Organic Chemistry of Dinuclear Metal Centres. Part 6.[1] μ-Vinylidene and μ-Ethylidyne Diruthenium Complexes: Crystal Structures of *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ and *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$ †

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The dimetallacycles $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2HR\}(\eta\text{-}C_5H_5)_2]$ (R = H or Ph) isomerise in boiling toluene to the μ-vinylidene complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCHR)(\eta\text{-}C_5H_5)_2]$, shown by a deuterium-labelling experiment to involve an intramolecular hydrogen shift. Protonation of the $\mu\text{-}C{=}CH_2$ complex with $HBF_4{\cdot}OEt_2$ gives the μ-ethylidyne species $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$, which deprotonates readily when treated with water, triethylamine, or methyl-lithium; with $NaBH_4$ the cation is attacked by hydride to produce the μ-ethylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$. Successive addition of methyl-lithium and $HBF_4{\cdot}OEt_2$ to $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ also yields the complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$, whose subsequent conversion to $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ or $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ provides an excellent route to these complexes. Similar successive addition of phenyl-lithium, $HBF_4{\cdot}OEt_2$, and $NaBH_4$ to $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ gives $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPh)(\eta\text{-}C_5H_5)_2]$ in high yield. The molecular structures of *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ and *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$ have been determined by *X*-ray diffraction studies. Crystals of both compounds are monoclinic, space group $P2_1/n$ with $Z = 4$ and unit-cell dimensions $a = 8.620(6)$, $b = 15.712(9)$, $c = 10.844(8)$ Å, $\beta = 92.57(4)°$ and $a = 9.121(2)$, $b = 9.724(3)$, $c = 20.666(6)$ Å, $\beta = 106.42(3)°$ respectively. The structures were solved by heavy-atom methods and refined by least squares to give final residuals *R* of 0.051 and 0.026 for 2 503 and 3 044 unique, observed, diffractometer data respectively. Both *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ and *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2]^+$ show approximate C_s symmetry in the solid state, with Ru–Ru single bond distances of 2.696(1) and 2.714(1) Å respectively. In both cases each ruthenium atom is co-ordinated by terminal carbonyl and η-cyclopentadienyl ligands in addition to bridging carbonyl and hydrocarbon (vinylidene and ethylidyne) groups. The geometry and orientation of the bridging vinylidene ligand is consistent with a C–C bond order of two [C–C 1.326(11) Å] and contact carbon bonding to the Ru_2 fragment *via* donor and acceptor interactions of σ and π symmetry in the Ru_2C plane. The μ-ethylidyne ligand in *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$ shows average Ru–C distances shorter than those of the μ-vinylidene ligand in *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ [1.937(4) *vs.* 2.030(7) Å], and has a longer C–C distance [1.462(6) Å] consonant with a C(*sp*)–C(*sp*^{3}) single bond. These geometric features, and the reactivity of the cationic μ-ethylidyne complex towards nucleophiles, are explained in terms of a simple molecular orbital model.

The synthesis of the dimetallacycle $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2H_2\}(\eta\text{-}C_5H_5)_2]$ (1) was reported in an earlier Part [2] of this series. The most intriguing aspect of its chemistry is that the carbon–carbon bond formed by linking of acetylene with a carbon monoxide ligand is easily broken. Thus in Part 3 of this series [3] we described how upon protonation a μ-vinyl cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]^+$ is produced. This is an irreversible process, but in solution below 100 °C (1) undergoes fluxional breaking and regeneration of the carbon–carbon bond.[2] We now report that at the higher temperature of boiling toluene (111 °C) the breaking becomes irreversible; it is accompanied by a hydrogen shift to yield a complex of the vinylidene ligand, $\mu\text{-}CCH_2$, which is readily converted to $\mu\text{-}CMe^+$ and μ-CHMe. The synthesis of these species through the transformation of a co-ordinated carbon monoxide ligand of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ is also described. Such simple but important C_2 hydrocarbon fragments co-ordinated at a dinuclear metal centre in a complex are of interest because of the insights they may provide into the behaviour of the same species on a metal surface in catalysis; [4–6] related or identical fragments are probably involved in the rearrangements suffered by acetylene and ethylene upon chemisorption.[7] Aspects of this work have appeared as a preliminary communication.[8]

Results and Discussion

Synthesis and Characterisation.—In boiling toluene the dimetallacycles $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2HR\}(\eta\text{-}C_5H_5)_2]$ [R = H (1) or Ph (2)] isomerise slowly over *ca.* 1 d to the μ-vinylidene complexes (3) (*ca.* 60%) and (4) (*ca.* 20%) respectively. Each exists as *cis* (a) and *trans* (b) isomers, separable by chromatography and isolated as air-stable bright yellow crystals. In solution at room temperature both (3a) and (3b) slowly transform to an equilibrium mixture of the two; in [$^2H_8$]toluene the (3a) : (3b) ratio attained is *ca.* 1.2 : 1. Isomerisation of (4a) occurs at a significant rate only on warming and at 70 °C in [$^2H_8$]toluene the isomers are present in about equal amount. It is likely that the mechanism of

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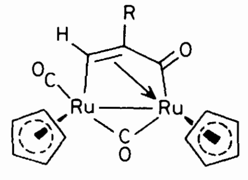
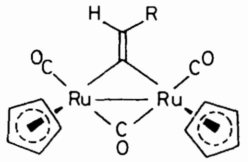
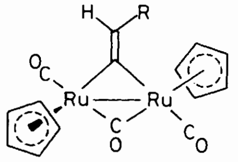
† *cis*-μ-Carbonyl-μ-vinylidene-bis[carbonyl(η^5-cyclopentadienyl)-ruthenium](*Ru–Ru*) and *cis*-μ-carbonyl-μ-ethylidyne-bis-[carbonyl(η^5-cyclopentadienyl)ruthenium](*Ru–Ru*)(1+) tetrafluoroborate.

Supplementary data available (No. SUP 23732, 42 pp.): structure factors, isotropic and anisotropic thermal parameters, H-atom co-ordinates. See Instructions for Authors, Section 4.0, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

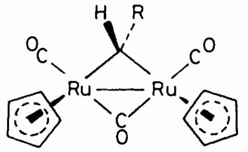


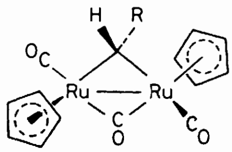
(1) R = H
(2) R = Ph



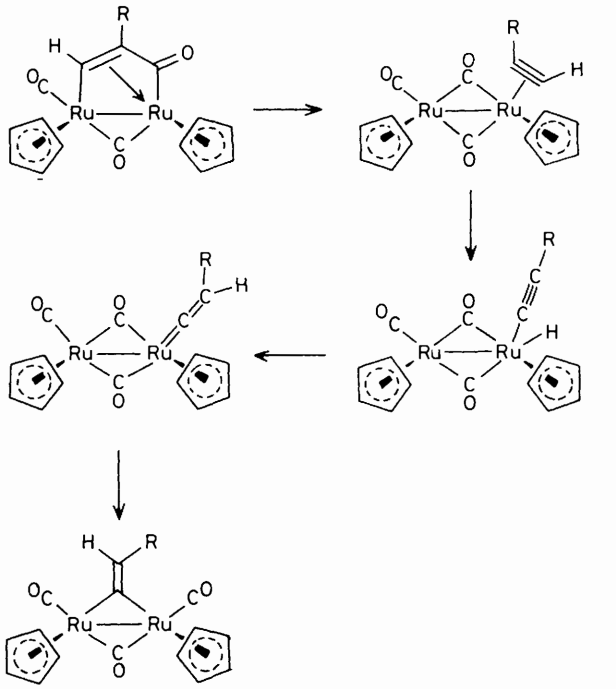


(3a) R = H (3b)
(4a) R = Ph (4b)





(6a) R = Me (6b)
(7a) R = Ph (7b)



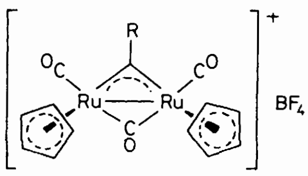
Scheme 1.

cis–trans isomerisation is analogous to that proposed[3] for isostructural μ-alkylidene complexes like (6) and (7), *i.e.* concerted bridge-opening to produce a transient terminal vinylidene complex, rotation about the unsupported metal–metal bond, and then bridge closure. However, the μ-alkylidene complexes undergo *cis–trans* isomerisation much more rapidly than does (3), sometimes even on the n.m.r. time-scale,[9] a feature attributable to the ease with which the alkylidene ligand leaves the bridging mode compared with the vinylidene ligand.

Spectroscopic characterisation (see Experimental section) of the μ-vinylidene complexes was straightforward. This is exemplified by (3a) and (3b): the *cis* isomer (3a) displays two terminal carbonyl stretching absorptions in the i.r., and the *trans* form (3b) only one, as expected on symmetry grounds, while the ^{1}H n.m.r. spectrum of each contains a single η-C_5H_5 resonance and single vinylidene proton resonance in accord with C_s (3a) or C_2 (3b) symmetry. This indication that all the atoms of the Ru_2(μ-CCHR) unit lie in the same plane was confirmed by the existence of two η-C_5H_5 signals for (4a) and by an *X*-ray diffraction study on (3a), described below. The ^{13}C n.m.r. spectra of (3a) and (3b) have signals for the μ-C*C*H_2 carbon at *ca.* 123 p.p.m., and for the μ-*C*CH_2 carbon at *ca.* 250 p.p.m., the latter being a substantially lower field shift than that (142.9 p.p.m.) observed[3] for the μ-*C*HMe carbon of (6a).

An insight into the mechanism of vinylidene formation was obtained by preparing complex (2) with deuterium in the C(O)-CRC^{2}H site, and studying its isomerisation. Treatment of phenylacetylene with n-butyl-lithium to give the lithium acetylide, followed by addition of water [99.9% $^2H_2$], gave phenylacetylene [98.6% ^{2}H, by mass spectrometry]. Using the deuteriated alkyne, complex (2) was synthesised by the literature method;[2] computer matching of the molecular ion (M^+) isotope pattern of (2) with $(M + 1)^+$ now provided a best fit to the observed pattern for 87.5% deuterium incorporation. Similar treatment of the $(M - 2CO)^+$ ion indicated 92.5% incorporation. Finally, heating the deuteriated complex in toluene at reflux afforded a sample of (4a) containing 74.3% deuterium by mass spectrometry. It is therefore evident that the hydrogen migration involved in vinylidene formation is substantially intramolecular. This leads us to propose the pathway laid out in Scheme 1. The first step yields a terminal alkyne complex which has a well established ethylene analogue;[10,11] moreover, the related acetonitrile complex $[Ru_2(CO)(MeCN)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$[12] reacts with acetylene at room temperature to form (1), and this synthesis is very likely to comprise an initial replacement of labile MeCN by a terminally bound HC_2H molecule, followed by alkyne–CO linking, *i.e.* the reverse of our proposed high-temperature step. The transformation of a terminal alkyne to terminal vinylidene ligand has several precedents,[13–16] and it seems plausible for it to occur *via* the oxidative addition depicted in Scheme 1. Subsequent migration of the terminal vinylidene to a lower-energy bridging site[3] completes the process. Hydrogen (or deuterium) terminally bound to a transition metal is susceptible to exchange and the slight deuterium loss observed in the labelling experiment described earlier is therefore consistent with the suggested metal hydride intermediate.

The μ-vinylidene complex (3) is converted quantitatively to the μ-ethylidyne species $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$ (5) upon addition of $HBF_4 \cdot OEt_2$. The orange, crystalline salt appears indefinitely stable under vacuum, but decomposes slowly in air. Both i.r. and n.m.r. spectra (Experimental section) identify the presence only of a *cis* isomer in solution.



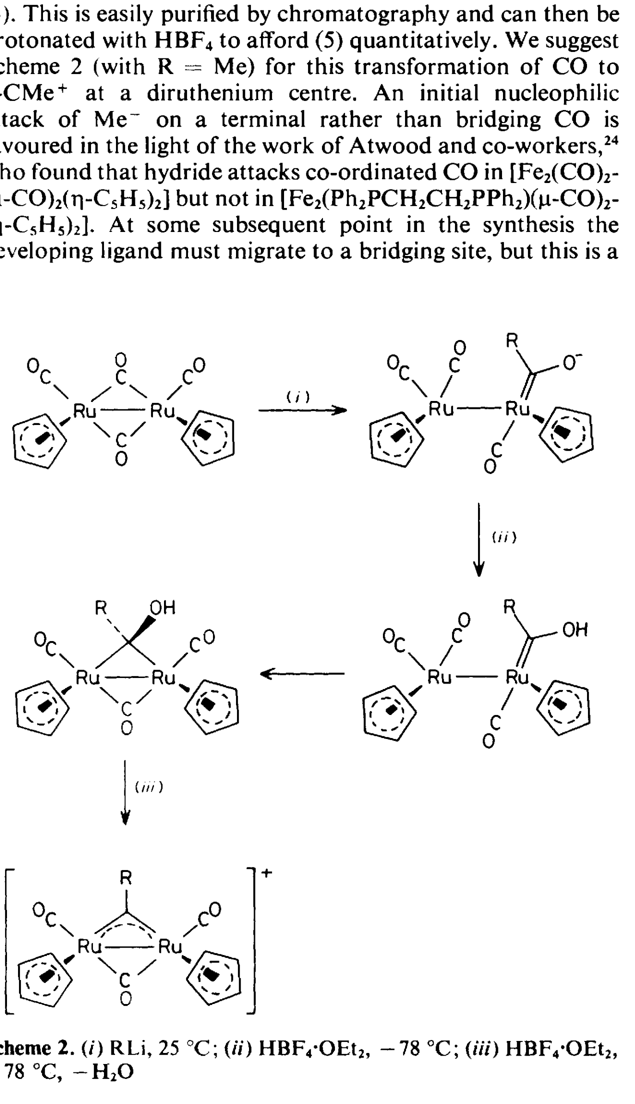
(5) R = Me
(8) R = Ph

The ^{13}C n.m.r. spectrum is additionally notable for the very low field shift (469.7 p.p.m.) of the μ-*C*Me carbon, among the lowest observed for a diamagnetic organometallic complex; *cf.* $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)(\eta\text{-}C_5H_5)_2]^+$ (490.2)[17] and $[Fe_5C(CO)_{15}]$ (486.0 p.p.m.).[18] The molecular structure of (5) was determined by *X*-ray diffraction (see below).

Protonation of $[Mn_2(CO)_4(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$[19] and $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$[20,21] likewise yields μ-ethylidyne cations, but unaccountably $[Rh_2(CO)_2(\mu\text{-}CCH_2)(\eta^5\text{-}C_9H_7)_2]$[22] differs in forming the μ-vinyl cation $[Rh_2(CO)_2(\mu\text{-}CHCH_2)(\eta^5\text{-}C_9H_7)_2]^+$.

The methyl group of the μ-CMe ligand in (5) is very acidic, and the cation is rapidly and quantitatively deprotonated to regenerate (3) on shaking a dichloromethane solution with water, triethylamine, or methyl-lithium. Similar behaviour is shown by the iron analogue, which is readily synthesised from $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ through nucleophilic attack of methyl-lithium upon a co-ordinated CO ligand.[21,23] This pathway is also applicable to $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, and provides the best route to (5) and thence (3).

Treatment of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with methyl-lithium at room temperature quickly yields an unisolated species whose i.r. spectrum contains only terminal carbonyl stretching bands at 2 029s and 1 966s, br cm^{-1}. Addition of $HBF_4{\cdot}OEt_2$ then equally quickly provides a solution of the μ-ethylidyne complex (5), but in order to obtain this pure it is best to add water or triethylamine at this stage to form the μ-vinylidene complex (3). This is easily purified by chromatography and can then be protonated with HBF_4 to afford (5) quantitatively. We suggest Scheme 2 (with R = Me) for this transformation of CO to μ-CMe$^+$ at a diruthenium centre. An initial nucleophilic attack of Me$^-$ on a terminal rather than bridging CO is favoured in the light of the work of Atwood and co-workers,[24] who found that hydride attacks co-ordinated CO in $[Fe_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ but not in $[Fe_2(Ph_2PCH_2CH_2PPh_2)(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$. At some subsequent point in the synthesis the developing ligand must migrate to a bridging site, but this is a well established feature of alkylidene and alkylidyne species (see ref. 3 and refs. therein).



Scheme 2. (*i*) RLi, 25 °C; (*ii*) $HBF_4{\cdot}OEt_2$, −78 °C; (*iii*) $HBF_4{\cdot}OEt_2$, −78 °C, $-H_2O$

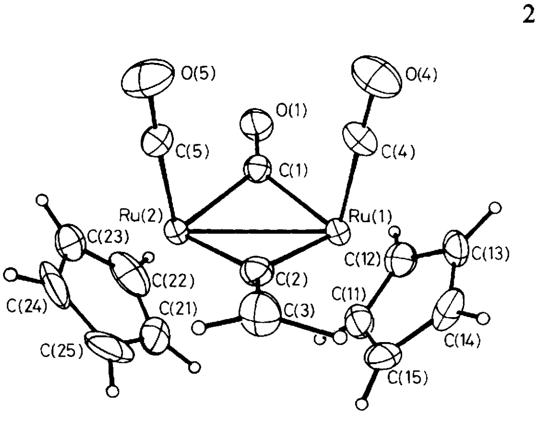


Figure 1. Molecular structure of *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ (3a)

Unlike methyl-lithium, which as described earlier abstracts a proton from (5), hydride (in the form of $NaBH_4$) attacks the bridging carbon of the μ-ethylidyne ligand to form the μ-ethylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ (6). Although prepared previously[3] by sequential addition of HBF_4 and $NaBH_4$ to (1), the direct route from $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ *via* (5) is better. It is unnecessary actually to isolate (5); successive addition of methyl-lithium, $HBF_4{\cdot}OEt_2$, and $NaBH_4$ to $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ provides (6) in high yield. An attempt to obtain a μ-C(Me)OMe complex by reaction of (5) with methoxide ion gave only a dark red cluster complex which will be the subject of a future publication.

The new complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPh)(\eta\text{-}C_5H_5)_2]$ (7) is also prepared efficiently by adding phenyl-lithium, $HBF_4{\cdot}OEt_2$, and $NaBH_4$ in succession to $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$. It is assumed that the first two of these reagents generate the μ-CPh cation (8), as in Scheme 2, and that this then suffers hydride attack to give (7). The i.r. and n.m.r. spectra of (7) reveal the presence of both a *cis*-(7a) and *trans*-(7b) isomer, in *ca.* 2 : 1 ratio in $CDCl_3$ at room temperature. Unlike the vinylidene isomers these were not separable by chromatography and their rapid interconversion in the same manner as (6a) and (6b) is likely.[3,9]

Molecular Structures of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ (3a) *and* $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$ (5).—The crystal and molecular structures of (3a) and (5) were determined at room temperature by *X*-ray diffraction studies. The molecular geometry of (3a) is illustrated in Figure 1 and that of the cation in (5) in Figure 2. The bond lengths and inter-bond angles derived are listed in Tables 1 and 2 for (3a) and 3 and 4 for (5), respectively. Both (3a) and the cation of (5) belong to the general class of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L)(\eta\text{-}C_5H_5)_2]$ complexes, where L is a two-electron donor ligand (*e.g.*, L = CO,[25] CH_2,[26] or CMe_2[9]). Thus in (3a), L = CCH_2, and in (5), L = CMe$^+$. In such complexes the formal metal–metal bond order is one, and the Ru(1)–Ru(2) lengths observed here are consistent with this formalism [2.696(1) in (3a) and 2.714(1) Å in (5)] and similar to those in other examples.[9,25,26] As is usual for the *cis* isomers of these complexes, (3a) and the cation of (5) show approximate C_s geometry. The *cis* conformations found here are reflected in the C(4)–Ru(1)–Ru(2)–C(5) torsion angles [−2.2(4) in (3a) and −2.6(2)° in (5)] being close to zero. In both (3a) and (5) there is substantial puckering of the central $Ru_2(\mu\text{-}C)_2$ unit, the dihedral angle between the Ru(1)–Ru(2)–C(1) and Ru(1)–Ru(2)–C(2) planes being 22.3 and 15.2° respectively.

This puckering in *cis*-$[M_2(CO)_2(\mu\text{-}L)_2(\eta\text{-}C_5H_5)_2]$ complexes is typical and its origin has been traced to electronic factors.[27]

The structures of this pair of complexes allow a detailed comparison of the bonding capabilities of the CCH_2 (vinylidene) and CMe (ethylidyne) ligands when bridging between two transition metals. In this case the comparison is strictly between CCH_2 and CMe^+, each acting as two-electron donor ligands with powerful π-acid properties. The most marked effects of protonation of the vinylidene ligand are in the geometry around the bridging carbon, C(2). Thus, the C(2)-C(3) bond length increases from 1.326(11) Å in (3a) to 1.462(6) Å in (5), the mean Ru-C(2) distance decreases from 2.030(7) to 1.937(4) Å, and the Ru(1)-C(2)-Ru(2) angle increases from 83.2(3) to 89.0(1)°. In both (3a) and (5) the contact carbon [C(2)] shows planar three-co-ordinate geometry, and symmetrically bridges Ru(1) and Ru(2).

The methylene moiety in (3a) is very close to being coplanar with the Ru(1)-Ru(2)-C(2) plane [Ru-C(2)-C(3)-H torsion angles are −4(4), −172(5), 170(4), and 2(5)°]. In this orientation the C(2)-C(3) π and π* orbitals lie in the plane perpendicular to the Ru(1)-Ru(2)-C(2) plane; we shall term this orientation ' out-of-plane ' and that in or close to the Ru(1)-Ru(2)-C(2) plane ' in-plane ' for convenience of discussion. Considering the CCH_2 to be a neutral, two-electron donor ligand and the contact carbon C(2) to be *sp* hydridised, one of the *p* orbitals of C(2) will not be involved in π bonding to C(3), and therefore acts as the principal π-acceptor function of the ligand. The orientation adopted by the vinylidene ligand places this acceptor function in-plane, just as μ-alkylidene ligands (CR_2) bonded to the $[Ru_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ moiety are oriented to have their π-acceptor *p* orbital in-plane.[9,26] This behaviour implies that the primary donor function of the $[Ru_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ unit lies in plane

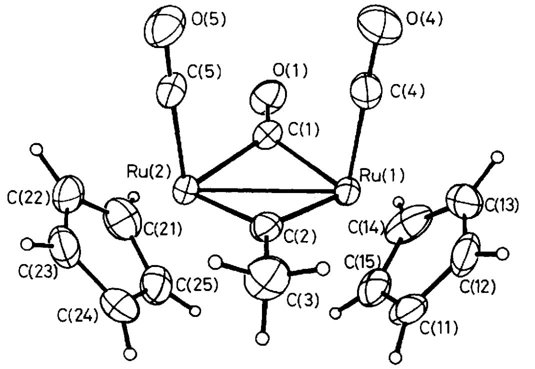


Figure 2. Molecular structure of the cation of *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$ (5)

Table 1. Bond lengths (Å) for (3a) *

Ru(1)-Ru(2)	2.696(1)	Ru(1)-C(1)	2.038(7)
Ru(1)-C(2)	2.033(7)	Ru(1)-C(4)	1.845(8)
Ru(1)-C(11)	2.275(9)	Ru(1)-C(12)	2.279(9)
Ru(1)-C(13)	2.231(8)	Ru(1)-C(14)	2.237(10)
Ru(1)-C(15)	2.277(9)	Ru(2)-C(1)	2.047(7)
Ru(2)-C(2)	2.026(7)	Ru(2)-C(5)	1.840(7)
Ru(2)-C(21)	2.266(9)	Ru(2)-C(25)	2.246(12)
Ru(2)-C(24)	2.207(10)	Ru(2)-C(23)	2.248(9)
Ru(2)-C(22)	2.273(11)	O(1)-C(1)	1.171(8)
O(4)-C(4)	1.138(10)	O(5)-C(5)	1.152(9)
C(2)-C(3)	1.326(11)	C(3)-H(31)	1.226(74)
C(3)-H(32)	0.892(69)	C(11)-C(12)	1.382(13)
C(11)-C(15)	1.376(17)	C(12)-C(13)	1.393(12)
C(13)-C(14)	1.428(14)	C(14)-C(15)	1.427(14)
C(21)-C(25)	1.390(18)	C(21)-C(22)	1.382(17)
C(25)-C(24)	1.362(17)	C(24)-C(23)	1.380(20)
C(23)-C(22)	1.342(16)		

* The estimated standard deviation in the final digit is given in parentheses here and throughout this paper.

Table 2. Bond angles (°) for (3a)

Ru(2)-Ru(1)-C(1)	48.9(2)	Ru(2)-Ru(1)-C(2)	48.3(2)	C(25)-Ru(2)-C(24)	35.6(4)	Ru(1)-Ru(2)-C(23)	148.6(3)
C(1)-Ru(1)-C(2)	94.7(3)	Ru(2)-Ru(1)-C(4)	98.5(2)	C(1)-Ru(2)-C(23)	110.5(4)	C(2)-Ru(2)-C(23)	152.6(4)
C(1)-Ru(1)-C(4)	87.8(3)	C(2)-Ru(1)-C(4)	87.0(3)	C(5)-Ru(2)-C(23)	106.3(4)	C(21)-Ru(2)-C(23)	58.6(4)
Ru(2)-Ru(1)-C(11)	102.3(2)	C(1)-Ru(1)-C(11)	100.2(3)	C(25)-Ru(2)-C(23)	59.5(4)	C(24)-Ru(2)-C(23)	36.1(5)
C(2)-Ru(1)-C(11)	112.5(3)	C(4)-Ru(1)-C(11)	157.9(3)	Ru(1)-Ru(2)-C(22)	115.2(3)	C(1)-Ru(2)-C(22)	91.9(3)
Ru(2)-Ru(1)-C(12)	123.3(2)	C(1)-Ru(1)-C(12)	93.7(3)	C(2)-Ru(2)-C(22)	138.6(4)	C(5)-Ru(2)-C(22)	136.7(7)
C(2)-Ru(1)-C(12)	147.9(3)	C(4)-Ru(1)-C(12)	124.3(3)	C(21)-Ru(2)-C(22)	35.4(4)	C(25)-Ru(2)-C(22)	59.4(4)
C(11)-Ru(1)-C(12)	35.3(3)	Ru(2)-Ru(1)-C(13)	159.1(2)	C(24)-Ru(2)-C(22)	58.9(4)	C(23)-Ru(2)-C(22)	34.5(4)
C(1)-Ru(1)-C(13)	120.8(3)	C(2)-Ru(1)-C(13)	144.0(3)	Ru(1)-C(1)-Ru(2)	82.6(2)	Ru(1)-C(1)-O(1)	139.8(6)
C(4)-Ru(1)-C(13)	99.0(3)	C(11)-Ru(1)-C(13)	59.2(3)	Ru(2)-C(1)-O(1)	137.6(5)	Ru(1)-C(2)-Ru(2)	83.2(3)
C(12)-Ru(1)-C(13)	36.0(3)	Ru(2)-Ru(1)-C(14)	144.4(3)	Ru(1)-C(2)-C(3)	135.9(7)	Ru(2)-C(2)-C(3)	140.7(7)
C(1)-Ru(1)-C(14)	154.7(3)	C(2)-Ru(1)-C(14)	106.9(3)	C(2)-C(3)-H(31)	111.7(37)	C(2)-C(3)-H(32)	104.5(47)
C(4)-Ru(1)-C(14)	105.9(3)	C(11)-Ru(1)-C(14)	59.8(4)	H(31)-C(3)-H(32)	142.0(57)	Ru(1)-C(4)-O(4)	177.8(7)
C(12)-Ru(1)-C(14)	61.0(3)	C(13)-Ru(1)-C(14)	37.3(3)	Ru(2)-C(5)-O(5)	176.1(7)	Ru(1)-C(11)-C(12)	72.5(5)
Ru(2)-Ru(1)-C(15)	110.4(3)	C(1)-Ru(1)-C(15)	132.1(3)	Ru(1)-C(11)-C(15)	72.5(5)	C(12)-C(11)-C(15)	111.5(8)
C(2)-Ru(1)-C(15)	92.0(3)	C(4)-Ru(1)-C(15)	140.0(4)	Ru(1)-C(12)-C(11)	72.2(5)	Ru(1)-C(12)-C(13)	70.1(5)
C(11)-Ru(1)-C(15)	35.2(4)	C(12)-Ru(1)-C(15)	60.1(4)	C(11)-C(12)-C(13)	106.6(8)	Ru(1)-C(13)-C(12)	73.9(5)
C(13)-Ru(1)-C(15)	60.9(3)	C(14)-Ru(1)-C(15)	36.8(4)	Ru(1)-C(13)-C(14)	71.6(5)	C(12)-C(13)-C(14)	108.8(8)
Ru(1)-Ru(2)-C(1)	48.6(2)	Ru(1)-Ru(2)-C(2)	48.5(2)	Ru(1)-C(14)-C(13)	71.1(5)	Ru(1)-C(14)-C(15)	73.1(5)
C(1)-Ru(2)-C(2)	94.7(3)	Ru(1)-Ru(2)-C(5)	97.1(2)	C(13)-C(14)-C(15)	106.4(9)	Ru(1)-C(15)-C(11)	72.3(5)
C(1)-Ru(2)-C(5)	88.5(3)	C(2)-Ru(2)-C(5)	84.4(3)	Ru(1)-C(15)-C(14)	70.0(5)	C(11)-C(15)-C(14)	106.7(9)
Ru(1)-Ru(2)-C(21)	101.4(2)	C(1)-Ru(2)-C(21)	107.4(4)	Ru(2)-C(21)-C(25)	71.3(6)	Ru(2)-C(21)-C(22)	72.6(6)
C(2)-Ru(2)-C(21)	104.3(3)	C(5)-Ru(2)-C(21)	160.9(3)	C(25)-C(21)-C(22)	107.7(9)	Ru(2)-C(25)-C(21)	72.9(6)
Ru(1)-Ru(2)-C(25)	120.0(3)	C(1)-Ru(2)-C(25)	143.2(4)	Ru(2)-C(25)-C(24)	70.6(7)	C(21)-C(25)-C(24)	106.8(11)
C(2)-Ru(2)-C(25)	93.8(4)	C(5)-Ru(2)-C(25)	128.0(4)	Ru(2)-C(24)-C(25)	73.8(6)	Ru(2)-C(24)-C(23)	73.6(6)
C(21)-Ru(2)-C(25)	35.9(5)	Ru(1)-Ru(2)-C(24)	155.6(3)	C(25)-C(24)-C(23)	108.8(11)	Ru(2)-C(23)-C(24)	70.3(6)
C(1)-Ru(2)-C(24)	146.6(4)	C(2)-Ru(2)-C(24)	117.8(4)	Ru(2)-C(23)-C(22)	73.8(6)	C(24)-C(23)-C(22)	108.2(10)
C(5)-Ru(2)-C(24)	101.7(4)	C(21)-Ru(2)-C(24)	59.2(4)	Ru(2)-C(22)-C(21)	72.0(6)	Ru(2)-C(22)-C(23)	71.7(6)
				C(21)-C(22)-C(23)	108.5(11)		

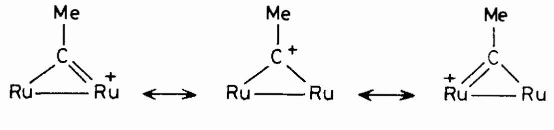
(and is Ru–Ru antibonding). The C(2)–C(3) π^* orbital lies at higher energy than the in-plane C(2) *p* orbital and is clearly of secondary importance as an acceptor function, a fact which has been noted in theoretical analyses of mononuclear vinylidene complexes.[28] That there is only limited occupancy of this π^* orbital is reflected in the C(2)–C(3) bond length [1.326(11) Å] which is close to the standard value for a C=C double bond [1.337(3) Å].[29] The mean Ru–C(2) length in (3a) is marginally shorter than the average Ru–C(1) length [2.030(7) *vs.* 2.043(7) Å] and markedly shorter than the corresponding Ru–C distances in μ-CR$_2$ complexes [$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CR_2)(\eta\text{-}C_5H_5)_2$] [R = H, Ru–C 2.078(6) Å;[26] R = Me, Ru–C 2.113(4) Å [9]].

Table 3. Bond lengths (Å) for (5) *

Ru(1)–Ru(2)	2.714(1)	Ru(1)–C(2)	1.933(3)
Ru(1)–C(1)	2.054(4)	Ru(1)–C(4)	1.900(4)
Ru(1)–C(11)	2.260(5)	Ru(1)–C(12)	2.223(5)
Ru(1)–C(13)	2.223(4)	Ru(1)–C(14)	2.271(6)
Ru(1)–C(15)	2.261(5)	Ru(2)–C(2)	1.941(4)
Ru(2)–C(1)	2.070(3)	Ru(2)–C(5)	1.897(4)
Ru(2)–C(21)	2.286(5)	Ru(2)–C(22)	2.246(5)
Ru(2)–C(23)	2.228(4)	Ru(2)–C(24)	2.267(4)
Ru(2)–C(25)	2.256(6)	C(2)–C(3)	1.462(6)
C(1)–O(1)	1.164(4)	C(4)–O(4)	1.143(6)
C(5)–O(5)	1.134(6)	C(11)–C(12)	1.365(6)
C(11)–C(15)	1.380(7)	C(12)–C(13)	1.390(9)
C(13)–C(14)	1.406(10)	C(14)–C(15)	1.401(7)
C(21)–C(22)	1.384(8)	C(21)–C(25)	1.437(8)
C(22)–C(23)	1.402(8)	C(23)–C(24)	1.386(8)
C(24)–C(25)	1.378(8)	B–F(1)	1.364(8)
B–F(2)	1.356(9)	B–F(3)	1.271(13)
B–F(4)	1.278(9)	B–F(1′)	1.298(25)
B–F(2′)	1.284(21)	B–F(3′)	1.316(26)
B–F(4′)	0.982(70)		

* Primed atoms are those of the minor component of the disordered BF_4^- ion (as in Tables 4 and 6 also).

In the case of the μ-CMe$^+$ moiety in (5) there can be no comparable orientational preference. The contact carbon C(2), if described as *sp* hybridised, possesses *two* equivalent vacant *p* orbitals which act as in-plane and out-of-plane acceptor functions. The C(2)–C(3) bond length in (5) [1.462(6) Å] is consistent with *sp* hybridisation at C(2), corresponding exactly to the standard value for a C(*sp*)–C(*sp*^{3}) bond [1.460(3) Å].[29] The shortening of the Ru–C(2) bond lengths in (5) relative to (3a) would therefore appear to result from improved out-of-plane π back donation in (5) due to the presence of a better (lower energy) π-acceptor function on the contact carbon. This molecular orbital description of the bonding in the cation of (5) is equivalent to a valence-bond description invoking resonance between the three canonical forms (I)—(III). The extremely low-field ^{13}C n.m.r. chemical shift of the contact carbon of the μ-CMe moiety in (5) is consistent with canonical form (II) playing a significant role. The delocalisation of positive charge between Ru(1), Ru(2), and C(2), *via* the π back-donation interactions described above, results in reduced π-donation from the metals to the carbonyl ligand in (5) relative to (3a). This in turn results in longer Ru–C(O) distances in (5) than in (3a) (see below). In the



(I) (II) (III)

Table 4. Bond angles (°) for (5)

Ru(2)–Ru(1)–C(2)	45.6(1)	Ru(2)–Ru(1)–C(1)	49.1(1)	C(5)–Ru(2)–C(24)	135.3(2)	C(21)–Ru(2)–C(24)	60.0(2)
C(2)–Ru(1)–C(1)	93.6(1)	Ru(2)–Ru(1)–C(4)	97.0(1)	C(22)–Ru(2)–C(24)	60.1(2)	C(23)–Ru(2)–C(24)	35.9(2)
C(2)–Ru(1)–C(4)	91.2(2)	C(1)–Ru(1)–C(4)	87.0(2)	Ru(1)–Ru(2)–C(25)	105.3(1)	C(2)–Ru(2)–C(25)	109.8(2)
Ru(2)–Ru(1)–C(11)	117.7(1)	C(2)–Ru(1)–C(11)	94.4(2)	C(1)–Ru(2)–C(25)	101.6(2)	C(5)–Ru(2)–C(25)	158.8(2)
C(1)–Ru(1)–C(11)	135.9(2)	C(4)–Ru(1)–C(11)	136.0(2)	C(21)–Ru(2)–C(25)	36.9(2)	C(22)–Ru(2)–C(25)	60.4(2)
Ru(2)–Ru(1)–C(12)	151.1(1)	C(2)–Ru(1)–C(12)	112.8(2)	C(23)–Ru(2)–C(25)	60.0(2)	C(24)–Ru(2)–C(25)	35.5(2)
C(1)–Ru(1)–C(12)	151.0(2)	C(4)–Ru(1)–C(12)	103.3(2)	Ru(1)–C(2)–Ru(2)	89.0(1)	Ru(1)–C(2)–C(3)	134.8(3)
C(11)–Ru(1)–C(12)	35.4(2)	Ru(2)–Ru(1)–C(13)	159.3(2)	Ru(2)–C(2)–C(3)	135.7(3)	Ru(1)–C(1)–Ru(2)	82.3(1)
C(2)–Ru(1)–C(13)	149.3(2)	C(1)–Ru(1)–C(13)	116.3(2)	Ru(1)–C(1)–O(1)	139.1(3)	Ru(2)–C(1)–O(1)	138.5(3)
C(4)–Ru(1)–C(13)	96.7(2)	C(11)–Ru(1)–C(13)	59.8(2)	Ru(1)–C(4)–O(4)	179.2(3)	Ru(2)–C(5)–O(5)	177.5(3)
C(12)–Ru(1)–C(13)	36.4(2)	Ru(2)–Ru(1)–C(14)	123.0(1)	Ru(1)–C(11)–C(12)	70.8(3)	Ru(1)–C(11)–C(15)	72.3(3)
C(2)–Ru(1)–C(14)	145.1(2)	C(1)–Ru(1)–C(14)	91.2(2)	C(12)–C(11)–C(15)	108.8(4)	Ru(1)–C(12)–C(11)	73.8(3)
C(4)–Ru(1)–C(14)	123.5(2)	C(11)–Ru(1)–C(14)	59.7(2)	Ru(1)–C(12)–C(13)	71.8(3)	C(11)–C(12)–C(13)	108.4(5)
C(12)–Ru(1)–C(14)	60.4(2)	C(13)–Ru(1)–C(14)	36.4(2)	Ru(1)–C(13)–C(12)	71.8(3)	Ru(1)–C(13)–C(14)	73.6(3)
Ru(2)–Ru(1)–C(15)	104.9(1)	C(2)–Ru(1)–C(15)	109.4(2)	C(12)–C(13)–C(14)	107.9(4)	Ru(1)–C(14)–C(13)	69.9(3)
C(1)–Ru(1)–C(15)	101.5(2)	C(4)–Ru(1)–C(15)	156.9(1)	Ru(1)–C(14)–C(15)	71.6(3)	C(13)–C(14)–C(15)	106.5(5)
C(11)–Ru(1)–C(15)	35.6(2)	C(12)–Ru(1)–C(15)	59.7(2)	Ru(1)–C(15)–C(11)	72.2(3)	Ru(1)–C(15)–C(14)	72.4(3)
C(13)–Ru(1)–C(15)	60.2(2)	C(14)–Ru(1)–C(15)	36.0(2)	C(11)–C(15)–C(14)	108.3(4)	Ru(2)–C(21)–C(22)	70.7(3)
Ru(1)–Ru(2)–C(2)	45.4(1)	Ru(1)–Ru(2)–C(1)	48.6(1)	Ru(2)–C(21)–C(25)	70.4(3)	C(22)–C(21)–C(25)	106.7(5)
C(2)–Ru(2)–C(1)	92.9(1)	Ru(1)–Ru(2)–C(5)	95.2(1)	Ru(2)–C(22)–C(21)	73.8(3)	Ru(2)–C(22)–C(23)	71.1(3)
C(2)–Ru(2)–C(5)	88.2(2)	C(1)–Ru(2)–C(5)	87.9(1)	C(21)–C(22)–C(23)	108.5(5)	Ru(2)–C(23)–C(22)	72.4(3)
Ru(1)–Ru(2)–C(21)	123.4(1)	C(2)–Ru(2)–C(21)	146.3(2)	Ru(2)–C(23)–C(24)	73.6(3)	C(22)–C(23)–C(24)	108.3(5)
C(1)–Ru(2)–C(21)	91.1(2)	C(5)–Ru(2)–C(21)	125.3(2)	Ru(2)–C(24)–C(23)	70.5(3)	Ru(2)–C(24)–C(25)	71.8(3)
Ru(1)–Ru(2)–C(22)	158.5(1)	C(2)–Ru(2)–C(22)	151.0(2)	C(23)–C(24)–C(25)	108.4(5)	Ru(2)–C(25)–C(21)	72.7(3)
C(1)–Ru(2)–C(22)	115.4(2)	C(5)–Ru(2)–C(22)	98.5(2)	Ru(2)–C(25)–C(24)	72.7(3)	C(21)–C(25)–C(24)	107.9(5)
C(21)–Ru(2)–C(22)	35.5(2)	Ru(1)–Ru(2)–C(23)	152.7(2)	F(1)–B–F(2)	106.3(6)	F(1)–B–F(3)	113.2(7)
C(2)–Ru(2)–C(23)	114.5(2)	C(1)–Ru(2)–C(23)	150.5(2)	F(2)–B–F(3)	108.1(7)	F(1)–B–F(4)	115.1(7)
C(5)–Ru(2)–C(23)	103.1(2)	C(21)–Ru(2)–C(23)	60.1(2)	F(2)–B–F(4)	110.1(8)	F(3)–B–F(4)	103.9(8)
C(22)–Ru(2)–C(23)	36.5(2)	Ru(1)–Ru(2)–C(24)	118.7(2)	F(1′)–B–F(2′)	119.4(15)	F(1′)–B–F(3′)	108.8(15)
C(2)–Ru(2)–C(24)	95.5(2)	C(1)–Ru(2)–C(24)	136.1(2)	F(2′)–B–F(3′)	104.4(15)	F(1′)–B–F(4′)	96.8(39)
				F(2′)–B–F(4′)	111.0(34)	F(3′)–B–F(4′)	117.1(40)

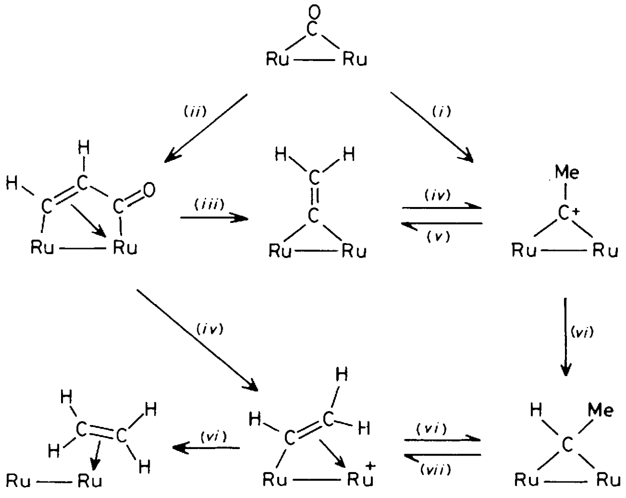
above description both the vinylidene and the cationic ethylidyne ligands donate two electrons to the Ru_2 unit *via* the (in-plane) $C(2)_{sp}$ σ-donor orbital. This interaction is thus between the lowest unoccupied molecular orbital (l.u.m.o.) of the $[Ru_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ fragment (an in-plane orbital which is Ru–Ru bonding) and the highest occupied molecular orbital (h.o.m.o.) of the C_2 ligand (the C_{sp} σ orbital).

The qualitative arguments above have been confirmed by an extended Hückel molecular orbital (EHMO) study of these and related molecules in the $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L)(\eta\text{-}C_5H_5)_2]$ class.[30] The calculations on the cation of (5) show that its l.u.m.o. is largely composed of the out-of-plane *p* orbital of C(2) (mixed with some out of phase contribution from the out-of-plane Ru_2 fragment donor orbital); this m.o. is isolated in energy from the higher lying virtual orbitals. In such circumstances nucleophilic attack on the cation is likely to proceed *via* direct attack on the contact carbon giving rise, in the case of H^- as nucleophile, to the observed μ-carbene complex (6). That nucleophilic attack on mononuclear alkylidyne complexes is similarly frontier-orbital controlled was the conclusion of a recent theoretical study.[31] The electrophilicity of the out-of-plane *p* orbital of the contact carbon in a μ-alkylidyne is noticeable in trinuclear complexes also, and has been observed to result in heteroatom stabilisation of the alkylidyne moiety [32] and interaction with a third metal atom.[33]

Other features of the molecular structures follow expected patterns. Thus Ru–μ-C(O) distances are longer [mean 2.043(7) *vs.* mean 1.843(7) Å in (3a); mean 2.062(4) *vs.* mean 1.899(4) Å in (5)] than the terminal Ru–C(O) lengths. The Ru–C–O angles for terminal carbonyl ligands show small deviations from linearity [mean 177.0(7)° in (3a) and mean 178.4(3)° in (5)]. The cyclopentadienyl ligands in both (3a) and (5) show only small variations in Ru–C distances and are η^5-bonded [Ru–C 2.207(10)—2.279(9), mean 2.254(8) Å in (3a); 2.223(4)—2.286(5), mean 2.252(7) Å in (5)]. Remaining geometric features are unremarkable.

Conclusions

The results of the synthetic work described in this paper are summarised in Scheme 3, which also includes observations recounted in an earlier Part.[3] The Scheme emphasises that there exists an extensive organic chemistry of the diruthenium centre which relates carbon monoxide, acetylene, ethylene, and the C_2 hydrocarbon species CCH_2, CMe, CHMe, and $CHCH_2$. The pathways for their interconversion may be relevant to the behaviour of acetylene and ethylene chemisorbed on metal surfaces. At 300—350 K on a Pt(111) surface both acetylene and ethylene rearrange to an ethylidyne fragment, bound at a trimetal site,[7] and on the evidence of our work a vinylidene intermediate is probably involved.



Scheme 3. (*i*) Me^-, $2H^+$, $-H_2O$; (*ii*) PhC_2Ph then HC_2H; (*iii*) boiling toluene; (*iv*) H^+; (*v*) H_2O, NEt_3, or Me^-, $-H^+$; (*vi*) H^-; (*vii*) Ph_3C^+, $-H^-$

In addition the structural studies reported here provide a useful insight into the characteristics of the vinylidene and ethylidyne C_2 hydrocarbon units. The geometric features of their binding to the diruthenium centre are readily understood in terms of a qualitative molecular orbital treatment. This treatment also allows an insight into the reactivity of the μ-CMe unit towards nucleophiles, which appears to be frontier-orbital controlled.

Experimental

Instrumentation and techniques were as described in Part 1 of this series.[2] Methyl-lithium (Ventron), phenyl-lithium, $NaBH_4$, and $HBF_4{\cdot}OEt_2$ (Aldrich) were used as supplied.

Preparation of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ (3).—(*a*) *From* $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2H_2\}(\eta\text{-}C_5H_5)_2]$ (1). A toluene (125 cm^3) solution of (1) (0.15 g, 0.34 mmol) was heated at reflux for 20 h. After evaporation to dryness at reduced pressure the residue was subjected to chromatography on an alumina column (40—50 × 2 cm). Elution with dichloromethane–hexane (2 : 3) developed two bright yellow bands which yielded, in turn, 43 mg (29%) of yellow crystalline *trans*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ (3b) [m.p. 178—180 °C; ν(CO) (in CH_2Cl_2) at 1 953s and 1 793m cm^{-1}; ^1H n.m.r. (in $CDCl_3$) δ 5.26 (s, 10 H, $2C_5H_5$) and 6.37 (s, 2 H, CH_2); ^{13}C n.m.r. (in CD_2Cl_2) δ 92.2 ($2C_5H_5$), 123.0 (CH_2), 199.1 (2CO), 244.1 (μ-CO), and 250.1 (*C*CH_2); Found: C, 41.3; H, 2.9%; *M*, 443. $C_{15}H_{12}O_3Ru_2$ requires C, 40.7; H, 2.7%; *M*, 443] and 51 mg (34%) of yellow crystalline *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ (3a) [m.p. 178—180 °C; ν(CO) (in CH_2Cl_2) at 1 994s, 1 951w, and 1 788m cm^{-1}; ^1H n.m.r. (in $CDCl_3$) δ 5.20 (s, 10 H, $2C_5H_5$) and 6.27 (s, 2 H, CH_2); ^{13}C n.m.r. (in CD_2Cl_2) δ 90.3 ($2C_5H_5$), 122.7 (CH_2), 199.6 (2CO), 245.2 (μ-CO), and 249.1 (*C*CH_2); Found: C, 40.7; H, 2.8%; *M*, 443. $C_{15}H_{12}O_3Ru_2$ requires C, 40.7; H, 2.7%; *M*, 443], each purified by crystallisation from dichloromethane–hexane.

(*b*) *From* $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Methyl-lithium in diethyl ether (2 cm^3 of a 1 mol dm^{-3} solution) was added to a tetrahydrofuran (60 cm^3) solution of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.79 g, 1.78 mmol) and the mixture stirred for 0.75 h. After cooling to −78 °C an excess of $HBF_4{\cdot}OEt_2$ (2 cm^3) was added, giving an orange precipitate identified by i.r. as (5). The mixture was allowed to warm to room temperature over 0.5 h, an excess of NEt_3 (*ca.* 5 cm^3) added, and stirred for a further 10 min. After evaporation to dryness at reduced pressure the residue was extracted with dichloromethane; the extract was shaken with water, and then evaporated and chromatographed as in (*a*) to give *cis*- and *trans*-(3) in a combined yield of 0.6 g (77%).

(*c*) *From* $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2][BF_4]$ (5). Addition of water, NEt_3, or methyl-lithium to a dichloromethane solution of (5), and shaking, yields (3) quantitatively, identified by i.r. and n.m.r. spectroscopy.

Preparation of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCHPh)(\eta\text{-}C_5H_5)_2]$ (4).—A toluene (100 cm^3) solution of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2HPh\}(\eta\text{-}C_5H_5)_2]$ (2) (0.2 g, 0.34 mmol) was heated at reflux for 17 h. Chromatography as above, eluting with

Table 5. Atomic co-ordinates (× 10^4) for (3a)

Atom	*x*	*y*	*z*
Ru(1)	2 417(1)	1 213(1)	359(1)
Ru(2)	2 707(1)	2 845(1)	−365(1)
O(1)	−450(6)	2 047(4)	−821(5)
O(4)	2 741(8)	358(4)	−2 072(6)
O(5)	3 265(8)	2 450(5)	−3 006(5)
C(1)	858(8)	2 027(4)	−478(6)
C(2)	4 307(8)	1 918(5)	−45(6)
C(3)	5 831(10)	1 796(7)	−12(10)
C(4)	2 598(9)	695(5)	−1 156(7)
C(5)	3 021(10)	2 627(5)	−2 002(7)
C(11)	1 773(14)	1 358(6)	2 360(7)
C(12)	741(11)	787(5)	1 804(8)
C(13)	1 617(11)	97(5)	1 430(7)
C(14)	3 213(11)	250(6)	1 768(9)
C(15)	3 274(14)	1 060(7)	2 363(8)
C(21)	2 619(16)	3 542(5)	1 459(8)
C(25)	3 955(15)	3 787(7)	881(12)
C(24)	3 486(16)	4 179(6)	−191(11)
C(23)	1 884(16)	4 200(5)	−271(10)
C(22)	1 358(14)	3 808(6)	727(11)

dichloromethane–hexane (1 : 4), gave three yellow bands from which were obtained, in turn, 5 mg (3%) of yellow crystalline *trans*-[Ru$_2$(CO)$_2$(μ-CO)(μ-CCHPh)(η-C$_5$H$_5$)$_2$] (4b) [ν(CO) (in CH$_2$Cl$_2$) at 1 958s and 1 796m cm^{-1}; Found: *M*, 519. C$_{21}$H$_{16}$O$_3$Ru$_2$ requires *M*, 519], a small amount of i.r.-identified [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$], and 30 mg (17%) of yellow crystalline *cis*-[Ru$_2$(CO)$_2$(μ-CO)(μ-CCHPh)(η-C$_5$H$_5$)$_2$] (4a) [m.p. 167—169 °C; ν(CO) (in CH$_2$Cl$_2$) at 1 997s, 1 959w, and 1 791m cm^{-1}; ^{1}H n.m.r. (in CDCl$_3$) δ 5.13 (s, 5 H, C$_5$H$_5$), 5.25 (s, 5 H, C$_5$H$_5$), 7.30 (m, 5 H, C$_6$H$_5$), and 7.75 (s, 1 H, C*H*Ph); Found: C, 48.3; H, 3.1%; *M*, 519. C$_{21}$H$_{16}$O$_3$Ru$_2$ requires C, 48.6; H, 3.1%; *M*, 519].

Preparation of [Ru$_2$(CO)$_2$(μ-CO)(μ-CMe)(η-C$_5$H$_5$)$_2$][BF$_4$] (5).—A few drops of HBF$_4$·OEt$_2$ were added to a dichloromethane solution (100 cm^3) of [Ru$_2$(CO)$_2$(μ-CO)(μ-CCH$_2$)(η-C$_5$H$_5$)$_2$] (3) (0.2 g, 0.45 mmol), causing an immediate colour change from yellow to orange. After removal of solvent at reduced pressure the residue was washed with ether, then crystallised from dichloromethane to give 0.22 g (92%) of orange crystalline (5) [m.p. 170—172 °C (decomp.); ν(CO) (in CH$_2$Cl$_2$) at 2 049s, 2 014w, and 1 859m cm^{-1}; ^{1}H n.m.r. (in [^{2}H$_6$]acetone) δ 4.62 (s, 3 H, Me) and 5.72 (s, 10 H, 2C$_5$H$_5$); ^{13}C n.m.r. (in CD$_2$Cl$_2$) δ 68.2 (Me), 94.1 (2C$_5$H$_5$), 195.8 (2CO), 227.1 (μ-CO), and 469.7 (*C*Me); Found: C, 34.2; H, 2.7%; *M*, 444 (cation). C$_{15}$H$_{13}$BF$_4$O$_3$Ru$_2$ requires C, 34.0; H, 2.5%; *M*, 444 (cation)].

Preparation of [Ru$_2$(CO)$_2$(μ-CO)(μ-CHMe)(η-C$_5$H$_5$)$_2$] (6).—(*a*) *From* [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$]. Methyl-lithium in ether (2.3 cm^3 of a 1 mol dm^{-3} solution) was added to a tetrahydrofuran solution (40 cm^3) of [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (1 g, 2.25 mmol) and the mixture stirred for 1 h. After cooling to −78 °C an excess of HBF$_4$·OEt$_2$ (2 cm^3) was added, and the mixture stirred over a further 0.5 h. An excess of NaBH$_4$ (0.5 g, 13.2 mmol) was now added and the mixture allowed to warm to room temperature over 15 min. After this time the solvent was evaporated and the residue extracted with portions of dichloromethane which were then washed through a short alumina column. Subsequent chromatography, eluting with dichloromethane–hexane (1 : 1), gave one yellow-green band from which 0.89 g (89%) of (6) was obtained, identified by i.r. and n.m.r. spectroscopy.[3]

Table 6. Atomic co-ordinates (× 10^4) for (5)

Atom	*x*	*y*	*z*
Ru(1)	2 428(1)	2 259(1)	731(1)
Ru(2)	5 355(1)	3 167(1)	1 180(1)
C(2)	4 341(4)	1 431(4)	1 229(2)
C(3)	4 781(5)	116(5)	1 572(2)
C(1)	3 460(4)	3 976(4)	480(2)
O(1)	3 140(3)	4 940(3)	135(2)
C(4)	2 585(4)	1 470(4)	−88(2)
O(4)	2 666(4)	1 005(4)	−584(2)
C(5)	5 973(4)	2 436(4)	447(2)
O(5)	6 307(4)	1 961(3)	8(2)
C(11)	1 212(5)	1 729(5)	1 512(2)
C(12)	407(5)	1 204(6)	903(3)
C(13)	−110(5)	2 292(8)	460(3)
C(14)	392(6)	3 521(7)	811(3)
C(15)	1 245(5)	3 144(5)	1 463(2)
C(21)	6 005(6)	5 287(6)	1 651(3)
C(22)	7 298(5)	4 640(6)	1 575(2)
C(23)	7 562(5)	3 452(7)	1 976(3)
C(24)	6 439(6)	3 366(7)	2 307(2)
C(25)	5 440(6)	4 447(6)	2 100(2)
B	8 624(9)	2 801(7)	−1 612(3)
F(1)	8 351(8)	1 562(5)	−1 932(3)
F(2)	8 985(7)	3 685(5)	−2 051(2)
F(3)	7 469(10)	3 279(8)	−1 458(6)
F(4)	9 679(13)	2 798(12)	−1 052(3)
F(1′)	10 051(29)	3 148(23)	−1 378(13)
F(2′)	7 629(24)	3 723(22)	−1 878(9)
F(3′)	8 153(25)	2 292(22)	−1 116(11)
F(4′)	8 759(70)	2 152(61)	−1 954(34)

(*b*) *From* [Ru$_2$(CO)$_2$(μ-CO)(μ-CMe)(η-C$_5$H$_5$)$_2$][BF$_4$] (5).—A solution of (5) (0.1 g, 0.19 mmol) in tetrahydrofuran (100 cm^3) was stirred with NaBH$_4$ (0.1 g, 2.6 mmol) for 3 h, then chromatographed as in (*a*) to yield 42 mg (50%) of (6).

Preparation of [Ru$_2$(CO)$_2$(μ-CO)(μ-CHPh)(η-C$_5$H$_5$)$_2$] (7).—To [Ru$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] (0.508 g, 1.13 mmol) in ether (100 cm^3) at 0 °C was added 1.5 cm^3 of a 1.9 mol dm^{-3} solution of phenyl-lithium in ether. After stirring for 0.5 h the solution was cooled to −78 °C, HBF$_4$·OEt$_2$ (*ca.* 3 cm^3) added, and stirred for a further 15 min. The solution was then warmed to room temperature and evaporated. The residue was washed with ether and acetone (100 cm^3) added, followed by NaBH$_4$ (0.1 g, 2.6 mmol). After stirring for 15 min the solution was again evaporated, the residue extracted with dichloromethane, and the extracts passed through a short column prior to chromatography, eluting with dichloromethane–hexane (1 : 1), to yield 0.43 g (74%) of (7) [m.p. 208—211 °C; ν(CO) (in CH$_2$Cl$_2$) at 1 975s, 1 939m, and 1 784m cm^{-1}; ^{1}H n.m.r. (in CDCl$_3$), *cis* δ 5.24 (s, 10 H, 2C$_5$H$_5$), 7.3 (m, 5 H, Ph), 11.30 (s, 1 H, C*H*Ph), *trans* 4.94 (s, 5 H, C$_5$H$_5$), 5.28 (s, 5 H, C$_5$H$_5$), 7.3 (m, 5 H, Ph), 10.36 (s, 1 H, C*H*Ph); ^{13}C n.m.r. (in CDCl$_3$), *cis* δ 89.9 (2C$_5$H$_5$), 138.2 (*C*HPh), *trans* 91.7 (C$_5$H$_5$), 93.0 (C$_5$H$_5$), 139.0 (*C*HPh), *cis* and *trans* 124.8, 125.0, 127.8, 128.0, and 128.4 (Ph). Found: C, 47.3; H, 3.1%; *M*, 507. C$_{20}$H$_{16}$O$_3$Ru$_2$ requires C, 47.4; H, 3.2%; *M*, 507].

Structure Determinations of cis-[Ru$_2$(CO)$_2$(μ-CO)(μ-CCH$_2$)(η-C$_5$H$_5$)$_2$] (3a) *and cis*-[Ru$_2$(CO)$_2$(μ-CO)(μ-CMe)(η-C$_5$H$_5$)$_2$][BF$_4$] (5).—A single crystal of (3a), of octahedral habit and bounded by faces {1 1 1}, {1 1 $\bar{1}$} (*ca.* 0.37 × 0.27 × 0.21 mm), was sealed in a thin-walled glass capillary under N$_2$ for *X*-ray structure analysis. Preliminary oscillation and Weissenberg photography established the space group and approximate cell dimensions. A full quadrant of intensity data in the range $4 < 2\theta < 55°$ was collected at room temperature on a Nicolet $P2_1$ diffractometer using graphite-monochromated Mo-K_α X-radiation ($\lambda = 0.710\,69$ Å). Integrated intensities were measured by the $\theta/2\theta$ scan technique with scan widths $(2.0 + \Delta_{\alpha_1\alpha_2})°$ and scan speeds varying between 2.0 and 29.3° min^{-1} based on a 2-s pre-scan of the reflection. Two check reflections were remeasured after every 50 intensity measurements and showed no significant variation during the course of data collection. Lorentz-polarisation and absorption corrections were applied to the data, the latter by a Gaussian quadrature procedure based on the indexed faces and dimensions of the crystal. Averaging of duplicate and symmetry-related intensity data and deletion of systematic absences yielded 3 186 unique data; of these 2 503 with $F^2 > 1.5\,\sigma(F^2)$ were used in the structure solution and refinement. The diffraction measurements on (5) followed a very similar course, differing only in the following respects. An irregularly shaped crystal, of approximate dimensions $0.4 \times 0.5 \times 0.55$ mm, was used throughout. The minimum scan rate in data collection was 3.0° min^{-1} and the maximum value of 2θ was 50.0°. The absorption correction was applied by an empirical method based on a six parameter fit to 203 azimuthal scan data. Data reduction as above yielded 3 158 unique intensity data of which 3 044 with $F^2 > 2\sigma(F^2)$ were used in the structure analysis.

Crystal data. (3a): $C_{15}H_{12}O_3Ru_2$, M 418.1, Monoclinic, space group $P2_1/n$, $a = 8.620(6)$, $b = 15.712(9)$, $c = 10.844(8)$ Å, $\beta = 92.57(4)°$, $U = 1\,467(1)$ Å^3, $Z = 4$, $D_c = 1.893$ g cm^{-3}, $F(000) = 856$, $\mu(\text{Mo-}K_\alpha) = 20.2$ cm^{-1}.

Crystal data. (5): $C_{15}H_{13}BF_4O_3Ru_2$, M 505.9, Monoclinic, space group $P2_1/n$, $a = 9.121(2)$, $b = 9.724(3)$, $c = 20.666(6)$ Å, $\beta = 106.42(3)°$, $U = 1\,758(1)$ Å^3, $Z = 4$, $D_c = 1.911$ g cm^{-3}, $F(000) = 1\,044$, $\mu(\text{Mo-}K_\alpha) = 17.36$ cm^{-1}.

Both structures were solved by conventional heavy-atom (Patterson and Fourier) methods, all non-metal atoms, including hydrogens, being located in difference Fourier syntheses. Cyclopentadienyl group hydrogens were constrained to idealised angular geometry, with the C–H distance held fixed at 0.96 Å, and assigned a common isotropic thermal parameter. In (3a) vinylidene hydrogen atoms were assigned individual isotropic thermal parameters and refined without constraints. The methyl group in (5) was constrained to C_{3v} symmetry with H–C–H angles 109.5° and C–H lengths 0.96 Å, methyl hydrogens being assigned a common isotropic thermal parameter. The BF_4^- counter ion in (5) was disordered over two component sites, whose occupancies refined to 0.806(5) and 0.194(5) respectively. With the exception of hydrogen atoms and the fluorine atoms of the minor orientation of the BF_4^- anion in (5), all atoms were assigned anisotropic thermal parameters. Refinement was by blocked-cascade full-matrix least squares, these and all calculations being carried out with programs of the SHELXTL package on a Nicolet R3m/E structure determination system. Final residual indices on convergence of refinement were R 0.051, R' 0.057, S 1.51 for (3a) and R 0.026, R' 0.035, and S 1.67 for (5).* A weighting scheme of the form, $w = \sigma^2(F) + gF^2$ with $g = 0.0005$ for (3a) and $g = 0.0003$ for (5) gave satisfactory analyses of variance.

Final difference electron-density synthesis showed no features of chemical significance, the largest peaks being in the proximity (<1 Å) of the Ru atoms in (3a) (*ca.* ±1.5 e Å^{-3}) and around the disordered BF_4^- ion in (5) (±0.5 e Å^{-3}). The positional co-ordinates of the non-hydrogen atoms are given in Tables 5 and 6 for (3a) and (5) respectively.

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* $R = \Sigma|F_o - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; and $S = [\Sigma w(F_o - |F_c|)^2/(NO - NV)]^{\frac{1}{2}}$.