Organic Chemistry of Dinuclear Metal Centres. Part 4.[1] μ-Carbene and μ-Vinyl Complexes of Ruthenium from Allenes †

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Heating $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ with an allene $R^1CH{=}C{=}CHR^2$ ($R^1 = R^2 = H$ or Me; $R^1 = H$, $R^2 = Me$) in toluene at 100 °C displaces diphenylacetylene and produces allyl complexes $[Ru(CO)\{\eta^3\text{-}C_3H_{4-n}Me_n[2\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}(\eta\text{-}C_5H_5)]$ (2, $n = 0$, yield 90%; 3, $n = 1$, 70%; 4, $n = 2$, 10%). A Ru–Ru bond is broken in this process but is regenerated upon protonation of (2) with HBF_4, which yields the μ-vinyl species $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)CH_2\}(\eta\text{-}C_5H_5)_2][BF_4]$. Treatment of this with $NaBH_4$ effects hydride addition to the μ-vinyl to form the μ-dimethylcarbene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ in 77% yield. Similar sequential addition of H^+ and H^- to (3) gives $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)Et\}(\eta\text{-}C_5H_5)_2]$ in 60% yield, but (4) does not transform to a $\mu\text{-}CEt_2$ complex. The molecular structure of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ was established by *X*-ray diffraction. The two ruthenium atoms are 2.712(1) Å apart and are bridged symmetrically by the carbonyl and the dimethylcarbene ligands. The interplanar angle between the two bridge systems is 153°. Each Ru atom carries one terminal carbonyl group and one cyclopentadienyl ligand. These cyclopentadienyl ligands lie in an eclipsed *cis* orientation, skew to the Ru ··· Ru axis, on the convex side of the bridge system, giving the molecule as a whole C_s symmetry. The mean Ru–C (carbene) separation is 2.113(4) Å and the plane of the carbene ligand coincides with the molecular mirror plane. The structure is triclinic and has been refined to *R* 0.018 for 2 001 intensities measured on a four-circle diffractometer. In solution the complex exists as both *cis* and *trans* isomers which interconvert rapidly on the n.m.r. time-scale above room temperature. This, and related behaviour of the complex $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CMe_2)(PMe_2Ph)(\eta\text{-}C_5H_5)_2]$, is interpreted in terms of a bridge $\rightleftharpoons$ terminal carbene exchange. Minor products of the synthesis of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ are the isomers $[Ru_2(CO)_2(\mu\text{-}H)\{\mu\text{-}C(Me)CH_2\}(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)_2(\mu\text{-}H)\{\mu\text{-}CHC(H)Me\}(\eta\text{-}C_5H_5)_2]$; the former is dominant in solution but an *X*-ray diffraction study revealed the latter as the solid-state structure. The molecule comprises two $Ru(CO)(\eta\text{-}C_5H_5)$ fragments joined by a Ru–Ru bond [2.857(2) Å] which is bridged by hydrido- and 2-methylvinyl ligands. The vinyl ligand spans the Ru–Ru bond in a σ,η^2 mode, with a Ru–C(σ) separation of 2.013(4) Å and Ru–C(π) separations of 2.189(4) and 2.275(4) Å. The hydrido-ligand bridges with a small degree of asymmetry, but lies coplanar with the Ru(1)Ru(2)(μ-C) metallacycle. The terminal ligands on each ruthenium atom are arranged to give the molecule an overall *cis* configuration. However, the carbonyl ligands are not perfectly eclipsed, the torsion angle (O)C–Ru–Ru–C(O) being 15.7(2)°. The structure is monoclinic, and has been refined to *R* 0.028 for 2 041 intensities measured on a four-circle diffractometer at 200 K.

The previous Part[1] of this Series described the synthesis of μ-carbene complexes of iron and ruthenium using alkynes as the organic precursors. The path involved the formation of μ-vinyl cations and their reactions with hydride. We now describe how in a related manner allenes may be converted into μ-carbene ligands at a diruthenium centre *via* the same μ-vinyl cations. This unprecedented transformation is accompanied by an unusual breaking and regeneration of a metal–metal bond. Preliminary accounts of this work have appeared.[2,3]

Results and Discussion

Allyl Complexes.—The dimetallacycle $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (1) is readily obtained by u.v. irradiation of a mixture of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and diphenylacetylene.[4] It has been shown to contain an easily displaced molecule of the alkyne, and to act as an excellent source of the $Ru_2(CO)_3(\eta\text{-}C_5H_5)_2$ unit.[5] This is seen here in its reactions with allene, buta-1,2-diene ($MeCH{=}C{=}CH_2$), and penta-2,3-diene ($MeCH{=}C{=}CHMe$) at 100 °C overnight, which yield allyl complexes (2)—(4), (3) and (4) existing as isomers of form (a) and (b). These very soluble products are obtained as pale yellow or grey crystals in yields which diminish from *ca.* 90 to 70 to 10% as methyl substitution in the allene increases.

I.r. and n.m.r. spectra indicate that the new species must be formulated as η^3-allyl complexes of the $Ru(CO)(\eta\text{-}C_5H_5)$ fragment, with σ-bound $Ru(CO)_2(\eta\text{-}C_5H_5)$ as a 2-allyl substituent. The displacement of diphenylacetylene from the Ru_2 unit by an allene has coincided with the rupture of the metal–metal bond, the metal atoms now being held together solely by a μ-allyl group. Such a ligand is also seen in $[Fe_2(CO)_7(\mu\text{-}C_3H_4)]$,[6,7] where it supports a metal–metal bond, and in $[Os_3(CO)_{11}(\mu\text{-}C_3H_4)]$,[8] where it does not.

The i.r. spectrum (see Experimental section) of $[Ru(CO)\{\eta^3\text{-}C_3H_4[2\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}(\eta\text{-}C_5H_5)]$ (2) displays three strong and three weak terminal carbonyl-stretching frequencies. These are attributed to the existence of two rotamers, arising from restricted rotation about the Ru–η^3-allyl bond. Such behaviour has been observed[9] previously for the unsubstituted allyl complex $[Ru(CO)(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$, and the introduction of bulky $Ru(CO)_2(\eta\text{-}C_5H_5)$ into the allyl will ensure that rotation is at least as restricted in (2). The n.m.r. spectra (Experimental section) of compound (2) reveal that rotation is slow even on the n.m.r. time-scale, in that there are signals present corresponding to the two rotamers.

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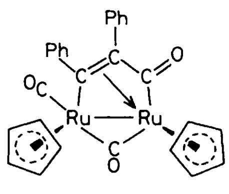
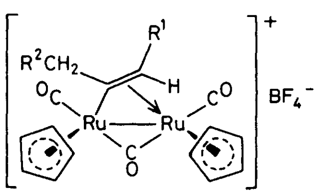
† *Supplementary data available* (No. SUP 23673, 46 pp.): complete atom co-ordinates, thermal and bond parameters, structure factors for complexes (8) and (12). See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

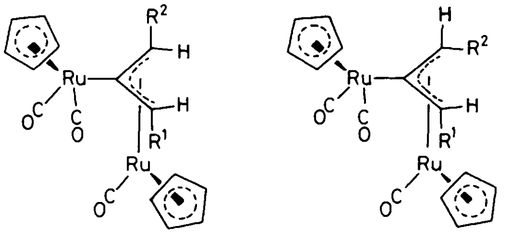
Non-S.I. unit employed: atm = 101 325 Pa.



(1)

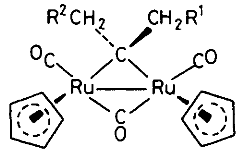


(5) $R^1 = R^2 = H$
(6) $R^1 = H$, $R^2 = Me$
(7) $R^1 = Me$, $R^2 = H$

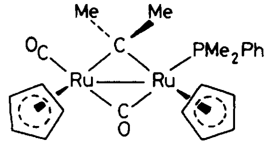


(a) (b)

(2) $R^1 = R^2 = H$
(3) $R^1 = H$, $R^2 = Me$
(4) $R^1 = R^2 = Me$



(8) $R^1 = R^2 = H$
(9) $R^1 = H$, $R^2 = Me$



(10)

Only one set of three terminal carbonyl bands is seen in the i.r. for each of $[Ru(CO)\{\eta^3\text{-}C_3H_3(1\text{-}Me)[2\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}(\eta\text{-}C_5H_5)]$ (3) and $[Ru(CO)\{\eta^3\text{-}C_3H_2(1,3\text{-}Me_2)[2\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}(\eta\text{-}C_5H_5)]$ (4), indicating that a single rotamer is now favoured, presumably as a result of the increased crowding. The n.m.r. spectra do, however, identify the existence of two isomers in solution arising from both *syn* and *anti* orientations of the allylic methyl substituents. Evidently the electronic differences between the two isomers are insufficient significantly to vary the carbonyl-stretching frequencies. When compared with the ^1H n.m.r. spectrum of compound (2), which shows the allylic protons at shifts characteristic of *syn* (δ 2.81, m, 2 H) and *anti* (1.43, m, 2 H) orientations, that of (3) clearly reveals that the major isomer has the methyl group *syn* since only one *syn* proton is now seen (δ 2.84, m, 1 H). The *syn* (3a) : *anti* (3b) ratio is *ca.* 2 : 1 in $[^2H_6]$-benzene at room temperature. In the same manner the dimethyl-substituted allyl complex is shown to exist as *syn-syn* (4a) and *syn-anti* (4b) isomers in *ca.* 1 : 5 ratio under the same conditions.

μ-Vinyl Cations.—Treatment of complex (2) with $HBF_4\cdot OEt_2$ results in protonation at a terminal allyl carbon to give the μ-vinyl species $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)CH_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ (5) in near quantitative yield. This transformation of a four-electron μ-allyl ligand to a three-electron μ-vinyl causes the regeneration of the Ru–Ru bond as the metal atoms seek to recoup the electron loss. The sequence (1) ⟶ (2) ⟶ (5) represents a nice example of the way in which metal–metal bond order can change to accommodate changes in the electronic properties of ligands.

A general synthesis of μ-vinyl cations like (5) was described in Part 3 [1] of this Series, and characterisation of (5) itself was therefore straightforward. The ^1H n.m.r. spectrum readily establishes the presence of the $\mu\text{-}CMe{=}CH_2$ ligand, whose vinylic protons are observed at the expected chemical shifts and with a *geminal* coupling constant of *ca.* 2 Hz. In our earlier work on such μ-vinyl cations a solution was generated containing both (5) and the $\mu\text{-}CH{=}C(H)Me$ isomer $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CHC(H)Me\}(\eta\text{-}C_5H_5)_2][BF_4]$. Evidence was presented that the latter is the kinetically controlled product, and rearranges to give (5). In solution, compound (5), prepared by protonation of (2), does not rearrange to any observable extent to the $\mu\text{-}CH{=}C(H)Me$ isomer; the ^1H n.m.r. spectrum shows the presence of only two species, each containing a $\mu\text{-}CMe{=}CH_2$ group, assigned as isomers of (5) with *cis* or *trans* arrangements of the terminal CO and $\eta\text{-}C_5H_5$ ligands. Such isomers are seen for a range of μ-vinyl cations like (5) and it has been concluded [1] that their relative stability is governed by steric interactions between the μ-vinyl and $\eta\text{-}C_5H_5$ groups. On this basis the *cis* and *trans* forms of a $\mu\text{-}CR{=}CH_2$ cation appear finely balanced and the two species present in $[^2H_6]$acetone solution at −30 °C are actually in *ca.* 2 : 3 ratio. The n.m.r. spectra cannot distinguish *cis* from *trans*, but the relative intensities of the carbonyl bands in the i.r. point to the *trans* being the major isomer.

On warming above −30 °C the $\eta\text{-}C_5H_5$ and $\mu\text{-}CMe{=}CH_2$ methyl-proton n.m.r. signals of the *cis* and *trans* isomers broaden, coalesce at ambient temperatures, and at 80 °C sharpen to give single $\eta\text{-}C_5H_5$ and methyl resonances at δ 5.88 and 3.32 respectively ($[^2H_5]$pyridine solvent). One of the vinylic CH_2 protons is seen as a doublet at δ 5.42 but the other is unobserved, perhaps obscured by the resonance of water as impurity. The production of a single time-averaged $\eta\text{-}C_5H_5$ resonance can be explained only by the occurrence of two fluxional processes for (5), a *cis* $\rightleftharpoons$ *trans* interconversion and the well known [10] σ–π oscillatory rearrangement of a μ-vinyl ligand. This phenomenon has been discussed at length for such μ-vinyl cations.[1]

μ-Carbene Complexes.—Addition of $NaBH_4$ to an acetone solution of the cation (5) effects nucleophilic attack by hydride specifically upon the β-vinylic carbon, producing the μ-dimethylcarbene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (8) in 77% yield; although prepared previously,[1] (8) is much better obtained by this new route. The μ-C(Me)Et species (9) [1] is also formed in good (56%) yield by successive addition of HBF_4 and $NaBH_4$ to (3). No attempt was made to isolate the intermediate μ-vinyl cation in this case; according to which terminal allyl carbon is protonated, either a $\mu\text{-}CEt{=}CH_2$ (6) or $\mu\text{-}CMe{=}C(H)Me$ (7) cation will be produced, but each will generate the μ-C(Me)Et complex (9) upon hydride attack at the β-vinyl carbon. Treatment of compound (4) with HBF_4 and $NaBH_4$ in succession surprisingly gave none of the expected $\mu\text{-}CEt_2$ analogue of (8) and (9).

Molecular Structure of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (8).—An *X*-ray diffraction study was undertaken on

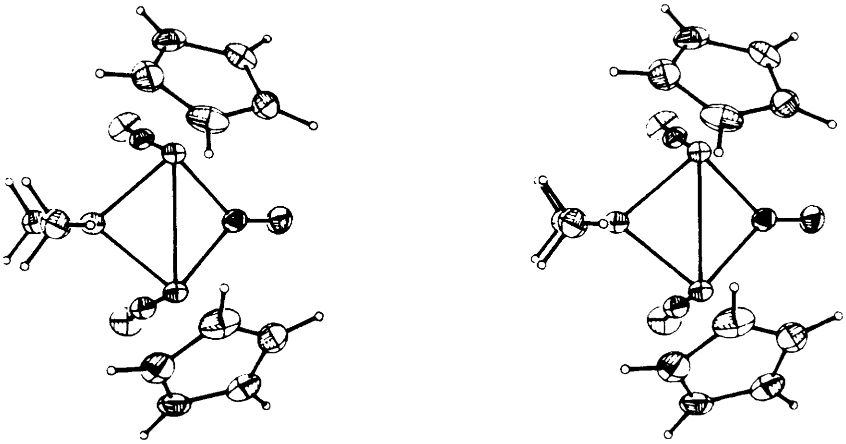


Figure 2. A stereoscopic view of (8)

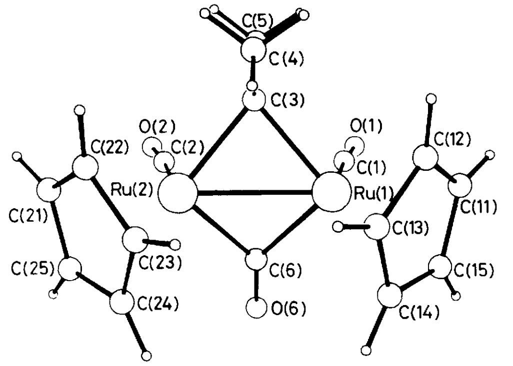


Figure 1. Molecular structure of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (8), showing the crystallographic numbering scheme

Table 1. Selected bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses, for $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (8)

Ru(1)-C(3)	2.113(3)	Ru(2)-C(3)	2.113(4)
C(3)-C(4)	1.536(6)	C(4)-C(5)	1.524(5)
Ru(1)-C(6)	2.011(5)	Ru(2)-C(6)	2.031(3)
C(6)-O(6)	1.179(5)	Ru(1)-Ru(2)	2.712(1)
Ru(1)-C(1)	1.829(4)	Ru(2)-C(2)	1.832(4)
C(1)-O(1)	1.158(5)	C(2)-O(2)	1.159(6)
C(11)-C(12)	1.397(7)	C(21)-C(22)	1.393(8)
C(12)-C(13)	1.411(7)	C(22)-C(23)	1.418(5)
C(13)-C(14)	1.417(6)	C(23)-C(24)	1.417(7)
C(14)-C(15)	1.394(6)	C(24)—C(25)	1.394(7)
C(15)—C(11)	1.426(6)	C(25)—C(21)	1.417(6)
Mean Ru-C (C_5H_5)	2.277(5)		

Ru(1)-C(3)-Ru(2)	79.8(1)	Ru(1)-C(6)-Ru(2)	84.3(2)
Ru(1)-Ru(2)-C(3)	50.1(1)	Ru(1)-Ru(2)-C(6)	47.6(1)
Ru(2)-Ru(1)-C(3)	50.1(1)	Ru(2)-Ru(1)-C(6)	48.2(1)
Ru(1)-Ru(2)-C(2)	102.8(1)	Ru(2)-Ru(1)-C(1)	101.8(1)
Ru(2)-C(2)-O(2)	175.2(4)	Ru(1)-C(1)-O(1)	175.5(3)
Ru(1)-C(6)-O(6)	138.4(3)	Ru(2)-C(6)-O(6)	137.4(3)
C(4)-C(3)-C(5)	105.8(3)	Mean C-C-C (C_5H_5)	108.0(4)

the μ-dimethylcarbene complex (8) and the results are summarised in Table 1; Figure 1 shows the molecular structure and the crystallographic numbering scheme, Figure 2 a stereoscopic view of the molecule. The core of the molecule comprises a double bridge system in which a dimethylcarbene ligand and a carbonyl ligand are each bonded to two ruthenium atoms which are themselves 2.712(1) Å apart. The interplanar angle between the two bridge systems is 153° [torsion angle C(6)-Ru(1)-Ru(2)-C(3) = −153°]. The two terminal carbonyl groups C(1)-O(1) and C(2)-O(2) lie in a plane which approximately bisects this angle, and the two cyclopentadienyl rings adopt an eclipsed *cis* orientation with respect to one another, skew to the Ru-Ru bond, on the convex side of the bridge system. Other workers have shown that it is the orbital composition of this *cis* configuration which induces the folding of the bridge system.[11]

The Ru-C(carbene) separations of 2.113(3) and 2.113(4) Å are significantly longer than the mean Ru-μ-C(O) separation of 1.98(2) Å in the parent carbonyl $[Ru_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$.[12] They are, however, comparable with other Ru-C(carbene) distances; for example, those of 2.079(5) and 2.077(6) Å in $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$,[13] of 2.079(3) and 2.107(3) Å (mean values) in $[Ru_2(CO)_2\{\mu\text{-}C(H)Me\}(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$,[14] and of 2.107(6) Å (mean) in $[Ru_2(\mu\text{-}CH_2)_3(PMe_3)_6]$.[15] This difference between μ-CR_2 and μ-CO reflects the stronger π-acceptor capability of CO due to the availability of two carbonyl π*-acceptor orbitals. It may thus seem paradoxical that the bridging Ru-C(O) distances in compound (8) [Ru(1)-C(6) 2.011(5) and Ru(2)-C(6) 2.031(3) Å] are longer than those [mean 1.98(2) Å] in $[Ru_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$,[12] because the smaller π-bonding capacity of the carbene might be expected to imply tighter carbonyl binding on the other side of the metal bridge. However, although the carbene ligand has only one π-acceptor orbital, it is a more effective π-acceptor than the corresponding carbonyl orbital; the relevant carbene orbital is a pure *p* orbital of b_2 symmetry and is lower in energy than the carbonyl π* orbital with which it competes for metal-centred π-electron density.

The plane of the carbene ligand [C(3)C(4)C(5)] lies orthogonal to the Ru(1)Ru(2)C(3) plane, and the angles at the carbenoid carbon atom are 79.8(1) [Ru(1)-C(3)-Ru(2)] and 105.8(3)° [C(4)-C(3)-C(5)], in accord with the results of previous crystallographic investigations.[16]

Substitution of μ-CMe_2 for μ-CO causes a decrease in the Ru-Ru distance from 2.735(2) Å in $[Ru_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ [12] to 2.712(1) Å in complex (8). This feature can be readily rationalised on molecular orbital grounds. The principal metal-ligand π interaction occurs with a metal-metal π* orbital [17] and transfer of electron density from this orbital occurs more readily into the low-energy p_π (b_2) acceptor

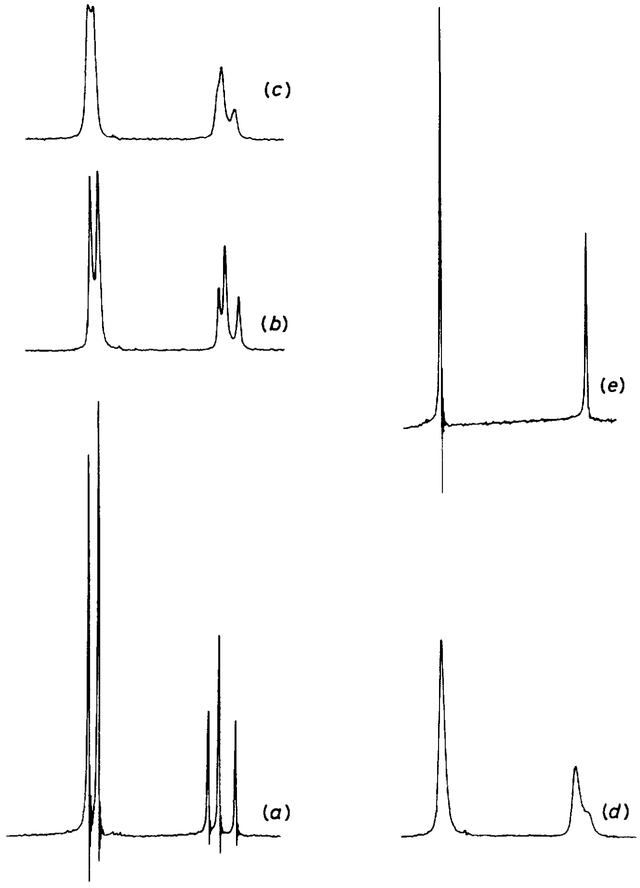


Figure 3. Proton n.m.r. spectrum of compound (8) at (*a*) 39, (*b*) 91, (*c*) 100, (*d*) 108, and (*e*) 140 °C; (*a*)—(*d*) in [$^2H_8$]toluene, (*e*) in *o*-dichlorobenzene

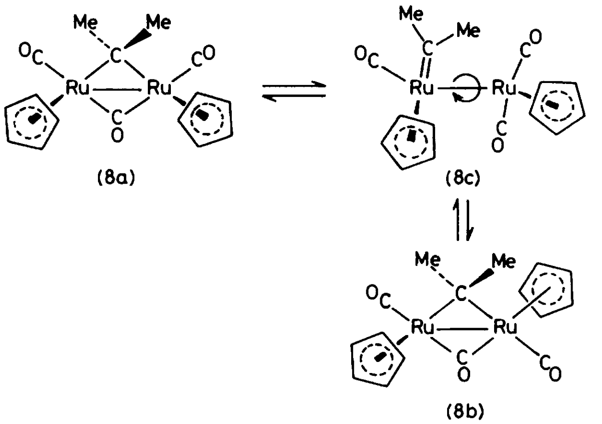


Figure 4. Proposed mechanism for the *cis* $\rightleftharpoons$ *trans* isomerisation of compound (8)

orbital of the carbene ligand than into the relevant carbonyl π^* orbital. Thus, for the carbene complex there is a relative transfer of electron density from the metal-centred antibonding orbital to the carbene ligand, strengthening the metal–metal interaction.

The *cis* cyclopentadienyl ligands give the molecule mirror (C_s) symmetry which is not crystallographically imposed. The cyclopentadienyl rings are planar to within 0.015 Å and show no significant deviations from C_{5h} symmetry. The terminal carbonyl ligands are distorted from linearity so that the oxygen atoms lean away from the bridges, giving angles Ru(1)–C(1)–O(1) of 175.5(3)° and Ru(2)–C(2)–O(2) of 175.2(4)°.

The molecules pack with no abnormally short intermolecular contacts, those less than 2.5 Å being O(2) $\cdots$ H(22) 2.47, O(6) $\cdots$ H(14) 2.29, O(6) $\cdots$ H(24) 2.38, and H(5C) $\cdots$ H(5C) 2.088 Å.

Molecular Dynamics of [$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2$] (8).—Although in the solid state (8) adopts a *cis* configuration, in [$^2H_8$]toluene solution the ^1H n.m.r. spectrum reveals the presence of both the *cis* (8a) [δ 2.78 (s, 3 H), 3.16 (s, 3 H), and 4.68 (s, 10 H)] and *trans* (8b) [δ 3.02 (s, 6 H) and 4.82 (s, 10 H)] isomers. At room temperature these are in *ca.* 1 : 1 ratio as seen in Figure 3. On warming, coalescence of the $\eta\text{-}C_5H_5$ and methyl signals of the two isomers is induced, until at 140 °C sharp signals are observed for each type of proton. These changes, which are reversible, are clearly due to *cis* $\rightleftharpoons$ *trans* isomerisation occurring on the n.m.r. time-scale.

Similar behaviour to (8) has been observed for the structurally analogous [$Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}GeMe_2)(\eta\text{-}C_5H_5)_2$].[18] In this case the *cis* $\rightleftharpoons$ *trans* isomerisation and consequent averaging of $\eta\text{-}C_5H_5$ and methyl environments was concluded to proceed *via* concerted bridge opening to afford a non-bridged form with terminal germylene ligand, rotation about the unsupported metal–metal bond, and subsequent bridge regeneration. Cotton and co-workers[19] have presented persuasive evidence and arguments that such a process occurs for a range of dinuclear metal systems with two bridges. We favour this mechanism for the fluxionality of (8), depicted in Figure 4, for several additional reasons. First, complexes akin to the transient terminal carbene species (8c) are known, *e.g.* [$(OC)_5ReRe\{C(OMe)C_6H_4Me\}(CO)_4$];[20] secondly, on treatment with tolyl-lithium and [OMe_3][BF_4] this complex yields [$(OC)_4Re\{\mu\text{-}C(OMe)C_6H_4Me\}_2Re(CO)_4$], showing that the terminal-to-bridge carbene transformation can occur. Thirdly, the reverse transfer of a μ-carbene to a terminal site has also been observed recently by Herrmann and Bauer,[21] in the reaction of [$Rh_2(CO)_2(\mu\text{-}CPh_2)(\eta\text{-}C_5Me_5)_2$] with SO_2 to give [$Rh_2(CO)(CPh_2)(\mu\text{-}SO_2)(\eta\text{-}C_5Me_5)_2$], and by Messerle and Curtis,[22] in the reaction of [$Mo_2(CO)_4\{\mu\text{-}C(C_6H_4Me)_2\}(\eta\text{-}C_5H_5)_2$] with $(C_6H_4Me)_2CN_2$ to give [$Mo_2(CO)_3\{C(C_6H_4Me)_2\}\{N_2C(C_6H_4Me)_2\}(\eta\text{-}C_5H_5)_2$], Fourthly, assuming a 1 : 1 ratio for the *cis* and *trans* isomers in solution, and with a coalescence temperature of 100 °C for the $\eta\text{-}C_5H_5$ signals, it is possible to estimate that the free energy of activation for the isomerisation of (8) is *ca.* 85 kJ mol^{-1}. This is double the value reported[23] for the *cis* $\rightleftharpoons$ *trans* isomerisation of [$Ru_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$], which involves only the movement of CO between bridging and terminal sites. Mechanisms for the fluxionality of (8) based on CO mobility with the dimethylcarbene remaining as a bridge throughout are therefore unlikely.

A one-for-one exchange of terminal and bridging CO has been observed for [$Rh_2(CO)(\mu\text{-}CO)\{P(OPh)_3\}(\eta\text{-}C_5H_5)_2$],[24] again with a low activation energy of *ca.* 40 kJ mol^{-1}, but study of a phosphine-substituted derivative of (8) rules out this process for the diruthenium μ-carbene system. The complex [$Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CMe_2)(PMe_2Ph)(\eta\text{-}C_5H_5)_2$] (10) was obtained by subjecting a toluene solution of (8) and PMe_2Ph to u.v. irradiation. Its ^1H n.m.r. spectrum shows that it exists in solution below 90 °C as a single isomer with inequivalent $\eta\text{-}C_5H_5$ rings and carbene methyl groups, the large chemical shift separation of the latter suggesting this to be the

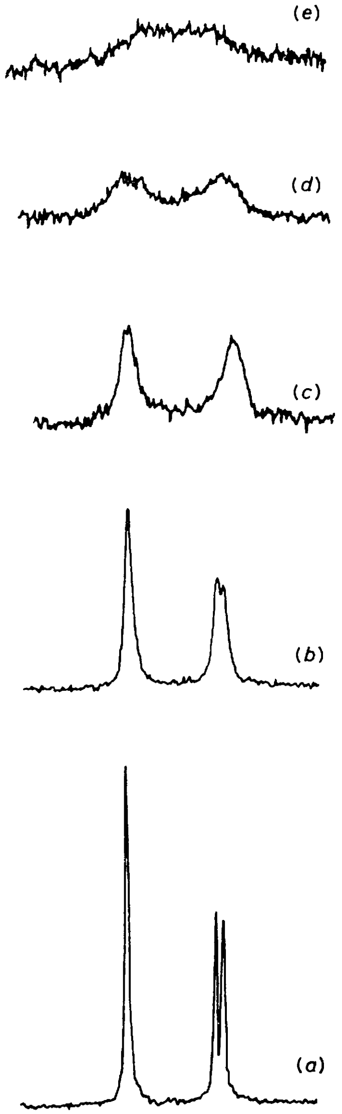
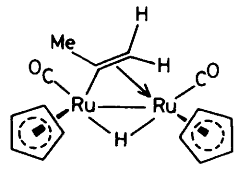
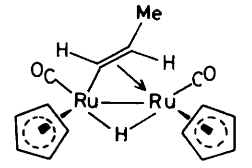


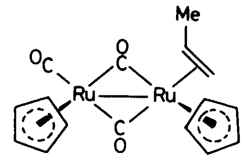
Figure 5. Proton n.m.r. spectrum (CMe_2 signals) of compound (10) at (*a*) 90, (*b*) 107, (*c*) 125, (*d*) 135, and (*e*) 146 °C; (*a*)—(*c*) in [$^2H_8$]toluene, (*d*) and (*e*) in *o*-dichlorobenzene



(11)



(12)



(13)

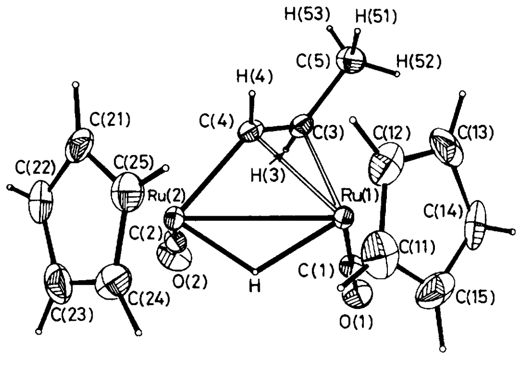


Figure 6. Molecular structure of $[Ru_2(CO)_2(\mu\text{-}H)\{\mu\text{-}CHC(H)Me\}(\eta\text{-}C_5H_5)_2]$ (12), showing the crystallographic numbering scheme

cis form illustrated. One of the carbene methyls, probably the one *anti* to the PMe_2Ph ligand shows much greater coupling to phosphorus than the other (see Figure 5). Above 90 °C the cyclopentadienyl and phosphine signals remain sharp but the carbene methyl signals broaden and coalesce at 146 °C (Figure 5). Higher temperatures were not accessible because of apparatus limitations, but it is evident that time-averaging of the methyl-group signals is occurring. This is clearly not caused by any movement of the phosphine from its terminal site since the η-C_5H_5 signals remain distinct. The μ-CMe_2 methyls are thus fixed *syn* or *anti* to the phosphine, ensuring that no process which leaves the carbene in its bridging site can render them equivalent. The carbene must therefore go terminal, demanding that the μ-CO does likewise to maintain an 18-valence-electron configuration for each ruthenium. We are thus led to the same mechanism which was suggested for compound (8), but with the additional requirement that the terminal carbene rotates to change the methyl orientations relative to the phosphine. An estimate of the free energy of activation for the averaging of the methyl environments, obtained from the coalescence temperature (146 °C) and their chemical shift separation of 50 Hz, provides a value of *ca.* 88 kJ mol^{-1}. This compares well with the 85 kJ mol^{-1} derived similarly for (8) and suggests that the same process of $Ru(\mu\text{-}CMe_2)(\mu\text{-}CO)Ru$ bridge-opening and -closure is indeed operative in each complex.

There is now a general consensus that surface methylene is the critical species in the Fischer–Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen.[25-27] The mobility of methylene on a metal surface is an important feature of any process in which it is involved and these studies suggest that a pathway exists analogous to that established [28] for carbon monoxide, namely a succession of bridge $\rightleftharpoons$ terminal 'jumps.'

μ-Hydrido-complexes.—The addition of $NaBH_4$ to the μ-$CMe{=}CH_2$ vinyl cation (5) gives not only the μ-CMe_2 complex (8) but also a mixture of the isomeric μ-hydrido-species $[Ru_2(CO)_2(\mu\text{-}H)\{\mu\text{-}C(Me)CH_2\}(\eta\text{-}C_5H_5)_2]$ (11) and $[Ru_2(CO)_2(\mu\text{-}H)\{\mu\text{-}CHC(H)Me\}(\eta\text{-}C_5H_5)_2]$ (12), with the former strongly favoured. The combined yield of (11) and (12) varied from 0 to 10% in reactions performed under apparently identical conditions, and was most often at or near 0%. Treatment of compound (5) with NaH or $K[BH\{CH(Me)Et\}_3]$ ('K-selectride') gave (8) equally well, but with no trace of (11) or (12). Clearly a carbon monoxide molecule is lost in the transformation of (5) to (11),(12), and the incoming hydride attacks a metal site rather than the μ-vinyl ligand, but u.v. irradiation of (5) prior to hydride addition, in an attempt to aid the elimination of CO, did not result in any increase in yield.

The ratio of (11) : (12) in solution is so high (*ca.* 15 : 1) that initially the ^1H and ^{13}C n.m.r. spectra (Experimental section)

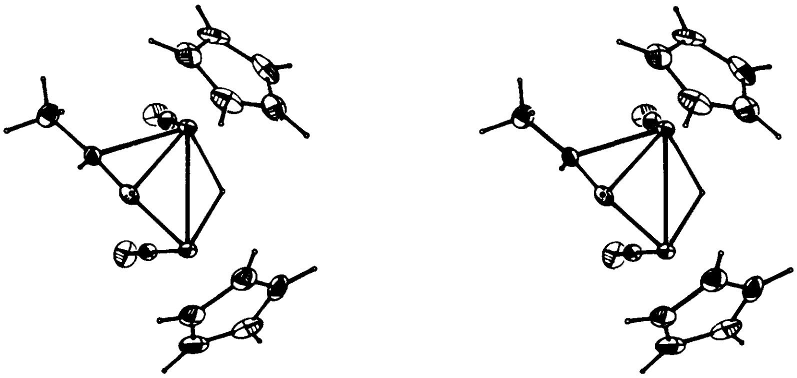


Figure 7. A stereoscopic view of (12)

of the mixture were interpreted as being due to (11) alone. It was therefore a surprise when an *X*-ray diffraction study (see below) revealed the structure (12), containing not μ-CMe=CH$_2$ but isomeric μ-CH=C(H)Me. Obviously either by chance a crystal of compound (12) had been selected from a mass of (11), or (12) is actually the preferred solid-state configuration. If the latter is true then (12) must isomerise rapidly to (11) in solution, because when the crystals from which the *X*-ray specimen was chosen were dissolved the ^{1}H n.m.r. spectrum at first inspection again indicated (11) to be the only species present in solution. However, at high amplitude it was possible to detect a doublet signal at δ 1.78 (J 6 Hz), which is characteristic [1] of a μ-CH=C(H)Me methyl group coupled to a *geminal* proton. It therefore appears that a small amount of (12) (*ca.* 7%) co-exists in solution with (11); such a situation has been noted previously for μ-CMe=CH$_2$ and μ-CH=C(H)Me complexes of iron, ruthenium, and molybdenum.[1,29]

Two complexes closely related to (11) and (12) are [Os$_3$(CO)$_{10}$(μ-H)(μ-CHCH$_2$)] [30,31] and [Re$_2$(CO)$_8$(μ-H)(μ-CHCH$_2$)],[32] in which hydrido and vinyl ligands also simultaneously bridge two metal atoms. Each of these complexes undergoes an interesting reaction with CO to link the μ-H and μ-CHCH$_2$, releasing ethylene and forming [Os$_3$(CO)$_{12}$] and [Re$_2$(CO)$_{10}$] respectively. If a similar linking were induced by the reaction of CO with the major solution species (11) propene would be evolved. There are two plausible pathways by which the μ-H and μ-C(Me)CH$_2$ ligands could combine: (*a*) migration of the hydrogen to the α-carbon of the vinyl giving the propene complex (13),[33] or (*b*) migration of the hydrogen to the β-carbon of the vinyl to give the μ-CMe$_2$ complex (8). Each of these complexes is known and on heating each evolves propene.[34] It was hoped that treatment of compound (11) with CO would lead to the isolation of (8) or (13), thereby establishing the path of linking. In the event (11) reacted with CO only under 40 atm pressure at 100 °C, conditions which displaced the vinyl and hydrido-ligands entirely, presumably as propene, and provided [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] as the only organometallic product. However, after subjection to identical conditions the μ-CMe$_2$ complex (8) was found to be unchanged and can be ruled out as a possible intermediate. The propene in complex (13), on the other hand, was displaced by CO to form [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] even under 20 atm pressure. Complex (13) could, therefore, be an intermediate and it is likely that H-vinyl linking occurs by migration of the μ-H to the α-carbon of the vinyl.

Table 2. Selected bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses, for [Ru$_2$(CO)$_2$(μ-H){CHC(H)Me}(η-C$_5$H$_5$)$_2$] (12)

Ru(1)–Ru(2)	2.857(2)	Ru(1)–C(3)	2.275(4)
Ru(1)–C(4)	2.189(4)	Ru(2)–C(4)	2.013(4)
Ru(1)–C(1)	1.854(4)	Ru(2)–C(2)	1.828(3)
C(1)–O(1)	1.153(4)	C(2)–O(2)	1.167(4)
Ru(1)–H	1.764(1)	Ru(2)–H	1.648(1)
C(4)–H(4)	0.91(4)	C(3)–H(3)	0.99(4)
C(5)–H(51)	1.00(4)	C(5)–H(52)	1.00(4)
C(5)–H(53)	0.99(4)	Mean Ru–C (C$_5$H$_5$)	2.243(5)
Mean C–C (C$_5$H$_5$)	1.413(7)		
Ru(1)–H–Ru(2)	113.7(1)	Ru(1)–Ru(2)–H	34.4(1)
Ru(2)–Ru(1)–H	31.9(1)	Ru(1)–C(3)–C(4)	68.3(2)
Ru(1)–C(4)–C(3)	75.0(2)	Ru(1)–C(4)–Ru(2)	85.6(1)
Ru(1)–Ru(2)–C(4)	49.8(1)	Ru(2)–Ru(1)–C(4)	44.6(1)
Ru(2)–Ru(1)–C(3)	73.2(1)	Ru(1)–C(3)–C(5)	117.5(2)
C(4)–C(3)–C(5)	123.4(3)	Ru(2)–C(4)–H(4)	111(3)
Ru(1)–C(4)–H(4)	106(3)	C(3)–C(4)–H(4)	120(3)
C(4)–C(3)–H(3)	117(3)	C(5)–C(3)–H(3)	112(3)
Ru(1)–C(3)–H(3)	111(3)	C(3)–C(5)–H(51)	104(3)
C(3)–C(5)–H(52)	114(2)	C(3)–C(5)–H(53)	113(3)
Ru(1)–Ru(2)–C(2)	92.9(1)	Ru(2)–Ru(1)–C(1)	97.5(1)
Ru(2)–C(2)–O(2)	177.5(3)	Ru(1)–C(1)–O(1)	178.2(3)
Mean C–C–C (C$_5$H$_5$)	108.0(4)	Mean H–C–H (methyl)	109(4)

Molecular Structure of [Ru$_2$(CO)$_2$(μ-H){μ-CHC(H)Me}(η-C$_5$H$_5$)$_2$] (12).—The results of the crystal structure determination are summarised in Table 2; Figure 6 shows the molecular geometry with the crystallographic numbering scheme, and Figure 7 is a stereoscopic view of the molecule. Two ruthenium atoms, separated by 2.857(2) Å, are bridged by a hydrido-ligand and a 2-methylvinyl ligand. Each ruthenium atom carries a terminal carbonyl and cyclopentadienyl ligand, thus achieving an 18-electron configuration.

The vinyl ligand bridges the two ruthenium atoms in the familiar σ,η^2 mode, with C(4) σ-bound to Ru(2) and the C(3)=C(4) bond π-co-ordinated to Ru(1). This results in lengthening of the C(3)=C(4) bond to 1.406(5) Å, which corresponds to a bond order of between one and two. The Ru(2)–C(σ) separation is 2.013(4) Å, *cf.* the Ru–C(π) separations Ru(1)–C(3) and Ru(1)–C(4) of 2.275(4) and 2.189(4) Å respectively; these variations are typical of μ-vinyl complexes.[35–38] The geometry of the vinyl ligand reflects the partial double-bond character of the C(3)–C(4) linkage, with C(5) lying *trans* to Ru(2), with a torsion angle Ru(2)–C(4)–C(3)–C(5) of 179.1(3)°. A *cis* arrangement would involve substantial steric crowding about the methyl group C(5). The hydrogen atoms H(3) and H(4) are bent out of the Ru(2)C(4)C(3)C(5) plane, giving torsion angles Ru(2)–C(4)–C(3)–H(3) of 31(3)°, H(4)–C(4)–C(3)–H(3) of −157(4)°, and H(4)–C(4)–C(3)–

C(5) of −9(3)°. The transverse side of the Ru–Ru axis is bridged by the hydrido-ligand; it lies coplanar with Ru(1), Ru(2), and the vinyl bridgehead carbon atom C(4). The Ru(1)–H and Ru(2)–H separations are 1.76 and 1.65 Å respectively, lying in the expected range; a neutron-diffraction study of the complex $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)]$[40] revealed edge-bridging Ru–H separations of 1.789(5) and 1.796(5) Å. The ruthenium–ruthenium separation of 2.857(2) Å is consistent with a single bond, but is much longer than that of 2.735(2) Å found in $[Ru_2(\mu\text{-}CO)_2(CO)_2(\eta\text{-}C_5H_5)_2]$.[12]

Each ruthenium atom carries terminal carbonyl and cyclopentadienyl ligands, arranged in a *cis* orientation with respect to the ruthenium–ruthenium axis. The carbonyl ligands, however, are not perfectly eclipsed as in complex (8), but twisted, giving an (O)C–Ru–Ru–C(O) torsion angle of 15.7(2)°. This arises from the steric and orbital requirements of the μ-vinyl ligand. The carbonyl ligands show no substantial deviations from linearity, and the cyclopentadienyl ligands conform to their expected geometry.

The molecules pack relatively loosely, the only intermolecular contacts less than 2.5 Å being H(12) ··· O(1) 2.49, H(24) ··· O(2) 2.47, and some H ··· H interactions lying in the range 2.3—2.5 Å.

Experimental

Instrumentation and techniques were as described in Part 1 of this Series.[4] Tetrafluoroboric acid was employed as the diethyl ether complex. Chromatography was on alumina columns. Allene (B.D.H.), buta-1,2-diene (Phase Separations), and penta-2,3-diene (Phase Separations) were used as supplied.

Preparation of Allyl Complexes.—$[Ru(CO)\{\eta^3\text{-}C_3H_4[2\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}(\eta\text{-}C_5H_5)]$ (2). Allene (1.7 g, 42 mmol) was condensed at −196 °C into a Carius tube containing compound (1) (0.25 g, 0.42 mmol) in toluene (50 cm^3). The sealed tube was heated (100 °C, 17 h) to give a pale yellow solution which was evaporated and the residue chromatographed. Elution with dichloromethane–hexane (3 : 7) developed a yellow band from which 0.175 g (91%) of yellow crystalline (2) was obtained, m.p. 111—112° C; ν(CO) (in hexane) at 2 034w, 2 023s, 1 976w, 1 967s, 1 953w, and 1 945s cm^{-1}. N.m.r.: ^{1}H (in $CDCl_3$), (major rotamer) δ 1.43 (m, 2 H), 2.81 (m, 2 H), 5.06 (s, 5 H), and 5.37 (s, 5 H); (minor rotamer) δ 5.07 (s, 5 H) and 5.38 (s, 5 H); ^{13}C (in $CDCl_3$), 43.5 (CH_2), 82.9 (C_5H_5), 87.2 (CRu), 89.7 (C_5H_5), 201.5 (CO), and 210.5 p.p.m. (CO) (Found: C, 42.3; H, 3.2%; *M*, 457. $C_{16}H_{14}O_3Ru_2$ requires C, 42.1; H, 3.1%; *M*, 457).

$[Ru(CO)\{\eta^3\text{-}C_3H_3(1\text{-}Me)[2\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}(\eta\text{-}C_5H_5)]$ (3). Buta-1,2-diene (0.67 g, 12.4 mmol) and compound (1) (2.0 g, 3.4 mmol) in toluene (100 cm^3) were heated (100 °C, 17 h) in a Carius tube and the resulting solution chromatographed as above. Elution with dichloromethane–hexane (1 : 4) gave 1.13 g (71%) of grey crystals, m.p. 135—138 °C; ν(CO) (in hexane) at 2 018s, 1 964s, and 1 940s cm^{-1}. N.m.r.: ^{1}H (in C_6D_6), [*syn* isomer (3a)] δ 1.36 (m, 1 H), 1.69 (m, 1 H), 1.72 (s, 3 H), 2.84 (m, 1 H), 4.56 (s, 5 H), and 4.99 (s, 5 H); [*anti* isomer (3b)] 1.28 (d, *J* 6 Hz, 3 H), 2.17 (m, 1 H), 3.06 (m, 1 H), 3.90 (m, 1 H), 4.58 (s, 5 H), and 5.03 (s, 5 H); ^{13}C (in $CDCl_3$), [*syn* isomer (3a)] 25.7 (Me), 42.0 (CH_2), 56.5 (*C*HMe), 83.2 (C_5H_5), 89.5 (C_5H_5), 89.7 (CRu), 201.4 (CO), 202.6 (CO), and 211.4 (CO); [*anti* isomer (3b)] 19.8 (Me), 42.2 (CH_2), 57.8 (*C*HMe), 83.4 (C_5H_5), 89.3 (C_5H_5), 201.6 (CO), 202.8 (CO), and 211.0 p.p.m. (CO) (Found: C, 43.6; H, 3.8%. *M*, 471. $C_{17}H_{16}O_3Ru_2$ requires C, 43.4; H, 3.7%; *M*, 471).

$[Ru(CO)\{\eta^3\text{-}C_3H_2(1,3\text{-}Me_2)[2\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}(\eta\text{-}C_5H_5)]$ (4). Penta-2,3-diene (0.25 g, 5.1 mmol) and compound (1) (3.0 g, 5.0 mmol) in toluene (100 cm^3) were heated (100 °C, 18 h) and the resulting solution chromatographed as above. Elution with dichloromethane–hexane (1 : 9) yielded the product as grey crystals (0.22 g, 9%), m.p. 147—151 °C; ν(CO) (in hexane) at 2 017s, 1 961s, and 1 937s cm^{-1}. N.m.r.: ^{1}H (in C_6D_6), [*syn-anti* isomer (4b)] δ 1.27 (d, *J* 7, 3 H), 1.76 (d, *J* 6, 3 H), 2.42 (m, 1 H), 3.78 (m, 1 H), 4.60 (s, 5 H), and 4.99 (s, 5 H); [*syn-syn* isomer (4a)] 1.38 (m, 2 H), 1.74 (d, *J* 7 Hz, 6 H), 4.57 (s, 5 H), and 4.93 (s, 5 H); ^{13}C (in $CDCl_3$), [*syn-anti* isomer (4b)] 20.0 (Me), 26.1 (Me), 53.9 (*C*HMe), 56.2 (*C*HMe), 84.0 (C_5H_5), 89.2 (C_5H_5), 90.7 (CRu) 201.5 (CO), 203.1 (CO), and 212.1 (CO); [*syn-syn* isomer (4a)] 54.5 (*C*HMe), 89.7 (C_5H_5), 202.5 p.p.m. (CO), and 212.8 (CO) p.p.m. (other signals unobserved or obscured) (Found: C, 44.4; H, 3.8%. *M*, 485. $C_{18}H_{18}O_3Ru_2$ requires C, 44.6; H, 3.7%; *M*, 485).

Protonation of $[Ru(CO)\{\eta^3\text{-}C_3H_4[2\text{-}Ru(CO)_2(\eta\text{-}C_5H_5)]\}(\eta\text{-}C_5H_5)]$ (2).—A few drops of $HBF_4\cdot OEt_2$ were added to a diethyl ether solution (20 cm^3) of compound (2) (65 mg, 0.14 mmol), resulting in immediate precipitation of yellow powder. After decanting off the supernatant liquid the powder was washed thoroughly with ether then crystallised from acetone–ether to give 71 mg (91%) of yellow (5) [m.p. 221—224 °C (decomp.); ν(CO) (in CH_2Cl_2) at 2 036s, 2 015s, and 1 867m cm^{-1}. N.m.r.: ^{1}H (in [$^2H_6$]acetone at −30 °C), (*trans* isomer) δ 3.33 (s, 3 H), 3.61 (d, *J* 2, 1 H), 4.92 (d, *J* 2, 1 H), 5.80 (s, 5 H), and 5.84 (s, 5 H); (*cis* isomer) 3.13 (d, *J* 1, 1 H), 3.46 (s, 3 H), 4.72 (d, *J* 1 Hz, 1 H), 5.94 (s, 5 H), and 6.09 (s, 5 H); ^{13}C (in [$^2H_6$]acetone at −40 °C), (*trans* isomer) 45.2 (Me), 56.8 (CH_2), 93.7 (C_5H_5), 94.3 (C_5H_5), 189.9 (*C*Me), 196.7 (CO), and 249.7 (μ-CO); (*cis* isomer) 45.9 (Me), 57.4 (CH_2), 93.7 (C_5H_5), and 95.8 p.p.m. (C_5H_5) (other signals unobserved) [Found: C, 35.0; H, 2.8%; *M*, 458 (cation). $C_{16}H_{15}BF_4O_3Ru_2$ requires C, 35.3; H, 2.8%; *M*, 458 (cation)].

Preparation of μ-*Carbene Complexes.*—$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (8). The adduct $HBF_4\cdot OEt_2$ was added to a diethyl ether solution (120 cm^3) of compound (2) (0.80 g, 1.76 mmol) to precipitate (5) as above. After washing with ether the complex was dissolved in acetone (100 cm^3) and $NaBH_4$ (0.13 g, 3.5 mmol) added, causing the solution to change from yellow to brown over 5 min. The solution was then evaporated and the residue introduced to an alumina column. Elution with dichloromethane removed a yellow band which gave 0.62 g (77%) of (8), identified by i.r., mass, and ^{1}H n.m.r. spectra.[1] Further elution with acetone gave a red band which, after rechromatography and elution with dichloromethane–hexane (7 : 3), provided 75 mg (10%) of red crystalline (11),(12); ν(CO) (in CH_2Cl_2) at 1 962s and 1 907s cm^{-1}. N.m.r.: ^{1}H (in $CDCl_3$), δ −14.40 (s, 1 H), 2.25 (s, 1 H), 2.72 (s, 3 H), 4.13 (s, 1 H), 4.82 (s, 5 H), and 4.91 (s, 5 H); ^{13}C (in $CDCl_3$), 44.6 (Me), 52.0 (CH_2), 84.6 (C_5H_5), 85.1 (C_5H_5), 175.8 (*C*Me), and 205.5 p.p.m. (CO) (Found: C, 41.5; H, 3.8%; *M*, 431. $C_{15}H_{16}O_2Ru_2$ requires C, 41.8; H, 3.8%; *M*, 431).

$[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)Et\}(\eta\text{-}C_5H_5)_2]$ (9). A few drops of $HBF_4\cdot OEt_2$ were added to a dichloromethane solution (100 cm^3) of compound (3) (0.5 g, 1.06 mmol), resulting in a colour change from brown to dark yellow-green. The solvent was evaporated and the residue washed with diethyl ether then dissolved in acetone (100 cm^3), to which $NaBH_4$ (0.2 g, 5.3 mmol) was added. After stirring (0.5 h), chromatography gave one yellow band with dichloromethane–hexane (2 : 3); this yielded 0.28 g (56%) of yellow crystalline (9), identified by i.r., mass, and ^{1}H n.m.r. spectra.[1]

Table 3. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for [Ru$_2$(CO)$_2$(μ-CO)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$] (8)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
C(11)	0.143 5(8)	0.289 4(4)	−0.212 7(5)	H(11)	0.085 5(8)	0.352 2(4)	−0.244 4(5)
C(12)	0.343 7(8)	0.287 1(4)	−0.129 8(5)	H(12)	0.448 4(8)	0.347 2(4)	−0.097 6(5)
C(13)	0.364 6(8)	0.181 0(4)	−0.101 2(5)	H(13)	0.485 4(8)	0.157 3(4)	0.043 3(5)
C(14)	0.176 3(8)	0.115 8(4)	−0.172 9(5)	H(14)	0.147 5(8)	0.039 7(4)	−0.173 5(5)
C(15)	0.040 4(7)	0.181 7(4)	−0.242 5(5)	H(15)	−0.098 4(7)	0.158 7(4)	−0.300 2(5)
C(25)	0.330 5(8)	0.101 2(4)	0.423 8(5)	H(25)	0.230 8(8)	0.073 8(4)	0.457 5(5)
C(24)	0.358 0(7)	0.055 2(4)	0.281 2(5)	H(24)	0.279 8(7)	−0.008 8(4)	0.198 8(5)
C(23)	0.522 4(8)	0.120 0(4)	0.280 0(6)	H(23)	0.575 0(8)	0.107 7(4)	0.196 2(6)
C(22)	0.596 4(7)	0.206 0(4)	0.424 1(6)	H(22)	0.708 7(7)	0.261 4(4)	0.456 1(6)
C(21)	0.475 0(7)	0.195 7(4)	0.510 3(5)	H(21)	0.487 7(7)	0.244 2(4)	0.611 7(5)
C(1)	−0.040 4(7)	0.366 7(4)	0.035 2(5)	H(4A)	0.614 8(7)	0.322 8(4)	0.197 7(5)
C(2)	0.123 7(6)	0.322 1(4)	0.400 5(5)	H(4B)	0.646 1(7)	0.426 2(4)	0.345 0(5)
C(3)	0.348 7(6)	0.375 6(3)	0.231 2(4)	H(4C)	0.572 1(7)	0.443 0(4)	0.179 0(5)
C(4)	0.565 8(7)	0.392 3(4)	0.238 3(5)	H(5A)	0.163 9(7)	0.492 2(3)	0.305 8(5)
C(5)	0.295 7(7)	0.493 0(3)	0.299 6(5)	H(5B)	0.307 6(7)	0.539 6(3)	0.236 3(5)
C(6)	0.025 5(6)	0.179 0(3)	0.113 4(4)	H(5C)	0.391 4(7)	0.522 8(3)	0.402 1(5)
O(1)	−0.167 1(5)	0.424 4(3)	0.036 4(4)				
O(2)	0.028 7(5)	0.371 2(3)	0.470 5(4)				
O(6)	−0.122 3(5)	0.119 5(3)	0.079 4(4)				
Ru(1)	0.151 31(5)	0.271 87(2)	0.016 86(3)				
Ru(2)	0.277 34(5)	0.236 57(2)	0.300 38(3)				

Table 4. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for [Ru$_2$(CO)$_2$(μ-H){μ-CHC(H)Me}(η-C$_5$H$_5$)$_2$] (12)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.184 00(3)	0.092 22(2)	0.270 02(2)	H(3)	0.126(5)	0.035(4)	0.063(3)
Ru(2)	0.451 27(3)	0.097 31(2)	0.173 82(2)	H(4)	0.323(4)	−0.082(4)	0.208(3)
O(1)	0.014 7(3)	0.261 9(3)	0.134 3(2)	H(51)	0.082(5)	−0.160(4)	0.182(3)
O(2)	0.313 8(4)	0.214 1(3)	−0.015 1(2)	H(52)	−0.065(4)	−0.085(3)	0.128(3)
C(1)	0.081 2(4)	0.196 6(3)	0.185 1(3)	H(53)	0.027(5)	−0.151(4)	0.058(3)
C(2)	0.364 8(4)	0.166 9(3)	0.058 3(3)	H(11)	0.367 8(6)	0.125 0(4)	0.460 2(3)
C(3)	0.146 5(4)	−0.014 1(3)	0.124 5(3)	H(12)	0.309 5(6)	−0.077 1(4)	0.412 4(3)
C(4)	0.292 7(4)	−0.020 9(3)	0.168 6(3)	H(13)	0.035 4(6)	−0.091 2(4)	0.358 1(3)
C(5)	0.039 4(5)	−0.110 0(4)	0.124 8(4)	H(14)	−0.074 4(6)	0.106 6(4)	0.373 2(4)
C(11)	0.272 3(6)	0.096 1(4)	0.436 7(3)	H(15)	0.136 4(6)	0.238 5(4)	0.436 1(3)
C(12)	0.240 3(6)	−0.016 1(4)	0.410 3(3)	H(21)	0.635 8(4)	−0.099 9(4)	0.177 0(3)
C(13)	0.088 1(6)	−0.024 0(4)	0.380 2(3)	H(22)	0.693 2(5)	0.061 3(4)	0.058 9(4)
C(14)	0.026 8(6)	0.085 9(4)	0.388 4(4)	H(23)	0.705 5(5)	0.242 4(4)	0.164 9(4)
C(15)	0.144 4(6)	0.159 0(4)	0.423 6(3)	H(24)	0.638 5(5)	0.193 5(4)	0.344 8(4)
C(21)	0.642 8(4)	−0.021 7(4)	0.195 9(3)	H(25)	0.594 8(5)	−0.019 6(4)	0.351 5(3)
C(22)	0.676 7(5)	0.067 8(4)	0.130 2(4)	H	0.346 59	0.165 09	0.249 30
C(23)	0.681 8(5)	0.168 7(4)	0.188 8(4)				
C(24)	0.645 5(5)	0.141 2(4)	0.289 2(4)				
C(25)	0.621 1(5)	0.022 4(4)	0.293 2(3)				

Preparation of [Ru$_2$(CO)(μ-CO)(μ-CMe$_2$)(PMe$_2$Ph)(η-C$_5$H$_5$)$_2$] (10).—A mixture of compound (8) (0.23 g, 0.50 mmol) and PMe$_2$Ph (0.375 g, 2.72 mmol) in toluene (200 cm^3) was subjected to u.v. irradiation for 17 h. Chromatography, eluting with dichloromethane–hexane (2 : 3), gave a yellow band from which 85 mg (30%) of yellow crystalline (10) was obtained, m.p. 178—179 °C; ν(CO) (in CH$_2$Cl$_2$) at 1 914s and 1 725m cm^{-1}. N.m.r.: ^{1}H (in C$_6$D$_6$), δ 1.27 (d, *J* 8, 6 H), 2.52 (d, *J* 4 Hz, 3 H), 3.02 (s, 3 H), 4.48 (s, 5 H), 4.92 (s, 5 H), and 7.14 (m, br, 5 H); ^{13}C (in CDCl$_3$), 16.1 [Me, d, *J*(P–C) 26], 21.6 [Me, d, *J*(P–C) 26], 53.9 [Me, d, *J*(P–C) 12 Hz], 55.9 (Me) 89.0 (C$_5$H$_5$), 90.3 (C$_5$H$_5$), 127.8 (Ph) 128.2 (Ph), 129.1 (Ph), 130.3 (Ph), 130.6 (Ph), and 167.5 p.p.m. (*C*Me$_2$) [Found: C, 49.1; H, 5.0%; *M*, 431 (*M* − PMe$_2$Ph). C$_{23}$H$_{27}$O$_2$PRu$_2$ requires C, 48.6; H, 4.8%; *M*, 569].

Reactions of CO.—(*a*) *With* [Ru$_2$(CO)$_2$(μ-H){μ-C(Me)CH$_2$}(η-C$_5$H$_5$)$_2$] (11). A toluene (25 cm^3) solution of compound (11) (17 mg) was subjected to 40 atm of CO at 100 °C in an autoclave for 10 h. I.r. spectroscopy revealed the presence only of [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] in the resultant solution, and chromatography gave only this complex as a product (8 mg, 46%).

(*b*) *With* [Ru$_2$(CO)$_2$(μ-CO)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$] (8). Under identical conditions to (*a*) complex (8) was recovered unchanged after 10 h.

(*c*) *With* [Ru$_2$(CO)(μ-CO)$_2$(C$_3$H$_6$)(η-C$_5$H$_5$)$_2$] (13). After heating a toluene (25 cm^3) solution of compound (13) (25 mg) at 80 °C under 20 atm of CO for 10 h in an autoclave, chromatography gave 10 mg (42%) of [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$], identified by its i.r. spectrum.

X-Ray Data Collection and Structure Determinations.—[Ru$_2$(CO)$_2$(μ-CO)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$] (8). Crystals of compound (8) grow as yellow needles of anisotropic cross-section. Diffracted intensities were collected in the range 2.9 ⩽ 2θ ⩽ 60° from a crystal of dimensions 0.05 × 0.15 × 0.325 mm on a Nicolet *P*3*m* four-circle diffractometer at

220 K. Those reflections with counts less than 20 on a 2-s pre-scan were not measured. Of the total 2 059 independent measured intensities, only those 2 001 with $I \geqslant 3\sigma(I)$ were used in structure solution and refinement. Check reflections $\bar{1}\ \bar{1}\ \bar{3}$ and $0\ \bar{2}\ 0$, which were remeasured every 50 reflections, showed no evidence of decay throughout the 91 h of data collection. Corrections were applied for Lorentz, polarisation, and *X*-ray absorption effects, the latter by a semi-empirical method based on azimuthal scan data.

Crystal data. $C_{16}H_{16}O_3Ru_2$, $M = 458.4$, Triclinic, $a = 7.124(4)$, $b = 12.373(3)$, $c = 9.494(4)$ Å, $\alpha = 105.94(3)$, $\beta = 108.61(3)$, $\gamma = 90.60(3)°$, $U = 758.2(5)$ Å^3, $Z = 2$, $D_c = 2.01$ g cm^{-3}, $F(000) = 448$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 19.6 cm^{-1}.

The structure was solved by heavy-atom methods and refined by blocked-cascade least squares, all non-hydrogen atoms being allowed anisotropic thermal parameters. Hydrogen atoms could not be adequately located from low sin θ electron-density difference maps, and were hence incorporated at calculated positions. They were allowed to refine: the methyl groups as rigid groups, and the cyclopentadienyl hydrogen atoms riding[41] on the carbon atoms of the ring. Chemically equivalent hydrogen atoms were given a common isotropic thermal parameter which was allowed to refine. Individual weights were ascribed according to the scheme $w = [\sigma^2(F_o) + 0.000\,09|F_o|^2]^{-1}$, and refinement converged at R 0.018 (R' 0.019). The final electron-density difference synthesis showed no features of modulus >0.57 e Å^{-3}. Scattering factors, including corrections for the effects of anomalous dispersion for all atoms, were taken from ref. 42. All computation was carried out within the laboratory on a Data General 'Eclipse' Minicomputer, using the SHELXTL[43] system of programs. Atomic co-ordinates are listed in Table 3.

$[Ru_2(CO)_2(\mu\text{-}H)\{\mu\text{-}CHC(H)Me\}(\eta\text{-}C_5H_5)_2]$ (12). Crystals of compound (12) grow as orange prisms. The crystal used for data collection was of dimensions 0.4 × 0.4 × 0.3 mm and was cut from a larger prism. Data were collected on a Nicolet *P*3*m* four-circle diffractometer in the range $2.9 \leqslant 2\theta \leqslant 50°$ at 200 K. Of the total 2 162 independent measured intensities, only those 2 041 with $I \geqslant 3\sigma(I)$ were used in structure solution and refinement. Check reflections $0\ 1\ \bar{7}$ and 3 6 1 were remeasured every 50 reflections and showed no evidence of crystal decay throughout the 39 h of data collection. Corrections for Lorentz and polarisation effects were applied, but no correction for the effects of *X*-ray absorption was carried out, due to the crystal splitting at the termination of data collection.

Crystal data. $C_{15}H_{16}O_2Ru_2$, $M = 429.4$, Monoclinic, $a = 9.151(6)$, $b = 11.849(6)$, $c = 13.042(6)$ Å, $\beta = 95.63(4)°$, $U = 1\,407(2)$ Å^3, $Z = 4$, $D_c = 2.02$ g cm^{-3}, $F(000) = 840$, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 21.0 cm^{-1}.

The structure was elucidated by conventional heavy-atom techniques and refined by blocked-cascade least squares. All non-hydrogen atoms were allowed anisotropic thermal parameters, the anisotropy of the cyclopentadienyl carbon atoms being the best model for their positional disorder; they were disordered *ca.* 85 : 15%, but the 15% component would not refine satisfactorily even with rigid geometrical constraints on the five-membered ring. The hydride ligand and the hydrogen atoms of the μ-methylvinyl ligand were located from difference-Fourier maps, but the cyclopentadienyl hydrogen atoms were included at calculated positions. The hydride ligand was fixed in position, but was allowed an isotropic thermal parameter which was refined. The positional parameters of the hydrogen atoms of the bridging vinyl moiety were allowed to refine, and they were each allowed a refining isotropic thermal parameter except for H(3). This was given a fixed isotropic thermal parameter 1.2 times that of the carbon atom to which it was attached [C(3)]. The hydrogen atoms of the cyclopentadienyl ligands were allowed to refine, 'riding' on the carbon atoms of the ring, but they were allocated fixed thermal parameters as for H(3).

Individual weights were apportioned according to the scheme $w = [\sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$, and refinement converged at R 0.028 (R' 0.033). The final electron-density difference synthesis showed no peaks >1.1 e Å^{-3}, Atomic co-ordinates are listed in Table 4. Other details as for complex (8).

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