (**3**), which may be formally described as a dimetallamethylenecyclopropane.

TABLE 3

Selected geometric features of bridging vinylalkylidene complexes

Molecular parameters	(1) [a]	(2) [b]	(3) [c]	(4) [d]	(5) [e]
M–C/Å (vinylidene C)	1.98(1) 1.98(1)	1.84(2) 1.90(2)	1.94(1) 1.99(1)	1.979(7) 1.971(6)	1.982(3) 1.988(3)
C=C/Å	1.33(1)	1.38(3)	1.35(2)	1.308(10)	1.304(5)
M–C–M/°	83(1)	82(2)	88.0(5)	88.6(3)	85.4(1)
M–M/Å	2.635(3)	2.511(4)	2.734(2)	2.759(2)	2.691(1)
Torsion angle (°) [f]	13.9	0.3	7	11	7

[a] $[Fe_2(\mu\text{-}C{=}CPh_2)(CO)_8]$, ref. 15. [b] $[Fe_2\{\mu\text{-}C{=}C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)_2]$, ref. 16. Two molecules per asymmetric unit. Values quoted are averages for the two molecules. [c] $[Mn_2(\mu\text{-}C{=}CHPh)(CO)_4(\eta\text{-}C_5H_5)_2]$, ref. 17. [d] $[Mn_2(\mu\text{-}C{=}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$, ref. 18. [e] $[Rh_2(\mu\text{-}C{=}CH_2)(CO)_2(\eta\text{-}C_9H_7)_2]$, this study. [f] The angle between the metallacyclopropane ring plane formed by the other carbon atom and its substituent atoms.

The geometries associated with the indenyl ligands are typical.[22–26] The rhodium atoms engage in η^5 co-ordination to the atoms of the five-membered ring, but the rhodium atom is significantly closer to the three end

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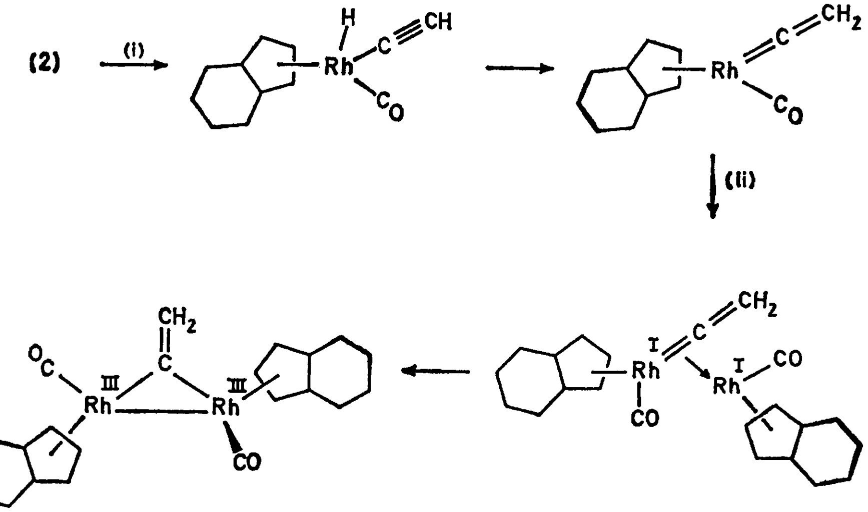
* On completion of this study the complexes $[M_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(\eta\text{-}C_5H_5)_2]$ M = Fe (G. M. Dawkins, M. Green, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1980, 1120) and M = Ru (D. L. Davies, A. F. Dyke, A. Endesfelder, S. A. R. Knox, P. J. Naish, A. G. Orpen, D. Plaas, and G. E. Taylor, *J. Organomet. Chem.*, 1980, **198**, C43) were described.

carbon atoms where Rh–C(mean) = 2.219(8) Å compared with the bridgehead carbons where Rh–C(mean) = 2.406(16) Å. The bond lengths and angles within the indenyl ligands conform to those previously observed.

The ^{1}H n.m.r. spectrum of (3) is temperature dependent, and it was thought that synchronous carbonyl exchange might be occurring *via* a triply bridged species $[Rh_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)_2(\eta^5\text{-}C_9H_7)_2]$; however, examination of the ^{13}C n.m.r. spectrum of a ^{13}CO-enriched sample of (3) showed in the temperature range −85 to +50 °C *one* terminal carbonyl C resonance coupled to only *one* ^{103}Rh nucleus. It was, therefore, concluded that in the temperature range studied only rotation of the η^5-indenyl ligands occurred.



SCHEME 1 (i) HC_2H; (ii) $[Rh(CO)(C_2H_4)(\eta^5\text{-}C_9H_7)]$

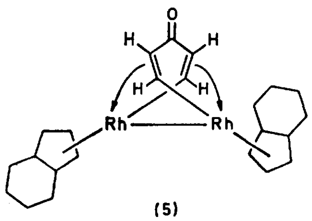
The only precedent for the formation of a μ-$C{=}CH_2$ complex from acetylene is in manganese chemistry, where it was observed [18] that reaction of HC_2H with $[Mn(thf)(CO)_2(\eta\text{-}C_5H_5)]$ (thf = tetrahydrofuran) followed by treatment with potassium hydroxide afforded in unspecified yield the binuclear complex $[Mn_2(\mu\text{-}C{=}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2]$. Whether this reaction involves the acetylide anion HC_2K or a deprotonated η^2-bonded HC_2H molecule is still not clear. In contrast, in the reaction leading to the formation of (3), no base is involved, and examination of the i.r. spectrum of the crude reaction mixture before column chromatography on alumina showed the presence of (3).

It is difficult to see how the possible intermediates $[Rh(\eta^2\text{-}HC_2H)(CO)(\eta^5\text{-}C_9H_7)]$, $[Rh_2\{\mu\text{-}(\sigma\text{-}HC_2H)\}(CO)_2(\eta^5\text{-}C_9H_7)_2]$, or $[Rh_2\{\mu\text{-}(\eta^2\text{-}HC_2H)\}(\mu\text{-}CO)(\eta^5\text{-}C_9H_7)_2]$ could rearrange at 60 °C to form (3), and it is suggested that the most plausible reaction path to (3) involves an oxidative-addition reaction between (2) and HC_2H followed by collapse to the illustrated (Scheme 1) hydrido(acetylide) complex, which could then rearrange with assistance from the π-accepting σ-acetylide ligand to form a mononuclear vinylalkylidene complex. Capture of this molecule by a $Rh(CO)(\eta^5\text{-}C_9H_7)$ fragment formed from the labile species (2) then affords (3) *via* co-ordination to a second rhodium centre followed by the formal oxidative formation of a Rh–Rh bond.

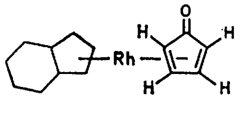
Further elution of the chromatography column from which (3) was obtained gave yellow crystals of (4), which on the basis of analysis, mass spectroscopy, i.r. and n.m.r. spectroscopy (see Experimental section for details) was characterised as $[Rh_2(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2]$. The third component of this reaction mixture, which was isolated on further elution of the column, was obtained only in very low yield; however, it was observed that direct reaction (60 °C, toluene) of $[Rh_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]$ with acetylene, whilst affording only trace amounts of the bridged vinylidene complex (3), gave a greatly enhanced yield (62%) of this third component, which was isolated as the orange crystalline complex (5).

Elemental analysis, mass spectroscopy, and the appearance in the i.r. spectrum of a ketonic carbonyl band at 1 649 cm^{-1} suggested that (5) was a bridged pentadienone complex as is illustrated. This was supported by the ^{1}H n.m.r. spectrum, which demonstrated the C_2 symmetry of the molecule, showing resonances at τ 1.62 and 5.82, which are assigned to the pentadienone protons. It is interesting that the vinylic proton attached to the symmetrically bridged carbon atom α to the rhodium occurs at low field, an assignment which is supported by the presence of coupling to equivalent ^{103}Rh nuclei.

This type of molecule has been previously observed both in cyclopentadienylrhodium [27-30] chemistry and



(5)



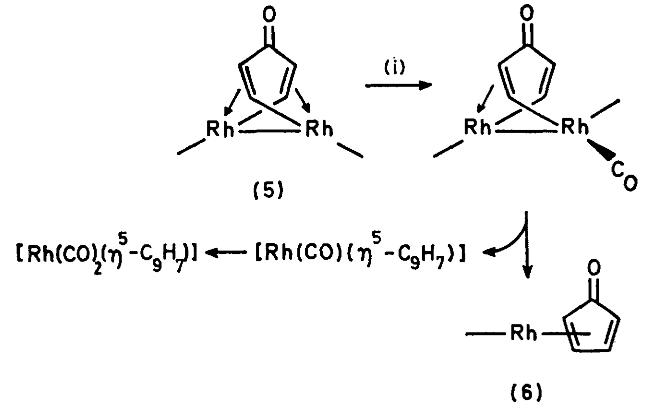
(6)

with iron complexes of the general formula $[Fe_2(CO)_6(C_4R_4CO)]$;[31,32] however, in all previously studied examples, the μ-pentadien-3-one fragment has carried alkyl or trifluoromethyl substituents, and therefore the isolation of (5) was of particular interest, and can be attributed to the enhanced reactivity of the η^5-indenyl systems.

Finally, elution with ethanol of the reaction mixture obtained from acetylene and (1) gave yellow crystals of (6), which was readily identified by elemental analysis, mass spectroscopy, i.r. and ^1H n.m.r. spectroscopy as a mononuclear unsubstituted cyclopentadienone complex. The same complex was also obtained on heating (5) at 100 °C, or more importantly on reaction of (5) at room temperature with carbon monoxide.

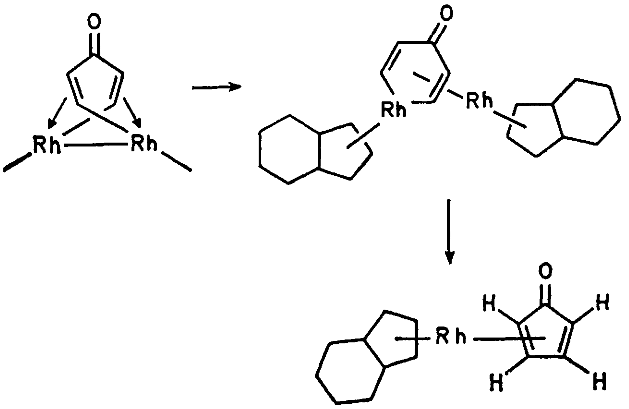
The formation of (5) throws no new light on the previously proposed[27,30] reaction paths to μ-pentadien-3-one binuclear complexes, however, the transformation of (5) into the mononuclear η^4-cyclopentadienone complex (6) merits further comment.

The most obvious reaction path for the thermal transformation of (5) into (6) involves the concerted elimination of cyclopentadienone *via* a C_{2v} transition site. However, this pathway is forbidden by symmetry considerations in the same way as is the suprafacial elimination of H_2 from ethane.[33] Co-ordination of carbon monoxide to one of the rhodium centres removes this symmetry restriction and as is illustrated (Scheme 2) a concerted carbon–carbon bond-forming reaction is then allowed. It is possible that the formation of (6) from (5) at room temperature in the presence of added carbon monoxide proceeds *via* this pathway. However, complex (6) is also formed on heating (100 °C) (5) in the complete absence of carbon monoxide, and it is likely that a different reaction path is followed under these conditions involving a reductive disproportionation reaction with cleavage of the Rh–Rh bond, and the formation of a rhodacyclohexadienone complex (Scheme 3). There is then no problem in forming the carbon–carbon bond needed to complete the cyclopentadienone by reductive coupling of adjacent vinyl groups σ bonded to one metal centre.



SCHEME 2 η^5-C_9H_7 ligands omitted for clarity. (i) CO, room temperature

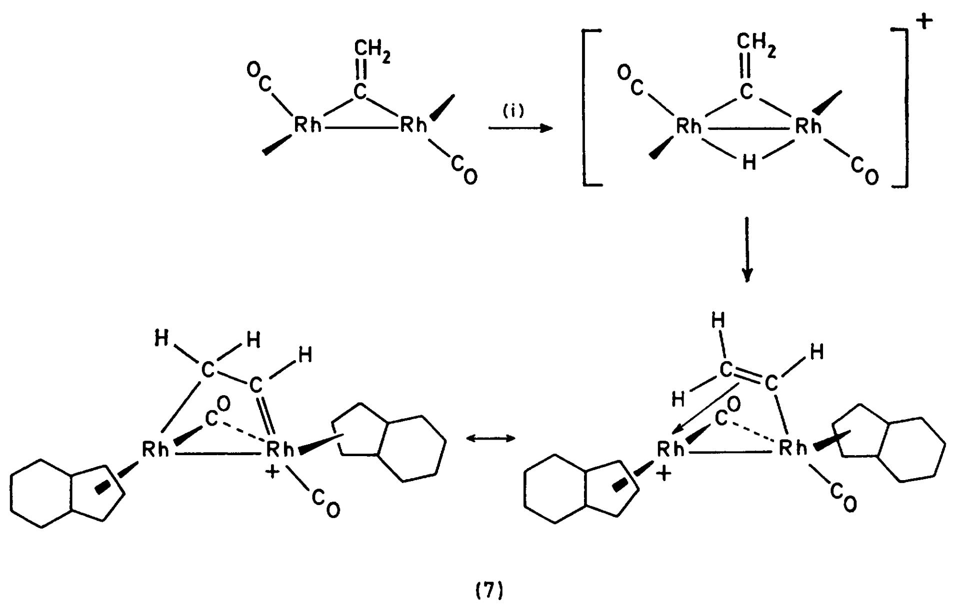
The availability of the bridged vinylidene complex (3) provided an opportunity to study its reactions with electrophiles. There are two possible sites for electrophilic attack, the metal–metal bond as recently observed[34] on protonation of the related dimetallacyclopropane $[Rh_2(\mu-CH_2)(CO)_2(\eta-C_5H_5)_2]$, and secondly on the methylene carbon atom[10] forming a bridged alkylidyne or carbyne complex. An example of this latter mode of attack is the formation[35] of $[Mn_2(\mu-CCH_3)(CO)_4(\eta-C_5H_5)_2][O_2CCF_3]$ on reaction of trifluoroacetic acid with $[Mn_2(\mu-C{=}CH_2)(CO)_4(\eta-C_5H_5)_2]$.



SCHEME 3 Some η^5-C_9H_7 ligands omitted for clarity

Treatment (0 °C) of a solution of (3) in diethyl ether with HBF_4–Et_2O led to an immediate change in colour, and the formation of the red crystalline tetrafluoroborate salt (7), which was characterised by elemental analysis and mass spectroscopy (field desorption). Examination of the ^1H n.m.r. spectrum showed that protonation had occurred to form a bridged cationic vinyl complex (7) similar to the complex $[Rh_2\{\mu-C(Me){=}CH_2\}(CO)_2(\eta^5-C_9H_7)_2][BF_4]$ (ref. 1) formed on protonation of a μ-allene complex. The i.r. spectrum showed carbonyl bands at 2 054s and 1 902s, br cm^{-1} similar to those observed[1] for the μ-vinyl cation obtained from $[Rh_2(\mu-C_3H_4)(CO)_2(\eta^5-C_9H_7)_2]$, the low-wavenumber band being assigned to an acceptor semi-bridging carbonyl ligand. Comparison of the ^1H n.m.r. spectrum of (7) with that of the complex $[Rh_2\{\mu-C(Me){=}CH_2\}(CO)_2(\eta^5-C_9H_7)_2][BF_4]$, which has been structurally identified by *X*-ray crystallography, allowed assignment of the chemical shifts detailed in the Experimental section. Analysis of the multiplets due to the μ-CH=CH$_2$ system afforded coupling constants fully consistent with the illustrated structure. The low-field chemical shift for the vinylic proton RhC*H*=CH$_2$ suggests that there is a contribution from a canonical form containing a bridged alkylidene complex. The low solubility of the cationic complex in suitable solvents precluded measurement of a satisfactory ^{13}C n.m.r. spectrum.

Thus, in contrast with the manganese system, but in parallel with the reactions of $[Rh_2(\mu-CH_2)(CO)_2(\eta-C_5H_5)_2]$, protonation probably occurs *via* attack on the electron density located between the two rhodium atoms of (3),



(7)

SCHEME 4 Some η^5-C_9H_7 ligands omitted for clarity. (i) HBF_4–Et_2O

forming a four-membered dimetallic μ-$C=CH_2$, μ-hydrido-frame (Scheme 4). This is followed by rapid intramolecular transfer of the μ-H to the bridging carbon of the μ-$C=CH_2$ ligand with formation of a μ-$CH=CH_2$ system. It is interesting that the related neutral osmium cluster $[Os_3(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}]$ (ref. 36) in solution reversibly isomerises to the tautomer $[Os_3(\mu\text{-}H)(\mu\text{-}CH_3)(CO)_{10}]$; however, in the case of the dirhodium system (7) there was no evidence for the related reaction shown below.

$$[Rh_2(\mu\text{-}CH=CH_2)(CO)_2(\eta^5C_9H_7)_2]^+ \longrightarrow [Rh_2(\mu\text{-}H)(\mu\text{-}C=CH_2)(CO)_2(\eta^5C_9H_7)_2]^+$$

EXPERIMENTAL

N.m.r. spectra (^1H, hydrogen-1 decoupled ^{13}C) were recorded on Varian Associates HA-100 and JEOL PS-, PFT-, and FX-200 spectrometers, with ^{13}C shifts relative to $SiMe_4$ (0.0 p.p.m.). Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer. Mass spectra were measured at 70 eV on an AEI 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.

Preparation of Tri-μ-carbonyl-tris(η^5-*indenyl*)-triangulo-*trirhodium* (1).—A solution of dicarbonyl(η^5-indenyl)-rhodium (0.30 g, 1.1 mmol) [prepared by bubbling carbon monoxide (15 min) through bis(ethylene)- or cyclo-octa-1,5-diene-(η^5-indenyl)rhodium dissolved in heptane] in heptane (30 cm^3) was heated under reflux for 24 h affording dark green *crystals* of $[Rh_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]$ (1) (0.23 g, 86%) (Found: C, 49.1; H, 3.0. $C_{30}H_{21}O_3Rh_3$ requires C, 48.8; H, 2.9%); ν_{CO} (CH_2Cl_2) at 1 852s and 1 805s cm^{-1}, $\nu_{max.}$ (Nujol) at 1 840s, 1 800s, 1 775s, 1 330w, 1 320m, 1 235w, 1 230w, 1 210w, 1 050m, 1 035w, 915w, 865m, 820m, 805m, 760m, 750s, 745m, and 740m cm^{-1}. The mass spectrum (base peak *m/e* 115) showed peaks at *m/e* 738 (*P*, 1%), 682 (*P* – 2CO, 2%), 654 (*P* – 3CO, 1%), 567 (*P* – 2CO – C_9H_7, 2%), and 539 (*P* – 3CO – C_9H_7, 30%). N.m.r.: ^1H ($CDCl_3$, room temperature), τ 2.75 (m, 12 H), 4.3 (m, 3 H), and 4.5 [d, 6 H, *J*(HH) 4.5 Hz]; ^{13}C (CD_2Cl_2, room temperature, 40% enriched) δ 223.0 p.p.m. [t, RhCORh, *J*(RhC) 50.35 Hz].

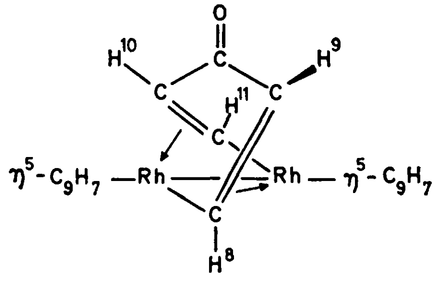
Preparation of Carbonylethylene(η^5-*indenyl*)*rhodium* (2).—A suspension of $[Rh_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3]$ (1.0 g, 1.34 mmol) in toluene (40 cm^3) was placed in a Fischer–Porter vessel (250 cm^3), which was flushed with ethylene and then pressurised to 2 atm. The stirred solution was heated (80 °C) for 6 h when the colour changed from dark green to bright yellow. The vessel was cooled and the ethylene vented. The solution was evaporated to dryness, avoiding prolonged pumping, and the residue extracted with hexane. The extract was rapidly passed through a short (2.5 cm) column of alumina, and the volume of the solvent reduced (10 cm^3) keeping the temperature at 0 °C. The solution was cooled (–78 °C) to give yellow *crystals* of (2) (1.0 g, 90%) (Found: C, 53.0; H, 4.3. $C_{12}H_{11}ORh$ requires C, 52.6; H, 4.1%), ν_{CO} (hexane) at 1 985 cm^{-1}. The mass spectrum (base peak *m/e* 115) showed peaks at *m/e* 274 (*P*, 4%) and 246 (*P* – C_2H_4, 4%). N.m.r.: ^1H ($CDCl_3$, 0 °C), τ 2.6—3.1 (m, 4 H, H^{4-7}), 3.9 [quartet, 1 H, H^2, $J(H^1H^2) = J(RhH^2) = 3$], 4.6 [d, 2 H, $H^{1,3}$, $J(H^2H^1)$ 3], and 7.2 [d, 4 H, C_2H_4, *J*(RhH) 3 Hz].

Reaction of Complex (2) *with Acetylene*.—A stream (1 bubble per second) of dry acetylene was passed through a solution of (2) (0.15 g, 0.55 mmol) in toluene (50 cm^3) at room temperature. After 15 min the temperature was raised to 60 °C, the acetylene continuing to bubble through the solution. After 30 min the solvent was removed *in vacuo*, the residue extracted with hexane, and the extract chromatographed on alumina. Elution with hexane afforded $[Rh(CO)_2(\eta^5\text{-}C_9H_7)]$ (5%). Further elution with hexane–toluene (5 : 1) gave a red band, which on recrystallisation (–20 °C) from hexane gave red *crystals* of $[Rh_2(\mu\text{-}C=CH_2)(CO)_2(\eta^5\text{-}C_9H_7)_2]$ (3) (0.07 g, 50%) (Found: C, 51.2; H, 3.2. $C_{22}H_{16}O_2Rh_2$ requires C, 51.0; H, 3.1%), ν_{CO} (hexane) at 1 987 cm^{-1}. The mass spectrum (base peak *m/e* 436) showed peaks at *m/e* 518 (*P*, 12%), 490 (*P* – CO, 21%), 462 ($P - 200$, 11%), 436 [$Rh_2(C_9H_7)_2$, 100%], 333 [$Rh(C_9H_7)_2$, 30%], and 218 (RhC_9H_7, 30%). N.m.r.: ^1H ([$^2H_6$]acetone, −85 °C), τ 2.4—3.3 (m, 8 H, H^{4-7}, $H^{4'-7'}$), 3.5 (br, s, 2 H, $H^{1,3}$), 4.1 (br, s, 2 H, $H^{2,2'}$), 4.55 (br, s, 2 H, $H^{8,9}$), and 5.20 (br, s, 2 H, $H^{1',3}$); ^{13}C (CD_2Cl_2, −90 °C), δ 196.5 [d, *C*O, *J*(RhC) 87 Hz], 124.8 (s, $C^{4,7'}$), 124.2 (s, $C^{4',7}$), 120.5 (s, $C^{5,6'}$), 119.9 (s, $C^{5',6}$), 116.4 (s, $C^{8',9}$), 115.6 (s, 2 C, $C^{8,9'}$), 111.2 (s, $C^{10,11}$), 95.4 (s, C^2), 80.1 (s, $C^{1',3}$), and 79.1 p.p.m. (s, $C^{1,3'}$).

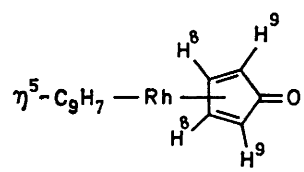
Further elution with hexane–toluene (5 : 1) gave yellow *crystals* (from hexane) (4) [$Rh_2(\mu-CO)(CO)_2(\eta^5-C_9H_7)_2$] (0.03 g, 10%) (Found: C, 48.4; H, 2.7. $C_{21}H_{14}O_3Rh_2$ requires C, 48.5; H, 2.7%), ν_{CO} (hexane) at 1 988s and 1 846 cm^{-1}. The mass spectrum (base peak *m/e* 218) showed peaks at *m/e* 520 (*P*, 1%), 492 ($P - CO$, 2%), 436 ($P - 3CO$, 15%), and 333 ($P - 3CO - Rh$, 4%). N.m.r.: ^1H ($CDCl_3$, 30 °C), τ 2.7—3.0 (m, 8 H, $H^{4-7,4'-7'}$), 4.2 [q, 2 H, $H^{2,2'}$, $J(H^1H^2) = J(H^2H^3) = J(RhH^2)$ 2.5], and 4.9 [d, 4 H, $H^{1,3,1',3'}$, $J(H^1H^2)$ 2.5 Hz].

Finally, elution with acetone–methylene chloride (1 : 9) gave a low yield of orange crystals of (5) (5%). This complex was obtained in higher yield by the following procedure.

Reaction of [$Rh_3(\mu-CO)_3(\eta^5-C_9H_7)_3$] *with Acetylene*.—A stream of dry acetylene (1 bubble per second) was passed through a solution of [$Rh_3(\mu-CO)_3(\eta^5-C_9H_7)_3$] (0.40 g, 0.54 mmol) in toluene (100 cm^3) at 60 °C for 3 h. The reaction mixture changed colour from dark green to deep red. The solvent was removed *in vacuo* and the residue extracted with methylene chloride. The reaction mixture was chromatographed on an alumina column. Elution with hexane, hexane–methylene chloride (10 : 1), and methylene chloride gave successively [$Rh(CO)_2(\eta^5-C_9H_7)$], complex (3) (trace), and starting material. Further elution with acetone–methylene chloride (10 : 1) gave on recrystallisation (−20 °C) from hexane–methylene chloride orange *plates* of (5) (0.26 g, 62%) (Found: C, 53.3; H, 3.5. $C_{23}H_{18}ORh_2$ requires C, 53.5; H, 3.5%), ν_{CO} (CH_2Cl_2) at 1 649 cm^{-1}. The mass spectrum (base peak *m/e* 298) showed peaks at *m/e* 516 (*P*, 5%), 488 ($P - CO$, 6%), 436 [$Rh_2(C_9H_7)_2$, 12%], 333 [$Rh(C_9H_7)_2$, 6%], and 298 ($P - RhC_9H_7$, 100%). N.m.r.: ^1H ($CDCl_3$, 30 °C), τ 1.62 [d of t, 2 H, $H^{8,11}$, $J(H^8H^9)$ 5, $J(RhH^8)$ 1.5], 2.5—3.1 (m, 8 H, $H^{4-7,4'-7'}$), 4.0 (s, 2 H, $H^{1,3'}$), 4.2 (s, 2 H, $H^{1',3}$), 4.66 (s, 2 H, $H^{2,2'}$), and 5.82 [d, 2 H, $H^{9,10}$, $J(H^9H^8)$ 5 Hz].



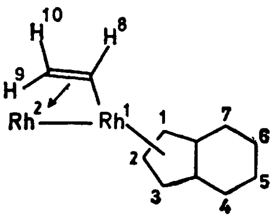
Finally, elution with ethanol followed by recrystallisation from hexane–methylene chloride gave yellow *crystals* of (6) (0.06 g, 12%) (Found: C, 56.2; H, 3.6. $C_{14}H_{11}ORh$ requires C, 56.4; H, 3.7%), ν_{CO} (CH_2Cl_2) at 1 603 cm^{-1}. The mass spectrum (base peak *m/e* 298) showed peaks at *m/e* 298 (*P*, 100%), 270 ($P - CO$, 70%), 218 (RhC_9H_7, 60%), and 115 (C_9H_7, 10%). N.m.r.: ^1H ($CDCl_3$, 30 °C), τ 2.5—3.0 (m, 4 H, H^{4-7}), 4.0 [d, 2 H, $H^{1,3}$, $J(H^2H^1)$ 2.5], 4.5 [quartet, 1 H, H^2, $J(H^1H^2) = J(RhH^2) = 2.5$ Hz], 5.1 (br, s, 2 H, H^8), and 5.3 (br, s, 2 H, H^9).



Pyrolysis of Complex (5).—A solution of (5) (0.02 g, 0.04 mmol) in toluene (30 cm^3) was heated (100 °C) in a sealed Carius tube for 3 d. Removal of the solvent *in vacuo*, followed by chromatography on alumina using ethanol as eluant, afforded yellow crystals of (6) (0.01 g, 50%).

Reaction of Complex (7) *with Carbon Monoxide*.—Carbon monoxide was bubbled through a solution of (5) (0.13 g, 0.35 mmol) in methylene chloride at room temperature. Chromatographic separation of the reaction mixture afforded [$Rh(CO)_2(\eta^5-C_9H_7)$] (45%) and complex (6) (0.07 g, 46%).

Reaction of Complex (3) *with Tetrafluoroboric Acid*.—A solution of HBF_4 in diethyl ether (3.0 cm^3, excess) was added dropwise with stirring (0 °C) to a solution of (3) (0.05 g, 0.08 mmol) in diethyl ether (30 cm^3). The resultant precipitate was washed (3 × 20 cm^3) with diethyl ether and dissolved in methylene chloride. Filtration followed by addition of diethyl ether and cooling (0 °C) gave red *crystals* of (7) (0.04 g, 92%) [Found: C, 43.5; H, 3.2%; *M*, 519 (field desorption mass spectroscopy). $C_{22}H_{17}BF_4O_2Rh_2$ requires C, 43.6; H, 2.8%; *M*, 519], ν_{CO} (CH_2Cl_2) at 2 054s and 1 902s, br cm^{-1}. N.m.r.: ^1H ($CDCl_3$, 30 °C), τ −0.85 (m, 1 H, H^8), 2.3—2.8 (m, 8 H, H^{4-7}, $H^{4'-7'}$), 3.41—4.30 (m, 6 H, H^{1-3}, $H^{1'-3'}$), 6.25 (m, 1 H, H^{10}), and 7.22 (m, 1 H, H^9).



Analysis of that part of the spectrum due to the μ-vinyl fragment using the program NUMARIT afforded the following coupling constants: $J(H^8H^{10})$ 5.8, $J(H^8H^9)$ 11.1, $J(Rh^2H^8)$ 2.1, $J(Rh^1H^8)$ 3.0, $J(H^9H^{10})$ 2.8, $J(Rh^2H^{10})$ 2.4, $J(Rh^1H^{10})$ 2.4, $J(Rh^2H^9)$ 1.2, and $J(Rh^1H^9)$ 1.8 Hz.

Crystal-structure Determination of Complex (3).—The crystal of (3) chosen for intensity measurement was mounted on a Syntex *P*2 four-circle diffractometer and orientated according to methods described earlier.[37] Of a total of 3 841 measured reflections in the range $0 < 2\theta \leqslant 50°$, 2 999 were deemed observed according to the criterion $I > 3.0\sigma(I)$, and only these were used in the solution and refinement of the structure.

Crystal data. $C_{22}H_{16}O_2Rh_2$, $M = 517.8$, Monoclinic, $a = 13.482(3)$, $b = 9.568(3)$, $c = 14.801(6)$ Å, $\beta = 100.69(3)°$, $U = 1\ 864.3(1.0)$ Å^3, $D_m = 1.81$ g cm^{-3}, $Z = 4$, $D_c = 1.84$ g cm^{-3}, $F(000) = 1\ 008$, space group $P2_1/c$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 16.2 cm^{-1}.

Structure solution and refinement. The structure was solved by conventional heavy-atom methods. All non-hydrogen atoms were assigned anisotropic thermal parameters for refinement. Hydrogen atoms for the η^5-indenyl ligands were located on a difference-Fourier map, and allowed to ride with their appropriate carbon atoms assuming sensible bond lengths and angles (C–H 1.08 Å, C–C–H 120°). Isotropic thermal parameters for the indenyl hydrogen atoms were all tied to a common variable.

Finally, hydrogen atoms for the μ-vinylidene fragment were located and were incorporated into the refinement process with no constraints. Weights were applied according to the scheme $w = 1.5106/\sigma^2(F)$ and the refinement converged at $R = 0.021$ ($R' = 0.021$). A final electron-density synthesis showed no peaks >0.3 e Å^{-3}, and no troughs < -0.5 e Å^{-3}. Numerical absorption corrections were applied prior to the structure solution. The atomic scattering factors used were those of ref. 38 for non-hydrogen atoms and of ref. 39 for hydrogens. A correction for the real and imaginary parts of anomalous dispersion for rhodium was also applied. All computational work was carried out at the South Western Universities Regional Computer Centre with the SHELX system[40] of programs. Observed and calculated structure factors, thermal parameters, and least-squares planes are listed in SUP 23161.

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