Synthesis of μ-Carbene and μ-Carbyne Complexes of Rhodium and Cobalt from Substituted Diazirines. Crystal Structures of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2\{\mu\text{-}C(C_6H_4F\text{-}4)(OMe)\}]$ and $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}C_6H_4Me\text{-}4)][BPh_4]$ †

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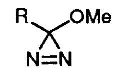
The reaction of aryl(methoxy)diazirines with $[M_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ (M = Rh or Co) affords the μ-carbene complexes $[M_2(\eta^5\text{-}C_5Me_5)(CO)_2\{\mu\text{-}CR(OMe)\}]$ (R = aryl) in excellent yield. The carbonyl groups are terminal in the rhodium complexes, as demonstrated conclusively in an X-ray diffraction study, but bridging for the cobalt complex. Thermolysis of the rhodium complexes results in loss of CO and the formation of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)\{\mu\text{-}CR(OMe)\}]$. Protonation of either the mono- or di-carbonyl rhodium complex with HBF_4 led to the formation of a stable cationic carbyne complex, $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}CR)][BF_4]$; the structure of the related $[BPh_4]^-$ salt was established in a diffraction study. Dynamic processes in the complexes were investigated by variable-temperature NMR spectroscopy.

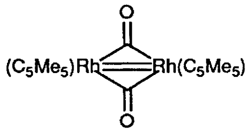
There has been considerable interest in the synthesis of μ-carbene complexes[1] because of their significance in catalytic reactions and as models for carbene species bound to metal surfaces. We now report a new approach to the synthesis of derivatives of cobalt and of rhodium, which should provide access to a wide range of carbene complexes of variable substitution. In our examples a diazirine, **1**, is used as the carbene precursor, and is added across a metal–metal double bond, in a manner directly analogous to the reactions in which cyclopropanes may be prepared from carbene addition to alkenes. There have been many reports of the preparation of metal carbene complexes from diazoalkanes, but our studies[2] on the reaction of methoxy(phenyl)diazirine with $[W(CO)_6]$ and related species represented the first examples of reactions with carbenes derived from diazirines. We have published some preliminary reports of this work.[3–5]

Results and Discussion

Synthesis and Reactions of Rhodium μ-Carbene Complexes.—The complex $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ **2** was originally prepared by Nutton and Maitlis,[6] and the work of Stone[7] and Herrmann[1] and co-workers established an isolobal analogy with the chemistry of alkenes. It was of some surprise to us therefore that the complex was unreactive towards dialkyl-substituted diazirines, such as **3**. This is in contrast to the reactions of diazoalkanes which proceed rapidly at −78 °C to give the μ-carbene complexes.[8]



1a R = C_6H_4Me-4
1b R = C_6H_4F-4



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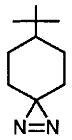

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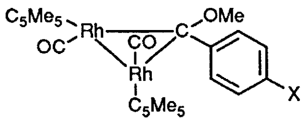

4a X = Me
4b X = F

By contrast, the reaction of complex **2** with arylmethoxydiazirines was rapid and facile. The addition of a pentane solution of an excess of the diazirine at 0 °C to a CH_2Cl_2 solution of **2** resulted in slow discharge of the deep blue colour of the double-bonded precursor. Removal of the solvent under reduced pressure gave a dark red solid residue of **4**. Initial attempts at purification met with considerable difficulties, owing to the presence of large amounts of diazirine decomposition products. Purification was eventually achieved by careful crystallisation from CH_2Cl_2–EtOH at −78 °C, to give **4a** and **4b** in yields of 63 and 49% respectively. The presence of terminal carbonyl ligands was based on IR spectroscopy of the complexes [ν/cm^{-1}(CO) 1961, 1942, **4a**; 1967, 1938, **4b**].

The structures of the complexes in solution were investigated by variable-temperature ^{13}C NMR spectroscopy. At room temperature for each of **4a** and **4b** the carbene carbon centre could be identified unambiguously as a well resolved triplet. The carbonyl resonances, however, were broad featureless signals, barely discernible. Upon cooling to 253 K the carbonyls became clearly visible as two distinct rhodium-coupled triplets. Lowering the temperature to 193 K resulted in no further significant changes to the spectrum. Thus the carbonyls exhibit spin–spin coupling to both ^{103}Rh nuclei, with the magnitude of the coupling approximately half the value expected for a terminal rhodium carbonyl, in addition to being somewhat lower than that expected for a true bridging carbonyl.

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† μ-(4-Fluorophenyl)methoxymethylene-bis[carbonyl(η^5-pentamethylcyclopentadienyl)rhodium] (*Rh–Rh*) and μ-carbonyl-μ-*p*-tolylmethylidyne-bis[(η^5-pentamethylcyclopentadienyl)rhodium] (2*Rh–Rh*) tetraphenylborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

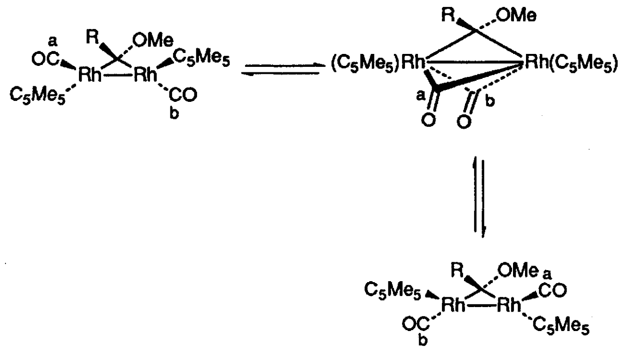


Fig. 1 Mechanism of carbonyl migration in $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2\{\mu\text{-}CR(OMe)\}]$ **4** (R = aryl)

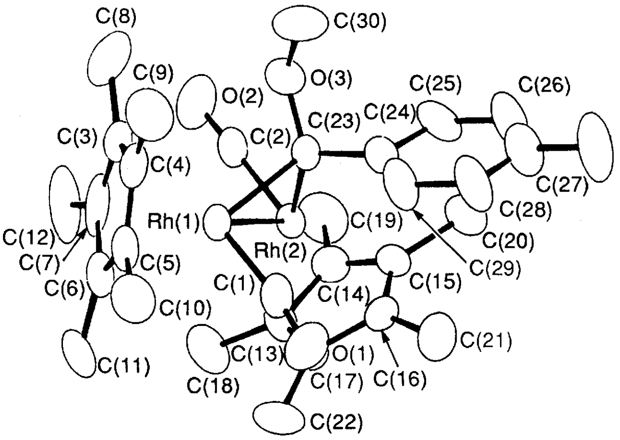
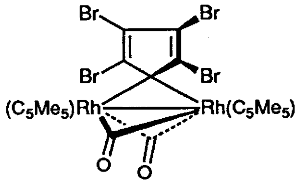


Fig. 2 Structure of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2\{\mu\text{-}C(C_6H_4F\text{-}4)(OMe)\}]$ **4b**



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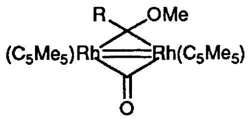


6a R = $C_6H_4Me\text{-}4$
6b R = $C_6H_4F\text{-}4$

Since the IR spectroscopic data and the structure determined in an X-ray diffraction study (see below) clearly establish that the carbonyls are terminal, we could attribute our NMR spectroscopic data to a rapid migration of the carbonyls between the two rhodium atoms, which is not frozen out at 193 K. An alternative explanation, that each carbonyl is coupled directly to one of the rhodium atoms, and virtually to the other, may be ruled out by Stone's work on $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CHCO_2Et)(CO)_2]$, for which the signals for the terminal carbonyls are observed as rhodium-coupled doublets at 223 K, suggesting that virtual coupling is not observed in these systems.[7] Since two separate carbonyl signals are observed at low temperature we can conclude that each migrates across only one stereochemically distinct face of the dimetallacyclopropane ring. This may be achieved by a concerted rotation of the metal centres about the Rh–CR(OMe) axis. This facilitates the formation of a transient triply bridged structure in which the carbonyls adopt a bridging mode of co-ordination above and below the plane of the three-membered ring (Fig. 1). On reverting to the terminal carbonyl species, both carbonyl ligands can be seen to retain their original chemical environment. The broadness of the signals at room temperature may signify the onset of a more comprehensive reorganisation of the carbonyl ligands, but the complex is not sufficiently thermally stable for this to be fully investigated. Full ^1H and ^{13}C NMR data for the complexes are given in Tables 5 and 6.

The structure of the 4-fluorophenyl derivative, **4b**, was established in an X-ray diffraction study (Fig. 2). Atomic co-ordinates are given in Table 1, and intramolecular distances and angles in Table 2. The presence of the terminally bonded carbonyls is confirmed, with the adoption of *trans* stereochemistry to minimise steric interactions between the pentamethylcyclopentadienyl ligands. There is no evidence for any semi-bridging character. It is significant that the arylmethoxycarbene is small enough to permit such an arrangement of carbonyl ligands, since analogous complexes of bulkier carbenes, such as **5**, are forced into the isomeric triply bridging geometry.[8] There are no interactions between the rhodium atoms and the methoxy group. The distance of 2.639(1) Å between the rhodium atoms is unremarkable, and occupies a central position in the range previously reported for rhodium–rhodium single bonds.[9–11] Other bond lengths and angles within the dimetallacyclopropane are also similar to those reported previously, irrespective of the differences in the nature of the bridging carbene ligand.

A notable feature of the chemistry of the μ-dialkylcarbene complexes prepared by Herrmann *et al.*[12] was their ability to undergo decarbonylation under thermal or photochemical conditions, resulting in the adoption by the remaining carbonyl group of a bridging mode of co-ordination, with the restoration of the metal–metal double bond. An entirely analogous process was noted for **4**. Thermolysis in refluxing toluene resulted in a colour change from deep red to turquoise, with the progress of the reaction monitored by IR spectroscopy. Upon completion of the decarbonylation, blue-black microcrystals of compound **6** could be isolated in *ca.* 60% yield. Photochemical decarbonylation of a hexane solution was complete in 45 min, giving **6** as the sole product. An interesting contrast, however, with the dialkylcarbene derivatives is that in our case the decarbonylation appears to be irreversible. Prolonged bubbling of CO through solutions of **6** left the complexes unchanged.

For compound **6a** the observation in the IR spectrum of a carbonyl absorption band at 1762 cm^{-1} indicated the bridging nature of the carbonyl ligand, and fast atom bombardment (FAB) mass spectrometry allowed the observation of the appropriate molecular ion. However, at room temperature, the ^1H NMR spectrum in the aromatic region was essentially featureless, although the remainder of the spectrum was as expected. When the spectrum was recorded at 253 K four multiplets were noted in the aromatic region, each corresponding to one proton. A selective population-transfer experiment established that these were due to two pairs of protons undergoing exchange. At room temperature the signals are so broad as to be unobservable. Irradiation of the methyl protons gave Overhauser enhancements of the signals at δ 7.11 and 6.92, establishing that these arise from the nearby protons H^3 and H^5. The remaining pair of signals, at δ 8.07 and 6.39 due to H^2 and H^6, indicate that these protons are in highly distinct environments in the static structure. The exchange process showed similar effects on the ^{13}C NMR spectrum of **6a**, and at 253 K the six carbon atoms of the aromatic ring were clearly revealed. At room temperature two of these, those at δ 127.3 and 126.1, had coalesced into a single broad resonance, thus allowing us to identify the exchanging pairs.

The asymmetry of the aromatic ring in compound **6** must arise from a lack of free rotation about the bond between the bridging carbene carbon atom and the attached aryl carbon. Whilst this could be due simply to steric interactions with the pentamethylcyclopentadienyl ligand, it could also be attributed to a weak interaction of the aryl ring with one of the rhodium atoms, as in **7**. There is ample precedent for such interactions in, for example, $[Ru_2(cp)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CPh_2)]$, (cp = $\eta\text{-}C_5H_5$), $[Mo_2(cp)_2(CO)_3(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4Me\text{-}4)_2\}]$ and $[(Me_3P)_2Pt\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}CO)W(cp)(CO)]^+$, and

Table 1 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for compound **4b**

Atom	*x*	*y*	*z*
Rh(1)	4266.9(9)	2568.6(5)	2958.6(5)
Rh(2)	4089.0(9)	3742.8(5)	1951.9(5)
F	9190(9)	5497(5)	4395(5)
O(1)	7222(8)	2257(6)	2902(6)
O(2)	1096(9)	3998(6)	1962(6)
O(3)	3337(8)	4096(5)	3469(5)
C(1)	6084(11)	2443(6)	2921(7)
C(2)	2287(11)	3879(6)	2002(6)
C(3)	2204(12)	2236(7)	3352(7)
C(4)	3291(12)	1878(7)	3848(8)
C(5)	3987(11)	1357(7)	3383(7)
C(6)	3276(11)	1365(6)	2598(7)
C(7)	2162(12)	1938(7)	2599(9)
C(8)	1083(14)	2731(9)	3611(10)
C(9)	3607(17)	1949(9)	4737(8)
C(10)	5182(14)	819(7)	3690(9)
C(11)	3557(17)	883(8)	1928(9)
C(12)	1044(15)	2059(8)	1913(11)
C(13)	4203(12)	3512(6)	680(7)
C(14)	4070(12)	4327(7)	824(6)
C(15)	5264(12)	4605(6)	1294(7)
C(16)	6145(11)	3945(7)	1487(7)
C(17)	5477(12)	3269(6)	1082(7)
C(18)	3230(15)	2967(8)	159(8)
C(19)	2879(15)	4868(8)	458(8)
C(20)	5648(15)	5478(7)	1490(8)
C(21)	7620(14)	3959(8)	1904(8)
C(22)	6090(14)	2449(8)	1040(7)
C(23)	4457(10)	3782(6)	3154(6)
C(24)	5754(12)	4192(6)	3489(7)
C(25)	5804(15)	5024(8)	3370(7)
C(26)	6960(15)	5439(7)	3673(8)
C(27)	8040(14)	5063(8)	4091(8)
C(28)	8111(15)	4267(8)	4243(8)
C(29)	6907(13)	3847(7)	3932(7)
C(30)	3539(15)	4220(10)	4278(7)

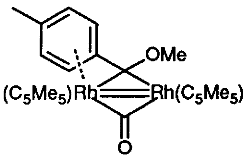
Table 2 Selected intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses for compound **4b**

Rh(1)–Rh(2)	2.639(1)	Rh(1)–Cen(1)	1.919
Rh(1)–C(1)	1.785(11)	Rh(1)–C(23)	2.081(10)
Rh(2)–Cen(2)	1.928	Rh(2)–C(2)	1.777(11)
Rh(2)–C(23)	2.079(10)	O(1)–C(1)	1.152(14)
O(2)–C(2)	1.164(14)	C(23)–O(3)	1.394(13)
Rh(1)–C(3)	2.280(12)	Rh(1)–C(4)	2.261(13)
Rh(1)–C(5)	2.206(11)	Rh(1)–C(6)	2.294(11)
Rh(1)–C(7)	2.304(12)	Rh(2)–C(13)	2.276(12)
Rh(2)–C(14)	2.203(11)	Rh(2)–C(15)	2.266(12)
Rh(2)–C(16)	2.288(11)	Rh(2)–C(17)	2.319(12)
C(27)–F	1.37(2)	C(23)–C(24)	1.476(14)
O(3)–C(30)	1.41(2)	C(24)–C(25)	1.42(2)
C(24)–C(29)	1.39(2)	C(25)–C(26)	1.36(2)
C(26)–C(27)	1.34(2)	C(27)–C(28)	1.37(2)
C(28)–C(29)	1.40(2)		
Rh(2)–Rh(1)–Cen(1)	132.7	Rh(2)–Rh(1)–C(1)	91.7(4)
Rh(2)–Rh(1)–C(23)	50.6(3)	Cen(1)–Rh(1)–C(1)	126.3
Cen(1)–Rh(1)–C(23)	136.0	C(1)–Rh(1)–C(23)	93.4(4)
Rh(1)–Rh(2)–Cen(2)	131.6	Rh(1)–Rh(2)–C(2)	91.7(3)
Rh(1)–Rh(2)–C(23)	50.7(3)	Cen(2)–Rh(2)–C(2)	127.3
Cen(2)–Rh(2)–C(23)	140.3	C(2)–Rh(2)–C(23)	88.1(4)
Rh(1)–C(1)–O(1)	171(1)	Rh(2)–C(2)–O(2)	173(1)
Rh(1)–C(23)–Rh(2)	78.8(4)	Rh(1)–C(23)–O(3)	112.6(7)
Rh(2)–C(23)–O(3)	112.7(6)	O(3)–C(23)–C(24)	109.5(9)
C(23)–O(3)–C(30)	116.9(9)	C(23)–C(24)–C(25)	117(1)
C(23)–C(24)–C(29)	126(1)	C(25)–C(24)–C(29)	117(1)
C(24)–C(25)–C(26)	120(1)	C(25)–C(26)–C(27)	120(1)
C(26)–C(27)–C(28)	126(1)	C(26)–C(27)–F	119(1)
C(28)–C(27)–F	116(1)	C(27)–C(28)–C(29)	114(1)
C(24)–C(29)–C(28)	124(1)		

Cen(1) and Cen(2) are the centroids of the cyclopentadienyl rings C(3)–C(7) and C(13)–C(17) respectively.

there are striking similarities in the NMR spectroscopic data reported for these species with those which we observe.[13,14] However, in these cases the aryl ring functions as a true two-electron donor to the metal centre. In the case of compound **6** this is unnecessary, since both rhodium atoms have a full complement of electrons, if we assume metal–metal double bonding. Thus any interaction would be weak. Furthermore, in order to account for the equivalence of the two rhodium centres, the interacting aryl ring must be switching between them. This must be fast on the NMR spectroscopic time-scale, and must occur without free rotation of the aromatic ring.

Synthesis and Dynamic Behaviour of Cobalt μ-Carbene Complexes.—The first μ-carbene complexes of cobalt were reported in 1967, and were the first examples of bridging carbene transition-metal derivatives.[15,16] A larger range of such complexes was reported by Herrman *et al.*,[17] who used diazoalkanes as carbene-transfer agents. The reaction between $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ and **1** proceeded smoothly and cleanly, resulting in conversion to a single new species, **8**. The complexes, which were extremely air-sensitive, were purified by crystallisation from EtOH–CH_2Cl_2 at −78 °C, to remove impurities derived from diazirine decomposition.



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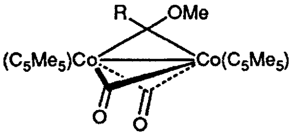
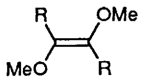


8a R = C_6H_4Me-4
8b R = C_6H_4F-4

There are a number of differences from the rhodium series. First, IR spectroscopy [ν/cm^{-1}(CO) 1817, 1781, **8a**; 1820, 1783, **8b**] indicated that the carbonyl groups were bridging rather than terminal. Furthermore, the aromatic region of the NMR spectrum showed rather broad signals at room temperature, which were partially resolved at lower temperature. The ^{13}C NMR spectrum showed related features, with six aromatic signals at low temperature, and coalescence of two pairs at room temperature. In the absence of definitive evidence from an X-ray diffraction study, we suggest that this dynamic process is similar to that noted for the rhodium monocarbonyl carbene derivatives, with a weak interaction between the aromatic ring and the metal centre, and switching between the metals without rotation of the arene ring. The carbonyl carbons are distinct at low temperatures, as expected, and their resonances fall in the range typical for bridging carbonyl ligands (δ 251.4, 249.2, **8a**; 252.0, 250.4, **8b**). At room temperature a single broad resonance is observed. We postulate that there is an equilibrium with an unseen terminal isomer, a process which is well documented for dicobalt complexes.[18]

Mechanism of Reaction of Diazirines with Metal–Metal Double Bonds.—Three distinct mechanistic pathways might be considered for the reactions of the diazirines with the metal–metal double bonds in $[M_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ (M = Rh or Co). These are a direct interaction of the diazirines with the complexes, decomposition to the diazoalkane followed by reaction, or decomposition to the carbene, and concerted addition. When the addition reaction was attempted at temperatures (−30 °C) below that at which the diazirine



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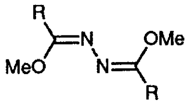

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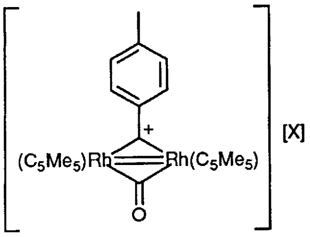
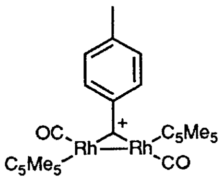


11 X = BF_4
12 X = BPh_4



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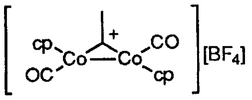

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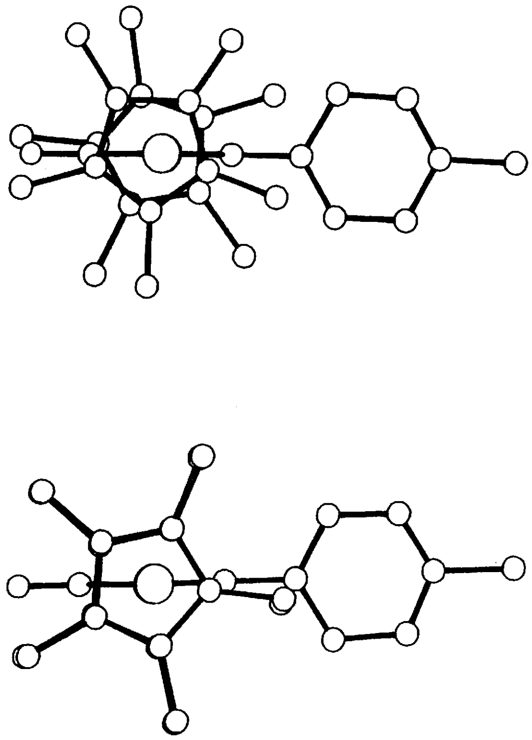

Fig. 3 Structure of the two crystallographically distinct cations of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)][BPh_4]$ **12**

decomposes no reaction was noted. This suggests that a pathway involving direct reaction of the complexes with intact diazirine is unlikely, a hypothesis which is reinforced by the lack of reactivity of the dialkyldiazirines.

The conclusions drawn by both Moss[19] and Liu[20] from studies of the thermal decomposition of methoxy(phenyl)diazirine are very strongly in favour of a direct decomposition to give the carbene. Whilst the data fall short of absolute proof of concerted dinitrogen loss, they restrict the lifetime of any diazoalkane transient intermediate to an extent that makes it an unlikely candidate for our high-yielding reaction. Thermolysis of the diazirine in pentane solution gave a mixture of the carbene dimer **9** and the azine **10**, in 14 and 44% yields respectively. When the decomposition was carried out in the presence of a catalytic amount of compound **4a** the products and their proportions were not significantly altered. This suggests that the bridging carbene product is relatively inert to reaction with either diazirine or further carbene. It was also notable that there was no reaction between the aryl(methoxy)-diazirines and $[Co_2(CO)_4(\mu\text{-}CO)_2(\mu\text{-}dppm)]$ (dppm = $Ph_2PCH_2PPh_2$), though this latter reacts readily with diazoalkanes. We would therefore suggest that our reactions proceed *via* a concerted addition of the carbene to the metal–metal double bond, this being followed in the rhodium series by a rearrangement of the initially formed triply bridged species.

Synthesis of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)][BF_4]$.—Simple mononuclear complexes of aryl(methoxy)-carbenes are not readily protonated, being susceptible instead to nucleophilic attack. The opposite is true for dinuclear bridging aryl(methoxy)carbene derivatives, with carbyne complexes formed from $[(Me_3P)(OC)_4M\{\mu\text{-}C(R)OMe\}Pt(PMe_3)_2]$ (R = aryl) on reaction with H^+ or $[Me_3O][BF_4]$.[21] Reaction of a diethyl ether solution of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2\{\mu\text{-}C(C_6H_4Me\text{-}4)(OMe)\}]$ with an excess of $HBF_4\cdot Et_2O$ resulted in the precipitation of a dark purple solid in quantitative yield. After recrystallisation, $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)][BF_4]$ **11** was obtained as purplish black fibrous crystals, with a greenish metallic lustre. The new complex dissolved readily in acetone, dichloromethane and ethanol, giving intensely coloured magenta solutions, which were stable to air and moisture, as was the solid material. The use of trimethyloxonium tetrafluoroborate gave an identical product, apparently in quantitative yield. Given that the product was shown to contain only one, bridging, carbonyl group (see below), its synthesis from **6a** was also studied. Addition of $HBF_4\cdot Et_2O$ to **6a** again resulted in the quantitative formation of **11**.

The complex was characterised spectroscopically; the bridging nature of the carbonyl group could be deduced from the IR spectrum [ν/cm^{-1} (CO) 1855 (in CH_2Cl_2)]. The marked shift to higher wavenumber relative to the precursors reflects a sharp decrease in the magnitude of the π-back donation to the ligand, as would be expected for a cationic species. In the ^{13}C NMR spectrum the carbonyl carbon atom was observed at δ 234.9 as a rhodium-coupled triplet (J = 54 Hz), again indicating a bridging mode of co-ordination. A second low-field rhodium-coupled triplet [δ 380.5, J(CRh) = 51 Hz] was assigned to the carbyne carbon atom.

Two possible mechanisms may be considered for the reaction forming the carbyne complex. The first involves CO loss from **4a** to give **6a** prior to protonation. This seems to be relatively unlikely, since the thermolytic or photolytic conversion of **4a** was relatively slow, and there is no reason to suppose that CO loss will be acid catalysed. A more probable route involves the initial formation of **13**, followed by rapid decarbonylation. The instability of **13** seems a little surprising in view of the synthetic accessibility of **14**,[22] and the generally greater stability of rhodium complexes over their cobalt congeners. The most likely explanation seems to involve the particular stability of the product, which is discussed further below.

Attempts to grow a crystal of the BF_4^- salt, **11**, suitable for an X-ray diffraction study were not successful, but good crystals of the BPh_4^- salt, **12**, were obtained. The complex crystallised in a triclinic unit cell in space group $P\bar{1}$. The unit cell contains four pairs of ions, two crystallographically independent pairs. Atomic coordinates are given in Table 3, and selected intramolecular bond lengths and angles in Table 4. The two distinct cations are shown in Fig. 3 and a view of one of them viewed perpendicular to the Rh_2C_2 plane in Fig. 4.

The two rhodium atoms in compound **12** are separated by 2.564(1) Å [2.571(1) Å, for the crystallographically distinct cation], and are doubly bridged, in a symmetrical manner, by

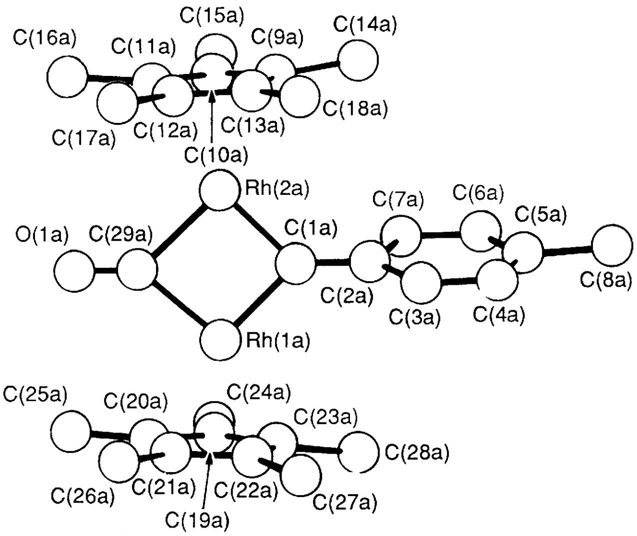

Fig. 4 Structure of one of the two crystallographically distinct cations of $[Rh_2(\eta^5-C_5Me_5)_2(\mu-CO)(\mu-CC_6H_4Me-4)][BPh_4]$ **12**, viewed perpendicular to the Rh_2C_2 plane

the carbonyl and carbyne ligand to form a planar $\{Rh_2C_2\}$ four-membered ring. The metal–metal distance is essentially identical to that in $[Rh_2(\eta^5-C_5Me_5)_2(\mu-CO)_2]$, clearly indicating formal double-bond character.[23] The centroids of the two pentamethylcyclopentadienyl rings and the rhodium atoms are arranged in essentially linear manner, with the rings being tilted away from the μ-carbyne ligand, this being more pronounced in one than in the other of the crystallographically distinct cations. Interestingly the relative orientation of the pentamethylcyclopentadienyl rings is eclipsed in one of the cations, and staggered in the other. In both cations the methyl groups are bent away from the metal centre to alleviate steric crowding. The plane of the aryl ring is close to parallel with those of the pentamethylcyclopetadienyl rings, again to minimise steric repulsion.

The single carbonyl ligand bridging the two rhodium atoms is symmetrically disposed, with a C–Rh bond distance of 1.96(1) Å. This is short, but not beyond the normal range. There is a marked shortening of the bond between the rhodium atoms and the carbyne carbon, relative to the carbene precursor, presumably in part due to the shortening of the metal–metal bond. An alternative approach would be to consider the complex as a dimetallacyclopropenyl cation, with some delocalisation, and hence bond shortening. However, there are considerable variations in the rhodium–carbon bond lengths. This analogy may also have some bearing on the unexpectedly high stability of the complex to air and moisture, not normally observed for complexes containing either metal–metal double bonds, or cationic carbyne ligands.

The addition of methoxide ion (though not methanol) to compound **11** resulted in the regeneration of **6a**. This route, if shown to be general for a range of nucleophiles, may offer considerable promise for the synthesis of previously inaccessible bridging carbene complexes.

Experimental

General Procedures.—All manipulations were carried out under an atmosphere of dry nitrogen according to standard vacuum-line techniques. Glassware was flame dried under vacuum prior to use. All manipulations involving diazirines were carried out with the rigorous exclusion of light. In view of their well known instability, and propensity towards detonation, the diazirines were not subjected to distillation, elemental analysis or mass spectrometry.

Preparations.—*Bromo*(4-*methylphenyl*)*diazirine.* This was prepared by the method of Graham[24] on a 4 g scale in 39% yield in two steps from 4-methylbenzonitrile.

Methoxy(4-*methylphenyl*)*diazirine* **1a**. Treatment of bromo(4-methylphenyl)diazirine (1.0 g) with sodium methoxide in dimethylethanamide–$P(NMe_2)_3O$, according to the method of Moss,[25] afforded a pentane solution of methoxy(4-methylphenyl)diazirine. Solutions were stored at −78 °C, and used within 24 h of preparation.

4-*Fluorobenzamidine.* Sodium methoxide (4 g) was added to a solution of 4-fluorobenzonitrile (100 g, 0.83 mol) in dry methanol (800 cm^3), and the solution stirred for 48 h at room temperature. Ammonium chloride (43 g, 0.804 mol) was added and the stirring continued for 24 h. The mixture was filtered, the solvent removed *in vacuo*, and the off-white residue taken up in a mixture of 2 mol dm^{-3} HCl (330 cm^3) and CH_2Cl_2 (80 cm^3). The aqueous layer was separated and washed with further CH_2Cl_2 (2 × 80 cm^3) to remove unreacted 4-fluorobenzonitrile. Addition of 5 mol dm^{-3} NaOH solution resulted in precipitation of the free amidine, which was extracted into CH_2Cl_2 (4 × 20 cm^3). The combined organic extract was dried and the solvent removed under reduced pressure to give crude 4-fluorobenzamidine (17.0 g, 15%) as an off-white solid, which was used without further purification. Infrared (KBr): 3485 (NH) and 1644 (C=N) cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.61 [dd, $^4J(HF) = 5.3$, $^3J(HH) = 9.0$, H^2, 2 H], 7.07 [t, $^3J(HH) = {}^3J(HF) = 8.7$, H^3, 2 H] and 5.73 [br s, $C(NH_2)NH$, 3 H]; ^{19}F, δ −110.4 [t of t, $^3J(HF) = 8.5$, $^4J(HF) = 5.3$]; $^{13}C-\{^1H\}$, δ 164.0 (C^1), 163.3 [d, $^1J(CF) = 250$, C^4], 127.4 [d, $^3J(CF) = 8$, C^2] and 115.0 [d, $^2J(CF) = 22$ Hz, C^3].

Bromo(4-*fluorophenyl*)*diazirine.* A three-necked flask (1 l) fitted with a thermometer, mechanical stirrer and pressure-equalising funnel was charged with lithium bromide (10.5 g), dimethyl sulphoxide (dmso) (105 cm^3), hexane (50 cm^3) and 4-fluorobenzamidine (3.4 g, 0.025 mol). The mixture was cooled to 10 °C and shielded from light. A solution of sodium hypobromite [prepared by dropwise addition of bromine (12 cm^3) to a cooled (−5 °C) solution of NaBr (78 g) and NaOH (25 g) in water (180 cm^3)] was added to the dropping funnel and added slowly to the reaction mixture with vigorous stirring, at a rate such that the temperature did not exceed 30 °C. The mixture was stirred for 1 h, quenched with water (180 cm^3) and separated. The aqueous layer was extracted further with hexane (4 × 25 cm^3), and the combined organic extract was dried ($MgSO_4$). Concentration under reduced pressure yielded a red oil, which was purified by column chromatography (SiO_2, pentane, exclusion of light). The diazirine was obtained as the first, yellow fraction. Removal of the solvent under reduced pressure afforded bromo(4-fluorophenyl)diazirine (2.2 g, 41%) as a greenish yellow oil. Infrared (liquid film): 1564 cm^{-1} (N=N). NMR ($CDCl_3$): ^1H (coupling constants from simulation using PANIC), δ 7.10 [dd, $^3J(HH) = 8.8$, $^4J(HF) = 5.0$, $^4J(HH) = 2.7$, $^5J(HH) = 0.4$, H^2, H^6, 2 H] and 7.03 [dd, $^3J(HF) = 8.2$, H^3, H^5, 2 H]; $^{13}C-\{^1H\}$, δ 163.4 [d, $^1J(CF) = 250$, C^4], 132.8 (C^1), 128.6 [d, $^3J(CF) = 9$, C^2, C^6], 115.6 [d, $^2J(CF) = 23$, C^3, C^5] and 37.1 (C_α), ^{19}F, δ −111.5 [tt, $^3J(HF) = 7.5$, $^4J(HF) = 5.8$ Hz].

(4-*Fluorophenyl*)*methoxydiazirine* **1b**. Treatment of bromo(4-fluorophenyl)diazirine with sodium methoxide in dimethylethanamide–$P(NMe_2)_3O$, according to the method of Moss,[25] yielded a pentane solution of (4-fluorophenyl)methoxydiazirine. Solvent was removed from a small volume of the pentane solution under reduced pressure (−30 °C; 10^{-1} Torr, *ca.* 13.3 Pa) to give the crude diazirine as a greenish yellow oil. NMR ($CDCl_3$, 243 K): ^1H, δ 7.07 [t, $^3J(HH) = {}^3J(HF) = 8.6$, H^3, H^5, 2 H], 6.95 [dd, $^3J(HH) = 8.8$, $^4J(HF) = 5.1$, H^2, H^6, 2 H] and 3.37 (OMe, 3 H); ^{19}F, δ −113.0 [tt, $^3J(HF) = 8.1$, $^4J(HF) = 5.6$ Hz].

Di-μ-carbonyl-bis[(η^5-*pentamethylcyclopentadienyl*)*rhodium*] **2**. The compound $[Rh_2(\eta^5-C_5Me_5)_2(\mu-Cl)_2Cl_2]$ was prepared by the method of Haszeldine[26] on a 4.4 g scale in 93% yield, $[Rh(\eta^5-C_5Me_5)_2(CO)_2]$ was prepared according to the method

Table 3 Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses for compound **12**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	10 356.3(8)	3 955.9(6)	1 214.7(3)	C(23a)	6 335(11)	2 181(7)	7 040(4)
Rh(2)	8 638.7(8)	2 754.3(6)	750.1(3)	C(24a)	8 017(14)	2 806(9)	6 633(6)
O(1)	8 775(11)	4 288(7)	285(4)	C(25a)	7 472(17)	903(11)	5 906(6)
C(1)	9 858(10)	2 863(7)	1 357(4)	C(26a)	5 413(17)	−151(11)	6 264(6)
C(2)	10 245(10)	2 386(7)	1 739(4)	C(27a)	4 773(17)	1 124(11)	7 258(7)
C(3)	9 725(12)	2 513(8)	2 160(5)	C(28a)	6 386(14)	2 942(9)	7 476(5)
C(4)	10 068(13)	2 026(8)	2 543(5)	C(29a)	4 435(11)	1 501(7)	5 566(4)
C(5)	10 950(12)	1 401(8)	2 480(5)	B(1)	2 340(13)	7 380(8)	5 976(5)
C(6)	11 466(13)	1 269(8)	2 064(5)	C(30)	2 234(11)	6 882(8)	5 374(4)
C(7)	11 160(12)	1 744(8)	1 687(5)	C(31)	1 424(11)	6 154(7)	5 122(4)
C(8)	11 331(15)	879(10)	2 907(6)	C(32)	1 457(12)	5 694(8)	4 637(5)
C(9)	7 116(14)	1 845(9)	748(5)	C(33)	2 317(13)	5 946(9)	4 382(5)
C(10)	8 035(16)	1 396(10)	478(6)	C(34)	3 151(15)	6 692(9)	4 623(6)
C(11)	7 989(16)	1 728(10)	79(6)	C(35)	3 121(13)	7 149(8)	5 106(5)
C(12)	7 205(15)	2 341(10)	40(6)	C(36)	3 743(10)	7 260(7)	6 280(4)
C(13)	6 632(14)	2 427(9)	436(5)	C(37)	4 393(12)	7 876(8)	6 693(4)
C(14)	6 551(29)	1 855(18)	1 218(10)	C(38)	5 614(13)	7 744(8)	6 947(5)
C(15)	8 669(30)	739(18)	771(11)	C(39)	6 173(12)	7 009(8)	6 785(5)
C(16)	8 800(31)	1 317(19)	−291(11)	C(40)	5 601(12)	6 405(8)	6 398(5)
C(17)	6 881(26)	2 842(16)	−387(10)	C(41)	4 389(11)	6 490(7)	6 126(4)
C(18)	5 593(25)	3 088(16)	514(9)	C(42)	1 321(10)	6 890(7)	6 200(4)
C(19)	12 365(11)	4 323(8)	1 501(4)	C(43)	14(11)	6 999(7)	6 043(4)
C(20)	11 914(11)	4 763(7)	1 081(4)	C(44)	−898(11)	6 556(8)	6 201(4)
C(21)	11 036(12)	5 335(8)	1 240(5)	C(45)	−567(11)	5 992(7)	6 519(4)
C(22)	10 880(12)	5 246(8)	1 724(5)	C(46)	663(11)	5 897(7)	6 692(4)
C(23)	11 718(11)	4 639(7)	1 885(4)	C(47)	1 606(10)	6 336(7)	6 531(4)
C(24)	13 360(14)	3 687(9)	1 501(5)	C(48)	2 055(12)	8 414(8)	6 038(5)
C(25)	12 342(15)	4 590(10)	590(6)	C(49)	2 195(14)	8 917(9)	5 663(5)
C(26)	10 390(14)	5 984(9)	930(5)	C(50)	2 008(17)	9 860(11)	5 791(7)
C(27)	10 070(16)	5 774(11)	2 020(6)	C(51)	1 716(16)	10 208(11)	6 205(6)
C(28)	11 945(15)	4 413(10)	2 400(6)	C(52)	1 581(16)	9 819(10)	6 593(6)
C(29)	9 075(12)	3 874(8)	594(5)	C(53)	1 771(14)	8 858(9)	6 484(5)
Rh(1a)	5 101.7(8)	1 982.5(5)	6 286.0(3)	B(1a)	2 872(14)	1 692(9)	8 871(5)
Rh(2a)	3 374.9(7)	2 492.5(5)	5 652.8(3)	C(30a)	2 882(11)	1 548(7)	9 433(4)
O(1a)	4 596(9)	921(6)	5 233(3)	C(31a)	3 717(12)	1 013(8)	9 689(5)
C(1a)	4 044(10)	2 914(7)	6 359(4)	C(32a)	3 745(14)	920(9)	10 175(5)
C(2a)	3 831(11)	3 601(7)	6 750(4)	C(33a)	2 942(14)	1 351(9)	10 452(5)
C(3a)	3 111(13)	3 428(8)	7 087(5)	C(34a)	2 101(13)	1 875(9)	10 222(5)
C(4a)	2 895(15)	4 116(9)	7 464(6)	C(35a)	2 066(12)	1 978(8)	9 730(5)
C(5a)	3 365(14)	4 914(9)	7 500(5)	C(36a)	1 454(12)	1 644(8)	8 526(5)
C(6a)	4 074(13)	5 140(9)	7 203(5)	C(37a)	1 322(16)	1 945(11)	8 066(6)
C(7a)	4 334(13)	4 457(8)	6 798(5)	C(38a)	48(21)	1 813(13)	7 732(8)
C(8a)	3 081(19)	5 716(12)	7 929(7)	C(39a)	−876(18)	1 498(12)	7 869(7)
C(9a)	2 030(11)	3 471(7)	5 461(4)	C(40a)	−792(19)	1 178(12)	8 295(7)
C(10a)	2 908(10)	3 365(7)	5 130(4)	C(41a)	446(14)	1 246(9)	8 641(5)
C(11a)	2 698(11)	2 492(7)	4 835(4)	C(42a)	3 622(12)	901(8)	8 568(4)
C(12a)	1 813(11)	2 052(7)	4 992(4)	C(43a)	4 949(13)	879(9)	8 729(5)
C(13a)	1 395(11)	2 662(7)	5 388(4)	C(44a)	5 573(15)	201(10)	8 498(6)
C(14a)	1 884(12)	4 321(8)	5 809(5)	C(45a)	4 973(15)	−445(10)	8 116(6)
C(15a)	3 744(13)	4 098(8)	5 065(5)	C(46a)	3 730(14)	−434(9)	7 943(5)
C(16a)	3 361(14)	2 118(9)	4 397(5)	C(47a)	3 036(12)	257(8)	8 179(5)
C(17a)	1 248(14)	1 106(9)	4 743(5)	C(48a)	3 503(12)	2 685(8)	8 896(5)
C(18a)	360(13)	2 447(8)	5 637(5)	C(49a)	3 266(14)	3 417(9)	9 241(5)
C(19a)	7 076(11)	2 116(7)	6 658(4)	C(50a)	3 706(15)	4 269(10)	9 247(6)
C(20a)	6 867(12)	1 265(8)	6 346(5)	C(51a)	4 487(16)	4 407(10)	8 942(6)
C(21a)	5 936(13)	786(9)	6 508(5)	C(52a)	4 813(18)	3 689(11)	8 610(7)
C(22a)	5 651(12)	1 379(8)	6 936(5)	C(53a)	4 311(15)	2 856(10)	8 589(6)

of Maitlis[27] in 78% yield on a 2 g scale, and [$Rh_2(\eta^5$-$C_5Me_5)_2(\mu$-$CO)_2$] was prepared according to the method of Stone[28] in 66% yield on an 0.8 g scale.

μ-*(4-Fluorophenyl)methoxymethylene-bis*[*carbonyl*(η^5-*pentamethylcyclopentadienyl*)*rhodium*] **4b**. A pentane solution of (4-fluorophenyl)methoxydiazirine was prepared using 0.4 g of the bromo-substituted precursor. This was added *via* a *cannula* in several portions with rapid stirring, over a period of *ca.* 3 h, to a solution of [$Rh_2(\eta^5$-$C_5Me_5)_2(\mu$-$CO)_2$] (464 mg, 0.87 mmol) in pentane (150 cm^3). Addition of the diazirine solution was continued until complete discharge of the intense blue colour of the unsaturated precursor was effected. The resulting deep red solution was stirred for 1 h, and then the solvent was removed under reduced pressure to give the crude product as a dark red solid. Recrystallisation (CH_2Cl_2–EtOH, −40 °C) afforded [$Rh_2(\eta^5$-$C_5Me_5)_2(CO)_2\{\mu$-$C(C_6H_4F$-$4)(OMe)\}$] (285 mg, 49%) as deep red prisms. Infrared (KBr): 1967 and 1938 cm^{-1}. ^{19}F NMR ($CDCl_3$, 298 K): δ −118.7 [tt, ^3J(HF) = 8.8, ^4J(HF) = 5.7 Hz].

μ-*Carbonyl*-μ-*(4-fluorophenyl)methoxymethylene-bis*[(η^5-*pentamethylcyclopentadienyl*)*rhodium*] **6b**. A solution of [$Rh_2(\eta^5$-$C_5Me_5)_2(CO)_2\{\mu$-$C(C_6H_4F$-$4)(OMe)\}$] (215 mg, 0.32 mmol) in toluene (20 cm^3) was stirred, and heated under reflux for 17 h. The resulting intensely coloured turquoise solution was filtered, and the solvent removed under reduced pressure. Recrystallisation of the solid (pentane, −78 °C) afforded

Table 4 Selected intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses for compound **12**

Rh(1)–Rh(2)	2.571(1)	Rh(1a)–Rh(2a)	2.564(1)	Rh(1)–C(1)	1.922(12)	Rh(1a)–C(1a)	1.882(11)
Rh(1)–C(29)	1.967(12)	Rh(1a)–C(29a)	1.958(11)	Rh(1)–Cp(2)	1.858	Rh(1a)–Cp(2a)	1.851
Rh(2)–C(1)	1.896(10)	Rh(2a)–C(1a)	1.913(10)	Rh(2)–C(29)	1.960(14)	Rh(2a)–C(29a)	1.960(12)
Rh(2)–Cp(1)	1.845	Rh(2a)–Cp(1a)	1.848	O(1)–C(29)	1.17(2)	O(1a)–C(29a)	1.197(14)
C(1)–C(2)	1.42(2)	C(1a)–C(2a)	1.42(2)	C(2)–C(3)	1.38(2)	C(2a)–C(3a)	1.40(2)
C(2)–C(7)	1.44(2)	C(2a)–C(7a)	1.41(2)	C(3)–C(4)	1.42(2)	C(3a)–C(4a)	1.39(2)
C(4)–C(5)	1.40(2)	C(4a)–C(5a)	1.32(2)	C(5)–C(6)	1.37(2)	C(5a)–C(6a)	1.33(2)
C(5)–C(8)	1.56(2)	C(5a)–C(8a)	1.62(2)	C(6)–C(7)	1.39(2)	C(6a)–C(7a)	1.46(2)
Rh(2)–Rh(1)–C(1)	47.2(3)	Rh(2a)–Rh(1a)–C(1a)	48.0(3)	Rh(2)–Rh(1)–C(29)	49.0(4)	Rh(2a)–Rh(1a)–C(29a)	49.1(4)
Rh(2)–Rh(1)–Cp(2)	174.0	Rh(2a)–Rh(1a)–Cp(2a)	175.2	C(1)–Rh(1)–C(29)	96.2(5)	C(1a)–Rh(1a)–C(29a)	97.1(5)
C(1)–Rh(1)–Cp(2)	138.4	C(1a)–Rh(1a)–Cp(2a)	136.8	C(29)–Rh(1)–Cp(2)	125.4	C(29a)–Rh(1a)–Cp(2a)	126.1
Rh(1)–Rh(2)–C(1)	48.1(3)	Rh(1a)–Rh(2a)–C(1a)	47.0(3)	Rh(1)–Rh(2)–C(29)	49.2(3)	Rh(1a)–Rh(2a)–C(29a)	49.1(3)
Rh(1)–Rh(2)–Cp(1)	173.7	Rh(1a)–Rh(2a)–Cp(1a)	176.0	C(1)–Rh(2)–C(29)	97.3(5)	C(1a)–Rh(2a)–C(29a)	96.0(5)
C(1)–Rh(2)–Cp(1)	137.9	C(1a)–Rh(2a)–Cp(1a)	136.9	C(29)–Rh(2)–Cp(1)	124.8	C(29a)–Rh(2a)–Cp(1a)	127.0
Rh(1)–C(1)–Rh(2)	84.7(5)	Rh(1a)–C(1a)–Rh(2a)	85.0(4)	Rh(1)–C(1)–C(2)	136.5(7)	Rh(1a)–C(1a)–C(2a)	137.9(8)
Rh(2)–C(1)–C(2)	138.8(8)	Rh(2a)–C(1a)–C(2a)	137.1(9)	C(1)–C(2)–C(3)	120(1)	C(1a)–C(2a)–C(3a)	120(1)
C(1)–C(2)–C(7)	120(1)	C(1a)–C(2a)–C(7a)	120(1)	C(3)–C(2)–C(7)	119(1)	C(3a)–C(2a)–C(7a)	120(1)
C(2)–C(3)–C(4)	122(1)	C(2a)–C(3a)–C(4a)	119(1)	C(3)–C(4)–C(5)	118(1)	C(3a)–C(4a)–C(5a)	120(2)
C(4)–C(5)–C(6)	121(1)	C(4a)–C(5a)–C(6a)	125(1)	C(4)–C(5)–C(8)	117(1)	C(4a)–C(5a)–C(8a)	120(2)
C(6)–C(5)–C(8)	122(1)	C(6a)–C(5a)–C(8a)	115(1)	C(5)–C(6)–C(7)	122(1)	C(5a)–C(6a)–C(7a)	118(1)
C(2)–C(7)–C(6)	118(1)	C(2a)–C(7a)–C(6a)	118(1)	Rh(1)–C(29)–Rh(2)	81.8(5)	Rh(1a)–C(29a)–Rh(2a)	81.8(4)
Rh(1)–C(29)–O(1)	138(1)	Rh(1a)–C(29a)–O(1a)	140(1)	Rh(2)–C(29)–O(1)	140(1)	Rh(2a)–C(29a)–O(1a)	138.0(9)

Cp(1), Cp(2), Cp(1a), Cp(2a) are the centroids of the cyclopentadienyl rings C(9)–C(13), C(19)–C(23), C(9a)–C(13a) and C(19a)–C(23a) respectively.

Table 5 Proton NMR spectroscopic data for carbene and carbyne complexes

			δ					
Complex	T/K	Solvent	H^2, H^6	H^3, H^5	OCH_3	$C_6H_4CH_3$	C_5Me_5	Coupling constant (Hz)
4a	298	$CDCl_3$	7.21	6.96	2.90	2.27	1.84	$^3J(H^2H^3) = 8.0$
4b	298	$CDCl_3$	7.31	6.86	2.89		1.86	$^3J(H^2H^3) = 8.7$ $^4J(H^2F) = 5.8$ $^3J(H^3F) = 8.7$
6a	298	C_7D_8	6.9 (br)[a]		2.98	2.31	1.34	
	253	C_7D_8	6.39[b] 8.07[d]	6.92[c] 7.11[e]	3.12	2.22	1.29	$^3J(H^2H^3) = 8.0$ $^3J(H^5H^6) = 8.0$
6b	253	CD_2Cl_2	6.16[b] 7.74[d]	6.67[c] 6.94[e]	2.92		1.31	Multiplets for aryl protons were not analysed
11	298	CD_2Cl_2	7.41[f]	6.63[f]		2.54	1.62	$^3J(H^2H^3) = 8.0$
8a	303	CD_2Cl_2	7.27[g]	6.99	3.17	2.23	1.29	$^3J(H^2H^3) = 7.9$
	223	CD_2Cl_2	*h*		3.09	2.21	1.27	$^3J(H^2H^3) = 7.4$
8b	293	CD_2Cl_2	7.40[g]	6.88	3.14		1.29	$^3J(H^2H^3) = 8.6$ $^3J(H^3F) = 8.6$
	253	CD_2Cl_2	7.14[b] 7.58[d]	6.88	3.09		1.27	Multiplets for aryl protons were not analysed

[a] All protons in a broad featureless signal. [b] H^2. [c] H^3. [d] H^6. [e] H^5. [f] Assignments may be reversed. [g] Broad signal. [h] H^2, H^3, H^5 appear as a complex multiplet at δ 6.97, H^6 as a doublet at δ 7.45.

[$Rh_2(\eta^5-C_5Me_5)_2(\mu-CO)\{\mu-C(C_6H_4F-4)(OMe)\}$] (140 mg, 68%) as a blue-black microcrystalline solid. Further attempts at purification resulted in decomposition. Infrared (KBr): 1756 cm^{-1}. ^{19}F NMR (CD_2Cl_2, 298 K): δ −118.6 [tt, $^3J(HF)$ = 8.1, $^4J(HF)$ = 6.6 Hz].

μ-Methoxy(4-methylphenyl)methylene-bis[carbonyl(η^5-pentamethylcyclopentadienyl)rhodium] **4a**. The procedure was identical to that adopted for the 4-fluorophenyl derivative (0.62 mmol scale, 63% yield). A second recrystallisation (CH_2Cl_2–EtOH, −78 °C) yielded microanalytically pure material (Found: C, 55.9; H, 6.6. $C_{31}H_{40}O_3Rh_2$ requires C, 55.9; H, 6.1%). Infrared (KBr): 1961 and 1942; (hexane) 1975 and 1950 cm^{-1}. Mass spectrum (chemical ionisation, CI): m/z = 666 ([M]$^+$), 638 ([M − CO]$^+$) and 607 ([M − CO −OMe]$^+$).

μ-Carbonyl-μ-methoxy(4-methylphenyl)methylene-bis[(η^5-pentamethylcyclopentadienyl)rhodium] **6a**. [$Rh_2(\eta^5-C_5Me_5)_2(CO)_2\{\mu-C(C_6H_4Me-4)(OMe)\}$] (80 mg, 0.13 mmol) was dissolved in toluene (10 cm^3), stirred and heated under reflux for 5 h. The red solution rapidly darkened in colour, becoming after 45 min an intense turquoise. Upon completion of the reaction the solution was filtered, and the solvent removed under reduced pressure to leave a blue-black residue. Recrystallisation (CH_2Cl_2–EtOH, −78 °C) afforded [$Rh_2(\eta^5-C_5Me_5)_2(\mu-CO)\{\mu-C(C_6H_4Me-4)(OMe)\}$], m.p. 208 °C (decomp.) (sealed tube) as a blue-black microcrystalline solid (43 mg, 56%) (Found: C, 56.8; H, 6.2. $C_{30}H_{40}O_2Rh_2$ requires C, 56.4; H, 6.3%). Infrared (KBr): 1762; (hexane) 1763 cm^{-1}. Mass spectrum (FAB): 638 (M^+) and 607 (M − CO).

μ-Carbonyl-μ-4-methylphenylmethylidyne-bis[(η^5-pentamethylcyclopentadienyl)rhodium]tetrafluoroborate **11**. *Method A*. An excess of $HBF_4{\cdot}OEt_2$ was added dropwise to a solution of [$Rh_2(\eta^5-C_5Me_5)_2(CO)_2\{\mu-C(C_6H_4Me-4)(OMe)\}$] (62 mg, 0.1 mmol) in ether (10 cm^3). Agitation of the mixture resulted in immediate precipitation of a dark purple solid. This was collected by filtration, washed thoroughly with ether (3 × 5 cm^3) and dried *in vacuo*. Recrystallisation (CH_2Cl_2–Et_2O) afforded [$Rh_2(\eta^5-C_5Me_5)_2(\mu-CO)(\mu-CC_6H_4Me-4)$][$BF_4$]·$CH_2Cl_2$, m.p. 235–236 °C (decomp., sealed tube) as air-stable purplish black prisms with a greenish metallic lustre.

Method B. A 5 mm NMR tube was charged with a solution of

Table 6 ^{13}C NMR spectroscopic data for carbene and carbyne complexes

		δ[a]											
Complex	*T*/K	CO	*C*(C$_6$H$_4$X)	C^1	C^2	C^3	C^4	C^5	C^6	OCH$_3$	C*C*H$_3$	*C*$_5$Me$_5$	C$_5$*Me*$_5$
4a	298	198.5 (br)	192.2 (t, 37)	151.5	129.2	126.9	134.7	126.9	129.2	56.3	20.6	101.2	10.3
[b]	253	198.2 (t, 45) 196.5 (t, 45)	191.7 (t, 37)	150.9			134.4					100.6	
4b	303	199.1 197.4 (br)	190.5 (t, 38)	151.1	131.1 (d, 7)	113.2 (d, 21)	161.2 (d, 244)	113.2 (d, 21)	131.1 (d, 7)	56.8		101.8	10.8
	253	198.5 (t, 46) 196.6 (t, 46)	190.2 (t, 38)	150.6	130.9 (d, 7)	112.8 (d, 21)	160.5 (d, 243)	112.8 (d, 21)	130.9 (d, 7)	56.3		101.1	10.5
6a	253	244.0 (t, 60)	221.8 (t, 44)	152.0	119.8	126.1	135.2	127.3	138.6	61.2	21.2	98.3	9.2
11	298	234.9 (t, 54)	380.5 (t, 51)	151.4	129.6	120.5	141.0	120.5	129.6		21.7	107.5	9.6
8a	308	250.2 (br)	194.1	151.8	[c]	127.4	134.3	127.4	[c]	58.3	20.1	99.0	6.9
	243	251.4 249.2	193.3	151.5	120.8	126.8	134.3	128.2	130.7	58.4	20.4	97.7	7.1
8b	308	[c]	191.0	[c]	[c]	114.1		114.4		59.4		99.2	8.0
	223	252.0 250.4	191.0	151.7	123.6 (d, 7)	113.7 (d, 21)	160.6 (d, 247)	115.5 (d, 21)	133.3 (d, 7)	59.6		98.9	8.3

[a] Multiplicities and couplings (Hz) to rhodium or fluorine are given below the relevant chemical shifts. Solvent was CD_2Cl_2 in all cases. [b] SEBBORD experiment, quaternaries only. [c] Not observed.

$[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)\{\mu\text{-}C(C_6H_4Me\text{-}4)(OMe)\}]$ (5 mg) in CD_2Cl_2 (0.5 cm^3). An excess of tetrafluoroboric acid was added dropwise, and the capped tube shaken vigorously. The turquoise solution became in rapid succession purple, red and finally an intense magenta colour. A ^1H NMR spectrum was recorded, which indicated the formation of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)][BF_4]$ as the sole product of the reaction.

Method C. Solid $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2\{\mu\text{-}C(C_6H_4Me\text{-}4)(OMe)\}]$ (12 mg, 0.018 mmol) was added to a suspension of trimethyloxonium tetrafluoroborate (2.7 mg, 0.018 mmol) in CD_2Cl_2 in a 5 mm NMR tube. The tube was capped and shaken vigorously, resulting in an immediate change in colour from deep red to an intense magenta. Examination of the ^1H NMR spectrum indicated clean conversion into the carbyne complex. (Found: C, 46.9; H, 5.3. $C_{31}H_{39}BCl_2F_4O_2Rh_2$ requires C, 46.3; H, 5.1%). Infrared (KBr): 1844vs, 1830 (sh); (CH_2Cl_2) 1855vs, 1947 (sh) cm^{-1}.

μ-*Carbonyl*-μ-4-*methylphenylmethylidyne*-*bis*[(η^5-*pentamethylcyclopentadienyl*)*rhodium*]*tetraphenylborate* **12**. The tetrafluoroborate salt of the carbyne complex (30 mg, 0.037 mmol) was dissolved in methanol (2 cm^3). Addition of $Na[BPh_4]$ (14 mg, 0.037 mmol) caused precipitation of a dark purple solid, which was collected by filtration and recrystallised (CH_2Cl_2–Et_2O) to give dark purple prisms of the tetraphenylborate salt of the carbyne suitable for an X-ray diffraction study.

Di-μ-*carbonyl*-*bis*[(η^5-*pentamethylcyclopentadienyl*)*cobalt*]. The complex $[Co(\eta^5\text{-}C_5Me_5)(CO)_2]$ was prepared by the method of Frith and Spencer[29] on a 10 g scale in 54% yield; $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ was prepared according to Cotton and co-workers[30] on a 1 g scale in 37% yield.

Di-μ-*carbonyl*-μ-(4-*fluorophenyl*)*methoxymethylene*-*bis*[(η^5-*pentamethylcyclopentadienyl*)*cobalt*] **8b**. A pentane solution of (4-fluorophenyl)methoxydiazirine was prepared from 0.4 g of the bromo precursor, according to the standard procedure. This was added dropwise in several portions, over a period of 2.5 h, to a rapidly stirred solution of $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ (345 mg, 0.78 mmol) in CH_2Cl_2 (20 cm^3). The solution was stirred for a further 2 h, gradually darkening to a muddy green colour. The solvent was removed under reduced pressure affording a dark green solid. Recrystallisation (EtOH–CH_2Cl_2, −78 °C) yielded $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2\{\mu\text{-}C(C_6H_4F\text{-}4)(OMe)\}]$ (292 mg, 65%) as an air-sensitive dark green microcrystalline solid, which was dried *in vacuo*. Analytically pure material was obtained by a further recrystallisation (EtOH, −78 °C) (Found: C, 61.3; H, 6.6. $C_{30}H_{37}Co_2FO_3$ requires C, 61.9; H, 6.4%). Infrared (Nujol): 1820 and 1783 cm^{-1}. ^{19}F NMR (CD_2Cl_2, 298 K): δ −116.7 [tt, ^3J(HF) = 8.5, ^4J(HF) = 5.9 Hz].

Di-μ-*carbonyl*-μ-*methoxy*(4-*methylphenyl*)*methylene*-*bis*-[(η^5-*pentamethylcyclopentadienyl*)*cobalt*] **8a**. A pentane solution of methoxy(4-methylphenyl)diazirine was prepared from 1.0 g of the bromo precursor, according to the standard procedure. This was added dropwise in several portions, over a period of 2.5 h, to a rapidly stirred solution of $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2]$ (425 mg, 0.96 mmol) in CH_2Cl_2 (20 cm^3). The intense green colour of the starting material underwent a slow darkening to give a dark muddy green solution. The solution was stirred for a further 2 h. The solvent was removed under reduced pressure affording a dark green solid. Recrystallisation (twice, EtOH, −78 °C) yielded $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2\{\mu\text{-}C(C_6H_4Me\text{-}4)(OMe)\}]$ (424 mg, 77%) as an air-sensitive dark green microcrystalline solid, which was dried *in vacuo*. (Found: C, 64.2; H, 7.0. $C_{31}H_{40}Co_2O_3$ requires C, 64.4; H, 7.0%). Infrared (KBr): 1817, 1781; (CH_2Cl_2) 1813, 1773 cm^{-1}.

X-Ray Structure Determinations of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(CO)_2\{\mu\text{-}C(C_6H_4F\text{-}4)(OMe)\}]$ **4b** *and* $[Rh_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)][BPh_4]$ **12**.—Suitable crystals were grown from an ethanol solution (**4b**) or by slow diffusion of ether into a solution of the complex in CH_2Cl_2 (**12**), and these were sealed in capillaries under argon. Data were collected on an Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (λ 0.710 69 Å), in the θ–2θ mode, with $\Delta\theta = (0.8 + 0.35 \tan\theta)°$, and a maximum scan time of 1 min. In both cases there was no crystal decay, and no absorption correction was applied. Reflections with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}$. The structures were solved by routine heavy-atom methods and non-hydrogen atoms refined by full-matrix least squares with anisotropic thermal parameters.

Table 7 Crystallographic data for compounds **4b** and **12**

	4b	**12**
Formula	$C_{30}H_{37}FO_3Rh_2$	$C_{53}H_{57}BORh_2$
M	670.4	926.7
Crystal size/mm	0.25 × 0.25 × 0.13	1.0 × 0.3 × 0.3
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	9.693(2)	10.996(8)
b/Å	16.883(2)	15.606(6)
c/Å	17.484(2)	27.692(4)
α/°	90	101.91(2)
β/°	98.65(2)	101.86(4)
γ/°	90	91.08(4)
U/Å^3	2828.5	4541.3
Z	4	4
D_c/g cm^{-3}	1.57	1.36
$F(000)$	1360	1912
μ/cm^{-1}	11.8	7.5
θ_{max}/°	25	22
Total unique reflections	5719	11 802
Significant reflections [($I > \sigma(I)$)]	2565	8172
R	0.045	0.077
R'	0.053	0.101

Difference maps did not reveal the positions of the hydrogen atoms of the pentamethylcyclopentadienyl groups, and since they are not uniquely defined by the geometry of the molecules it was decided to omit all hydrogen atoms. The weighting schemes were both $w = 1/\sigma^2(F)$. Programs from the Enraf-Nonius SDP-Plus package[31] were run on a PDP11/34 computer (**4b**) or a microVax computer (**12**). Further details are given in Table 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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