Organic Chemistry of Dinuclear Metal Centres. Part 12.[1] Synthesis, *X*-Ray Crystal Structure, and Reactivity of the Di-μ-alkylidene Complex $[Ru_2(CO)_2(\mu\text{-}CHMe)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$: Alkylidene Linking†

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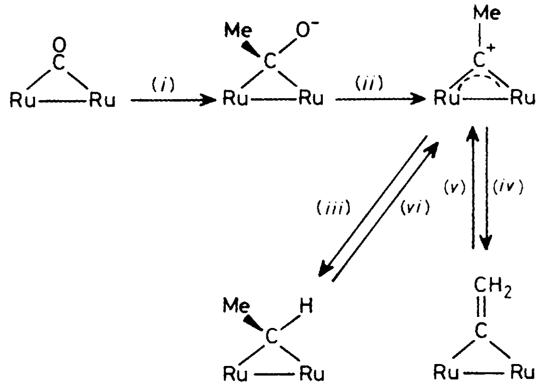
Upon treatment with methyl-lithium followed by $HBF_4{\cdot}OEt_2$ a carbon monoxide ligand of the μ-alkylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (**1**) is converted into μ-ethylidyne, giving $[Ru_2(CO)_2(\mu\text{-}CMe)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]^+$ (**2**). This is deprotonated readily by water to form the μ-vinylidene complex $[Ru_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (**3**), which quantitatively regenerates (**2**) with $HBF_4{\cdot}OEt_2$. Addition of $NaBH_4$ to (**2**) results in hydride attack on μ-CMe to yield the di-μ-alkylidene complex $[Ru_2(CO)_2(\mu\text{-}CHMe)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (**4**) as *cis* and *trans* isomers. The structure of the *trans* isomer has been established by *X*-ray diffraction. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell for which $a = 8.474(2)$, $b = 7.802(3)$, $c = 12.989(5)$ Å, $\alpha = 99.42(3)$, $\beta = 96.96(3)$, and $\gamma = 107.73(3)°$. The structure was solved by heavy-atom methods and refined to R 0.026 (R' 0.031) for 4 092 independent intensities. A ruthenium–ruthenium single bond of 2.701(1) Å is symmetrically bridged by ethylidene [mean Ru–C 2.079(3)] and isopropylidene [mean Ru–C 2.107(3) Å] ligands to form an approximately planar Ru_2C_2 ring with a non-bonding $Me_2C \cdot\cdot CHMe$ distance of 3.20 Å. Upon thermolysis the alkylidenes link to evolve $Me_2C{=}CHMe$, $Me_2CHCH{=}CH_2$, and $Et(Me)C{=}CH_2$. The absence of C_4 and C_6 hydrocarbons indicates that the alkylidene coupling occurs intramolecularly, and the electronic and stereochemical requirements of this process are discussed. Unlike mono-μ-alkylidene complexes, $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CR_2)(\eta\text{-}C_5H_5)_2]$, the *cis* and *trans* forms of (**4**) do not interconvert thermally below 145 °C, but u.v. irradiation effects a slow *trans* to *cis* isomerisation. U.v. irradiation of (**4**) in the presence of dimethyl acetylenedicarboxylate promotes ethylidene–alkyne linking to form $[Ru_2(CO)(\mu\text{-}CMe_2)\{\mu\text{-}C(CO_2Me)C(CO_2Me)CHMe\}(\eta\text{-}C_5H_5)_2]$, but with ethyne both of the alkylidenes are lost and the ruthenium–ruthenium double-bonded complex $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2H_2)(\eta\text{-}C_5H_5)_2]$ is produced.

The recognition[2] that methylene is an important surface species during transition-metal catalysed hydrogenation of carbon monoxide (the Fischer–Tropsch Synthesis) has prompted the synthesis and study of a wide range of μ-alkylidene complexes.[3] However, complexes which contain *two* μ-alkylidene ligands bridging a dinuclear metal centre are rare,[4–14] and at the time this work was begun their chemistry had been little explored. Yet such species provide an attractive model for alkene generation on a metal surface through alkylidene–alkylidene coupling. In order to investigate this process we have synthesised model di-μ-alkylidene diruthenium complexes. We report here on the chemistry of *trans*-$[Ru_2(CO)_2(\mu\text{-}CHMe)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$, which has been outlined in a preliminary form,[14] and in the following paper describe that of *cis*-$[Ru_2(CO)_2(\mu\text{-}CHMe)_2(\eta^5{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)]$.[15]



Scheme 1. (*i*)LiMe, 25 °C; (*ii*) $2HBF_4{\cdot}OEt_2$, −78 °C, $-H_2O$; (*iii*) $NaBH_4$; (*iv*) water, $-H^+$; (*v*) $HBF_4{\cdot}OEt_2$; (*vi*) CPh_3BF_4

Results and Discussion

Synthesis of Di-μ-hydrocarbyl Complexes.—In an earlier Part of this Series we described how, employing the technique of Rosenblum and co-workers,[16] a carbonyl ligand could be converted into μ-ethylidyne, μ-ethylidene, and μ-vinylidene at a diruthenium centre.[17] Scheme 1 summarises the steps involved in the transformations. Attempts to extend these procedures to the carbonyl ligands of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$,[18] $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$,[18] and $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$[19] were unsuccessful, perhaps because of preferential attack of methyl-lithium upon the ethylidene, vinylidene, and methylene ligands, respectively. However, the μ-iso-propylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (**1**)[20] is smoothly converted into the cation $[Ru_2(CO)_2(\mu\text{-}CMe)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]^+$ (**2**) upon successive

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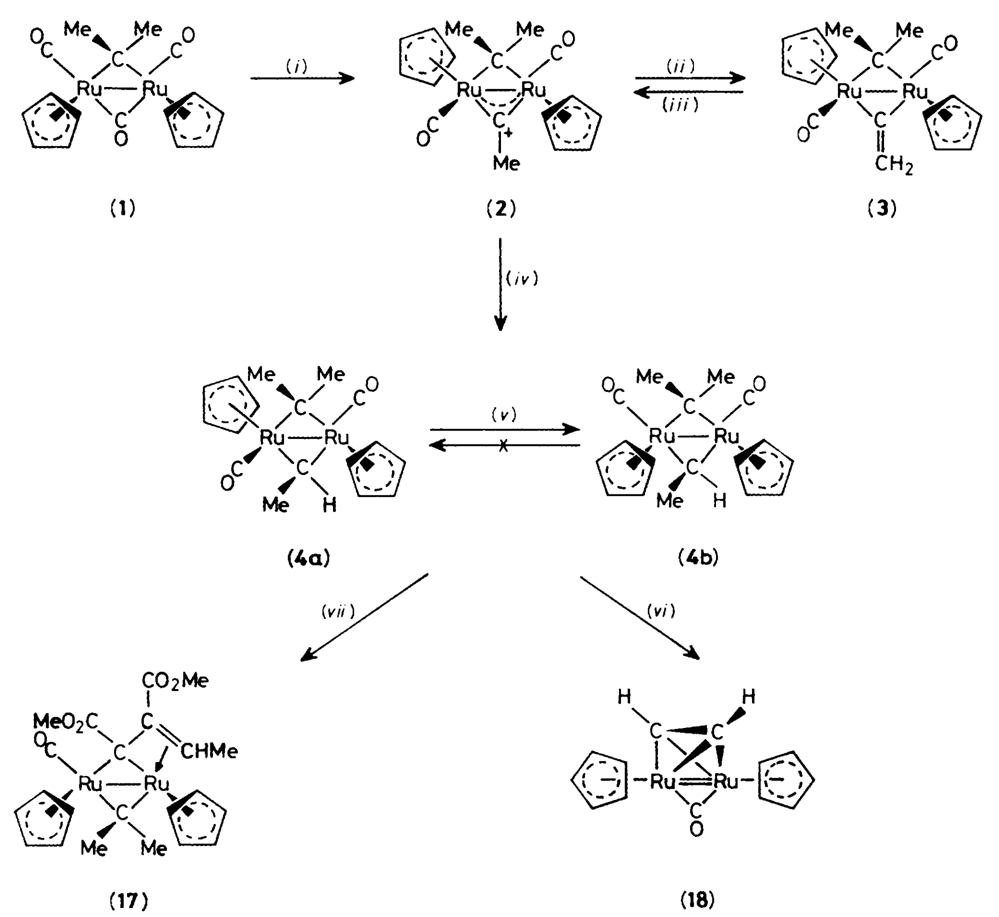
† μ-Ethylidene-$C'(Ru^{1,2})$-μ-isopropylidene-$C^{1'}(Ru^{1,2})$-bis[carbonyl-(cyclopentadienyl)ruthenium](*Ru–Ru*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii–xx.



Scheme 2. (*i*) LiMe, $2HBF_4$; (*ii*) water or LiMe; (*iii*) HBF_4; (*iv*) $NaBH_4$; (*v*) u.v. irradiation; (*vi*) HC_2H, u.v. irradiation; (*vii*) $MeO_2CC_2CO_2Me$, u.v. irradiation

treatment with methyl-lithium and $HBF_4·OEt_2$, as shown in Scheme 2. The cation readily deprotonates on shaking a dichloromethane solution with water, to give the μ-iso-propylidene–μ-vinylidene species $[Ru_2(CO)_2(\mu\text{-}CCH_2)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (**3**), which rapidly regenerates (**2**) on addition of $HBF_4·OEt_2$, and is attacked by hydride to yield the μ-iso-propylidene–μ-ethylidene complex $[Ru_2(CO)_2(\mu\text{-}CHMe)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (**4**). Treatment of (**2**) with methyl-lithium does not afford a bis(μ-iso-propylidene) complex; instead, deprotonation to give (**3**) occurs cleanly. Each of yellow, crystalline (**2**)—(**4**) is obtained in high yield, but while (**3**) and (**4**) are stable in air, apparently indefinitely, the tetrafluoroborate salt of (**2**) suffers some decomposition within days, probably as a result of hydrolysis. The neutral complexes (**3**) and (**4**) are readily soluble in hexane, and ionic (**2**) in dichloromethane.

The ^1H and ^{13}C n.m.r. characteristics of μ-CMe_2, μ-CHMe, μ-CCH_2, and μ-CMe^+ ligands co-ordinated at diruthenium centres have been established in our previous work,[17–20] and characterisation of (**2**)—(**4**) was therefore straightforward; the data and assignments are given in the Experimental section.

The i.r. [single ν(CO)] and n.m.r. (equivalent cyclopentadienyl groups and CMe_2 methyls) spectra of (**2**) and (**3**) clearly show that these complexes have the *trans* configuration illustrated. No evidence was obtained for the existence of *cis* isomers. However, while for the di-μ-alkylidene complex (**4**) the *trans* isomer (**4a**) was the major product, a small amount (*ca.* 1%) of the *cis* form (**4b**) was isolated, identified by the presence of the *two* i.r.-active carbonyl stretching modes required by this geometry. The di-μ-hydrocarbyl complexes (**2**)—(**4**) display a much stronger preference for the *trans* configuration than do mono-μ-hydrocarbyl species of the form $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L)(\eta\text{-}C_5H_5)_2]$. For the latter, in the absence of hydrocarbyl substituent steric effects, the *cis* form is thermodynamically favoured;[19,20] *e.g.* for L = CH_2 the equilibrium *cis*:*trans* ratio in $CDCl_3$ at 25 °C is 4:1.[19] This is shifted in favour of the *trans* isomer for complex (**1**) (L = CMe_2) (*cis*:*trans* ratio 3:4 in $CDCl_3$ at 25 °C), because in the *cis* form a propylidene methyl group must occupy a crowded site between a pair of cyclopentadienyl ligands.[18] Presumably this factor is also influential in determining a *trans* configuration for (**2**). The *trans* isomers of (**3**) and (**4**) would then evolve from (**2**) as kinetically controlled products. Whether these are also more thermodynamically stable than the *cis* forms is not clear since no low-energy pathway for *trans* $\rightleftharpoons$ *cis* isomerisation appears to be available. Mono-μ-hydrocarbyl complexes of type $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L)(\eta\text{-}C_5H_5)_2]$ undergo *trans* $\rightleftharpoons$ *cis* isomerisation readily [*e.g.* for L = CMe_2 (**1**) this occurs on the n.m.r. time-scale with $\Delta G^‡$ *ca.* 85 kJ mol^{-1}][18,20] *via* concerted opening of the μ-CO and μ-L bridges, rotation about the metal–metal bond, and bridge closure, but the di-μ-alkylidene isomers *trans*-(**4a**) and *cis*-(**4b**) do not interconvert on heating in xylene at 145 °C. Evidently the concerted opening of a pair of μ-alkylidene bridges is a high-energy process. This is perhaps not unexpected in view of the fact that substitution of even one CO in the $Ru_2(\mu\text{-}CO)_2$ system by μ-CMe_2 doubles the free energy of activation for concerted bridge opening to 85 kJ mol^{-1} (see refs. 18 and 21). Isomerisation of *trans*-(**4a**) to *cis*-(**4b**) can be achieved by u.v. irradiation of a toluene solution; after 2 h *ca.* 10% of the *cis* isomer is present and after 17 h it is the predominant form, but some decomposition is apparent. The

Table 1. Selected bond lengths (Å) and angles (°) for complex (**4a**)

Ru(1)–C(3)	2.106(3)	Ru(2)–C(3)	2.108(3)
C(3)–C(4)	1.521(4)	C(3)–C(5)	1.526(3)
Ru(1)–C(6)	2.073(3)	Ru(2)–C(6)	2.086(3)
C(6)–C(7)	1.514(4)	C(6)–H(6)	0.94(3)
Ru(1)–C(1)	1.835(3)	Ru(2)–C(2)	1.827(2)
C(1)–O(1)	1.158(4)	C(2)–O(2)	1.158(3)
C(11)–C(12)	1.391(5)	C(21)–C(22)	1.429(5)
C(12)–C(13)	1.403(5)	C(22)–C(23)	1.405(5)
C(13)–C(14)	1.427(5)	C(23)–C(24)	1.427(5)
C(14)–C(15)	1.370(6)	C(24)–C(25)	1.433(4)
C(15)–C(11)	1.444(6)	C(25)–C(21)	1.406(4)
Ru(1)–Ru(2)	2.701(1)	Mean Ru–C(cp)*	2.293(3)
Mean C–H(methyl)	0.99(5)	Mean C–H(cp)	0.90(5)
Ru(1)–C(3)–Ru(2)	79.7(1)	Ru(1)–C(6)–Ru(2)	81.0(1)
Ru(1)–Ru(2)–C(3)	50.1(1)	Ru(1)–Ru(2)–C(6)	49.3(1)
Ru(2)–Ru(1)–C(3)	50.2(1)	Ru(2)–Ru(1)–C(6)	49.7(1)
Ru(1)–Ru(2)–C(2)	92.1(1)	Ru(2)–Ru(1)–C(1)	91.5(1)
Ru(2)–C(2)–O(2)	175.7(3)	Ru(1)–C(1)–O(1)	175.6(3)
C(4)–C(3)–C(5)	107.4(2)	H(6)–C(6)–C(7)	104(3)
Mean C–C–C(cp)	108.0(3)		

* cp = η^5-Cyclopentadienyl ligand.

Table 2. Atomic co-ordinates for complex (**4a**)

Atom	*x*	*y*	*z*
C(11)	−0.117 0(4)	−0.070 3(5)	0.349 6(3)
C(12)	−0.039 4(4)	−0.188 3(4)	0.302 5(4)
C(13)	−0.065 2(4)	−0.203 1(4)	0.192 2(3)
C(14)	−0.169 5(4)	−0.095 6(5)	0.170 2(3)
C(15)	−0.199 5(4)	−0.013 3(5)	0.264 0(4)
C(21)	0.548 7(4)	0.406 4(4)	0.113 9(3)
C(22)	0.644 7(4)	0.345 2(5)	0.189 1(3)
C(23)	0.628 6(4)	0.422 4(4)	0.291 3(3)
C(24)	0.520 7(4)	0.530 4(4)	0.282 4(2)
C(25)	0.477 4(4)	0.523 4(3)	0.171 3(2)
C(1)	0.117 2(4)	0.333 6(4)	0.353 0(3)
C(2)	0.331 9(4)	0.000 7(4)	0.113 7(2)
C(3)	0.324 1(3)	0.106 4(3)	0.331 0(2)
C(4)	0.348 7(4)	−0.079 1(4)	0.328 9(3)
C(5)	0.408 3(4)	0.227 3(5)	0.440 6(2)
C(6)	0.125 6(3)	0.211 0(4)	0.138 6(2)
C(7)	0.084 8(4)	0.380 8(5)	0.120 3(3)
O(1)	0.130 2(4)	0.474 0(4)	0.405 5(2)
O(2)	0.314 6(4)	−0.136 5(3)	0.056 1(2)
Ru(1)	0.080 42(2)	0.104 16(2)	0.272 29(1)
Ru(2)	0.370 26(2)	0.225 81(2)	0.198 65(1)

mechanism of this process is unknown. Were it to involve the formation and recombination of $[Ru(CO)(CR_2)(\eta-C_5H_5)]$ radicals the symmetrical species $[Ru_2(CO)_2(\mu-CHMe)_2(\eta-C_5H_5)_2]$ and $[Ru_2(CO)_2(\mu-CMe_2)(\eta-C_5H_5)_2]$ would be produced, but no evidence of these was obtained.

Molecular Structure of trans-$[Ru_2(CO)_2(\mu-CHMe)(\mu-CMe_2)(\eta-C_5H_5)_2]$ (**4a**).—The molecular structure of (**4a**) was determined by *X*-ray diffraction and the results are summarised in Tables 1 and 2. The structure and the numbering scheme are shown in Figure 1, while Figure 2 gives a stereoscopic view of the molecule. The structure is based on a diruthenium unit symmetrically bridged by ethylidene and iso-propylidene ligands to give an approximately planar dimetallacyclobutane ring. Each metal atom carries terminal cyclopentadienyl and carbonyl ligands arranged to give the molecule a *trans* geometry. The planes of the two cyclopentadienyl ligands are thus approximately parallel (dihedral angle 2.7°) and the molecule possesses quasi C_{2h} symmetry.

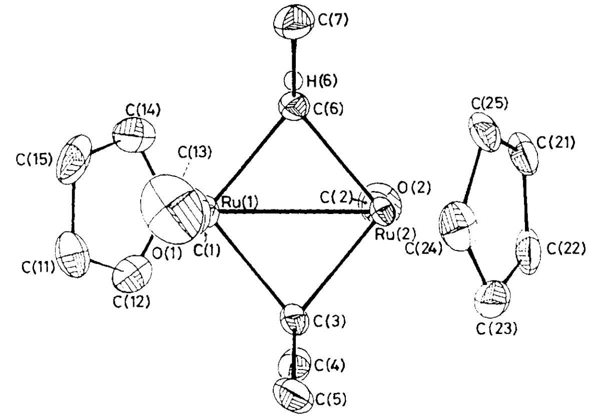


Figure 1. Molecular geometry of complex (**4a**), showing the atomic labelling scheme; thermal ellipsoids drawn to enclose 50% probability density. Methyl and cyclopentadienyl group hydrogens have been omitted for clarity

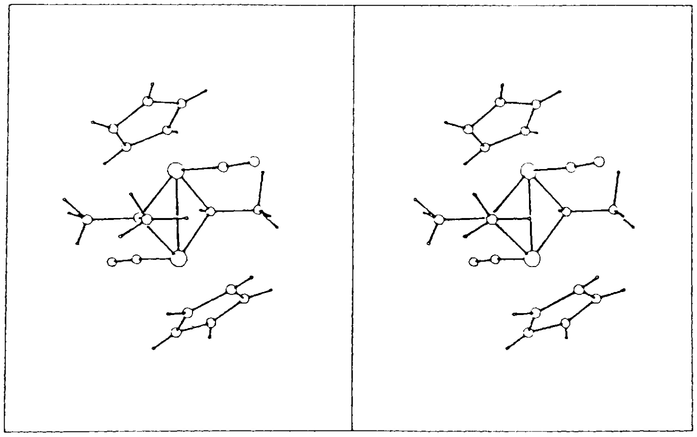


Figure 2. Stereoscopic view of complex (**4a**)

The ruthenium–ruthenium single bond distance of 2.701(1) Å is slightly shorter than that found in $[Ru_2(CO)_2(\mu-CO)(\mu-CH_2)(\eta-C_5H_5)_2]$ [2.707(1) Å],[19] $[Ru_2(CO)_2(\mu-CO)(\mu-CMe_2)(\eta-C_5H_5)_2]$ (**1**) [2.712(1) Å],[18] and $[Ru_2(CO)_2(\mu-CO)_2(\eta-C_5H_5)_2]$ [2.735(2) Å].[22] As discussed elsewhere,[18] this reflects the fact that the principal π interaction of the bridging ligands occurs with a metal–metal π* orbital, and that the more ready transfer of electron density from this orbital to alkylidene p_π orbitals rather than CO π* will result in metal–metal contraction as μ-CO are replaced by μ-alkylidene ligands.

Unlike the *cis* isomers of $[Ru_2(CO)_2(\mu-CO)(\mu-CH_2)(\eta-C_5H_5)_2]$[19] and $[Ru_2(CO)_2(\mu-CO)(\mu-CMe_2)(\eta-C_5H_5)_2]$,[18] which have substantially folded $Ru_2(\mu-C)_2$ cores [(μ-C)-Ru–Ru–(μ-C) torsion angles are 160.2(3) and 153.4(2)° respectively], the dimetallacyclobutane core of *trans*-(**4a**) is almost planar [torsion angle C(6)–Ru(1)–Ru(2)–C(3) −176.9(1)°], as predicted by molecular orbital considerations.[23]

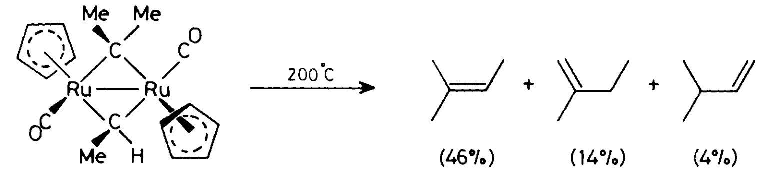
The planes of the ethylidene and iso-propylidene ligands lie approximately orthogonal to the planar $Ru_2(\mu-C)_2$ core, making angles of 90.7 and 89.7° respectively with the relevant $Ru_2(\mu-C)$ plane, again as expected on molecular orbital grounds and as observed generally for μ-alkylidene complexes.[24] The internal and external angles for the ethylidene [Ru–C–Ru 81.0(1), H–C–C 104(3)°] and isopropylidene [Ru–C–Ru 79.7(1), C–C–C 107.4(2)°] ligands are also typical.[24] The average Ru–C distances for the ethylidene and isopropylidene ligands are 2.079(3) and 2.107(3) Å respectively. These compare with mean Ru–CH_2 distances of 2.078(6) Å for $[Ru_2(CO)_2(\mu-CO)(\mu-$

$CH_2)(\eta-C_5H_5)_2]$[19] and mean Ru–CMe_2 distances of 2.113(4) Å for $[Ru_2(CO)_2(\mu-CO)(\mu-CMe_2)(\eta-C_5H_5)_2]$ (**1**).[18]

The terminal carbonyl ligands are approximately coplanar [torsion angle C(1)–Ru(1)–Ru(2)–C(2) −177.9(1)°] and lie orthogonal to the molecular core [Ru(1)–Ru(2)–C(2) 92.1(1), Ru(2)–Ru(1)–C(1) 91.5(1)°]. Both carbonyls are distorted slightly from linearity, leaning away from the molecular centre with angles Ru(1)–C(1)–O(1) 175.6(3) and Ru(2)–C(2)–O(2) 175.7(3)°.

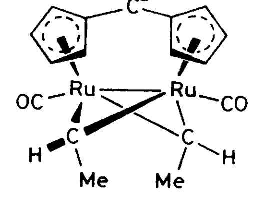
The molecules pack with just six intermolecular contacts of less than 2.5 Å, these being H(71) ··· H(43) 2.42, H(22) ··· H(15) 2.38, H(73) ··· H(22) 2.03, H(25) ··· H(21) 2.37, H(53) ··· H(53) 2.29, and H(6) ··· H(6) 2.41 Å.

Alkene Evolution from Complex (**4a**).—Upon thermolysis at 200 °C solid complex (**4a**) evolves (by g.l.c.) ethylene (20%) and propene (16%), and the C_5 hydrocarbons 2-methylbut-2-ene (46%), 2-methylbut-1-ene (14%), and 3-methylbut-1-ene (4%) (see below). The ethylene and propene can be readily attributed to the release and subsequent rearrangement of ethylidene and isopropylidene[25] respectively. The other three hydrocarbons each have the same carbon skeleton and are clearly derived by combination of C_2 ethylidene with C_3 isopropylidene, although in the case of the but-1-enes a subsequent hydrogen-shift isomerisation is required. Ample opportunity for such isomerisation, *via* attachment to low-co-ordinate ruthenium fragments, perhaps even ruthenium metal itself, will exist during the thermolysis. The important question is whether the alkylidenes combine in the gas phase, following their separate release from co-ordination, or combine intramolecularly at the diruthenium centre prior to their release as 2-methylbut-2-ene. If the former pathway were followed ethylidene–ethylidene and propylidene-propylidene coupling in the gas phase would also be expected, but no evidence for this was obtained; *i.e.* no C_4 or C_6 hydrocarbons were detected as products of the thermolysis. Some ethylidene and propylidene groups obviously do enter the gas phase, but they evidently rearrange to ethylene and propene, respectively, faster than they encounter another alkylidene. It is therefore concluded that alkylidene–alkylidene coupling does occur at the dinuclear metal centre.



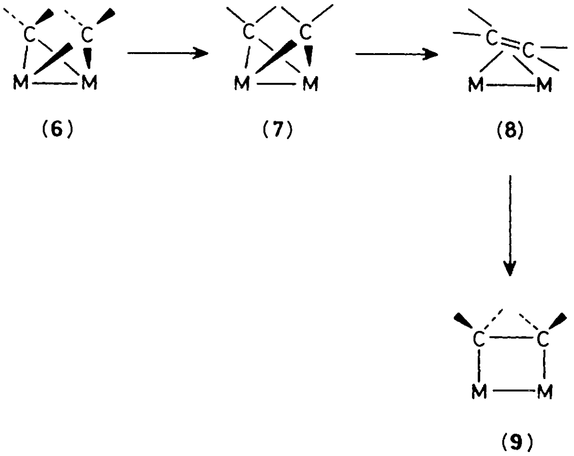
(**4a**)

This coupling appears to be a general phenomenon. Recently we have synthesised the di-μ-alkylidene complexes $[Ru_2(CO)_2(\mu-CH_2)(\mu-CHMe)(\eta-C_5H_5)_2]$ and $[Ru_2(CO)_2(\mu-CH_2)(\mu-CHEt)(\eta-C_5H_5)_2]$, by a a quite different route to that employed for (**4**), and upon thermolysis these yield propene (75%) and butenes (72%), respectively.[26] The bis-μ-ethylidene complex $[Ru_2(CO)_2(\mu-CHMe)_2(\eta^5:\eta^{5'}-C_5H_4CH_2C_5H_4)]$ (**5**), described in the following paper,[15] also generates butenes (36%) on heating at 230 °C. Subsequent to our first report[14] others have also observed such coupling; *e.g.* thermolysis of $[Co_2(\mu-CO)(\mu-CH_2)(\mu-CHMe)(\eta-C_5Me_5)_2]$ affords propene (83%),[27] $[Co_2(\mu-CO)(\mu-CHMe)_2(\eta-C_5Me_5)_2]$, butenes (91%),[27] $[Co_2(CO)_4(\mu-CH_2)(\mu-CHMe)(\mu-dppm)]$ [dppm = bis(diphenylphosphino)methane], propene (20%),[28] and $[Rh_2X_2(\mu-CH_2)_2(\eta-C_5Me_5)_2]$ species, ethylene.[29] In the evolution of propene from $[Rh_2Me_2(\mu-CH_2)_2(\eta-C_5Me_5)_2]$ ethylidene–methylene combination is regarded as a critical step.[29] Methylene–methylene coupling without release from the metal centre is also found, as in the reactions of $[Os_3(CO)_{10}(MeCN)(\mu-CH_2)]$ and $[Ru_2(CO)_2(MeCN)(\mu-CH_2)(\eta-C_5H_5)_2]$ with diazomethane to afford the μ-vinyl complexes $[Os_3(CO)_{10}(\mu-H)(\mu-CHCH_2)]$[30] and $[Ru_2(CO)_2(\mu-H)(\mu-CHCH_2)(\eta-C_5H_5)_2]$[26] respectively.



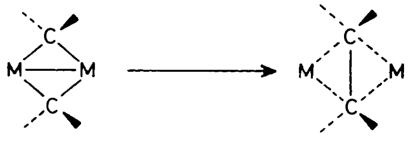
(**5**)

We turn now to the mechanism of alkylidene combination at the dinuclear metal centre. Hoffmann and co-workers[31] have approached this problem from a molecular orbital point of view for the case of two methylenes. Assuming a non-planar, or 'folded,' $M_2(\mu-C)_2$ core they considered the sequence of events illustrated in Scheme 3, in which the 'normal' orientation of the two methylenes in (**6**) changes to the 'coupling' orientation in (**7**), permitting transformation to the laterally bound μ-ethylene species (**8**), which subsequently rotates to the known dimetallacyclobutane form (**9**).

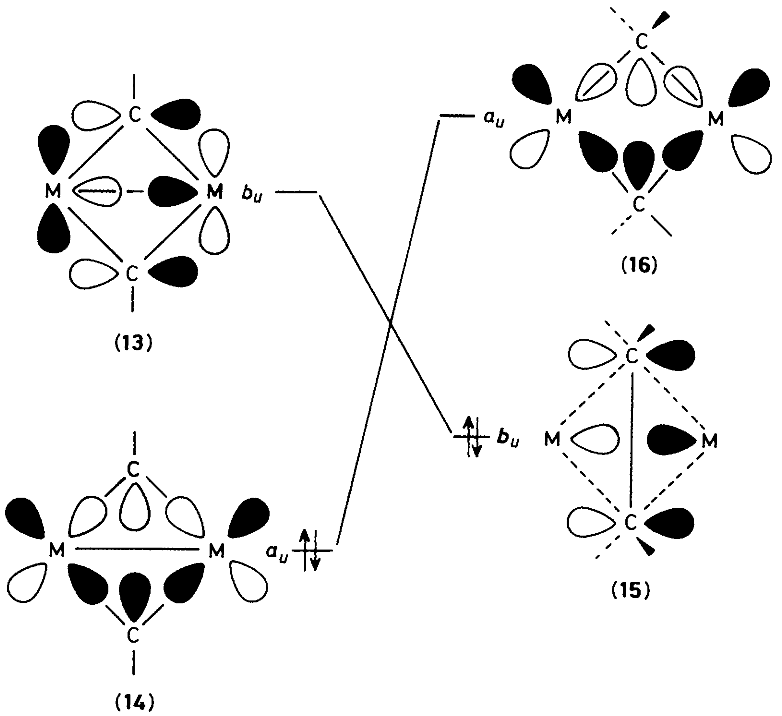


Scheme 3. Alkylidene coupling at a folded $M_2(\mu-C)_2$ centre[31]

However, while a folded conformation, (**6**), would be expected[23] for *cis*-(**4b**) a planar $M_2(\mu-C)_2$ unit is expected,[23]

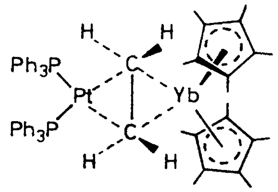


(**10**) (**11**)



Scheme 4. Orbital correlation for the coupling of two μ-alkylidene ligands at a planar $M_2(\mu\text{-}C)_2$ centre

and observed, for the *trans* isomer (**4a**). In this situation, (**10**), the alkylidenes appear ideally oriented for transformation to a μ-alkene species, (**11**), an arrangement recently established by *X*-ray diffraction for the ethylene complex $[(Ph_3P)_2Pt(\mu\text{-}C_2H_4)\text{-}Yb(\eta\text{-}C_5Me_5)_2]$ (**12**).[32]



(**12**)

This intriguing possiblility was not considered by Hoffmann and co-workers. The new reaction path involves cleavage of the Ru–Ru bond with concomitant formation of C–C σ and π bonds. In geometric terms the Ru–Ru distance must rise from *ca.* 2.7 to *ca.* 4.0 Å, while the μ-C • • • μ-C distance closes from *ca.* 3.2 to *ca.* 1.4 Å. The electronic structures of very closely related iron[33] and ruthenium[34] complexes $[M_2(\mu\text{-}CO)(\mu\text{-}L)(CO)_2(\eta\text{-}C_5H_5)_2]$ (L = CO, CH_2, *etc.*) have been investigated by Fenske–Hall and extended Hückel molecular orbital techniques, respectively. These show the lowest unoccupied molecular orbital (l.u.m.o.) in these metal–metal bonded species to be of the form (**13**) (symmetry species b_u under C_{2h} local symmetry), *i.e.* σ* with respect to the metal–metal interaction and π with respect to the μ-C • • • μ-C interaction (see Scheme 4). In addition there is a filled orbital of form (**14**) (symmetry species a_u) which is π with respect to the M–M interaction and σ* with respect to the μ-C • • • μ-C interaction. In the postulated reaction intermediate, (**11**), we would expect a filled orbital, (**15**), and a vacant orbital, (**16**), the alkene π and σ* orbitals respectively. Assuming these molecular orbitals correlate as in Scheme 4, the thermal reaction (**10**) ⟶ (**11**) is symmetry forbidden and a large barrier results. However, in view of the forcing conditions used in the thermolysis of (**4a**), such a pathway for alkene formation cannot be ruled out and a range of variations on this theme, involving lower-symmetry intermediate geometries, should be considered. Finally, we note that the reverse of the reaction observed here, *i.e.* C=C cleavage to yield bis-μ-alkylidene complexes, has been observed in cyclopropene chemistry.[35]

In the following paper[15] we report the coupling of μ-alkylidene ligands in the *cis*-bis-μ-alkylidene complex $[Ru_2(CO)_2(\mu\text{-}CHMe)_2(\eta^5\text{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4)]$ (**5**). As is usually the case, *cis* stereochemistry leads to a puckered Ru_2C_2 core in (**5**), which in turn implies a shorter C • • • C distance in (**5**) than in (**4a**) (3.11 *vs.* 3.20 Å). Thermolysis of (**5**) also results in linking of the μ-alkylidene ligands, but to give butenes in lower yield (36%) than the C_5 hydrocarbons evolved from (**4a**) (64%). It is therefore clear that least-motion of the μ-CR_2 groups is not the dominant factor in determining these yields. The implication is that the constraint of *cis* geometry imposed by the $\eta^5\text{:}\eta^{5'}\text{-}C_5H_4CH_2C_5H_4$ ligand in (**5**) hinders (but does not prevent) the alkylidene coupling reaction. This hindrance could either be the consequence of limited conformational flexibility in (**5**) in general, or, in particular, because a mechanism separating the ruthenium atoms [as in (**10**) ⟶ (**11**)] is not possible.

In any event, the intramolecular alkylidene linking observed for complexes (**4**) and (**5**) suggests that alkenes could be generated in this way at dinuclear metal centres on a metal surface in processes such as the Fischer–Tropsch synthesis. In this connection, it is noteworthy that decomposition of 2-diazopropane, Me_2CN_2, on Raney nickel at 100 °C gives tetramethylethylene in 40% yield.[36]

The linking of the two alkylidenes in (**4a**) suggested that thermolysis of complex (**3**) could afford 3,3-dimethylallene ($Me_2C{=}C{=}CH_2$), or isomers with the same C_5 skeleton, as a result of vinylidene–isopropylidene combination. Again, the mutual orientation of these ligands is ideal for this. Surprisingly, heating (**3**) at 200 °C under the same conditions as (**4a**) produced a very similar result; the volatile products were ethylene (2%), propene (10%), $Me_2C{=}CHMe$ (64%), $Et(Me)C{=}CH_2$ (18%), and $Pr^iCH{=}CH_2$ (6%). No C_4 or C_6

products were observed and, clearly, intramolecular linking of the vinylidene and isopropylidene ligands has occurred, but the intervention of hydrogen (presumably generated during the thermolysis) is evident. Thermolysis of an authentic sample of $Me_2C=C=CH_2$ at 200 °C, both in the presence and absence of (**3**), did not result in its transformation to the methylbutenes. The hydrogenation must therefore occur at the dinuclear metal centre either prior to or in association with the carbon–carbon bond formation, but its nature remains obscure.

Reactions of Complex (**4a**) *with Alkynes.*—We have previously described how the reactions of μ-alkylidene complexes [Ru$_2$(CO)$_2$(μ-CO)(μ-CR$_2$)(η-C$_5$H$_5$)$_2$] with alkynes (R′C$_2$R′) result in alkylidene–alkyne linking to give complexes of the form [Ru$_2$(CO)(μ-CO)(μ-σ,η^3-CR′CR′CR$_2$)(η-C$_5$H$_5$)$_2$].[37,38] The availability of (**4**) provided an opportunity to compare the reactivity of ethylidene and iso-propylidene towards such linking, and the complex was therefore treated with dimethylacetylenedicarboxylate under u.v. irradiation. The product, readily identified spectroscopically (see Experimental section), was complex (**17**) (10% yield), arising from preferential linking of the alkyne with ethylidene, perhaps because of the lower steric resistance to linking than is likely with isopropylidene.

Photolysis of (**4**) in the presence of ethyne gave a more surprising result; after 4 h a 10% yield of dark green [Ru$_2$(μ-CO)(μ-C$_2$H$_2$)(η-C$_5$H$_5$)$_2$] (**18**) was obtained. The diphenylacetylene analogue of (**18**) has previously been obtained by us *via* a different route and the presence of a ruthenium–ruthenium double bond confirmed by *X*-ray diffraction.[39] As with the thermolysis of (**4**), both alkylidenes are lost from the diruthenium centre in the reaction with ethyne, but their fate here is unknown.

Experimental

Techniques and instrumentation were as described in Part 1 of this series.[40] G.l.c. (gas–liquid chromatography) analyses of hydrocarbon products was carried out on a Pye Series 104 instrument, employing a 2-m Chromosorb 102 column (80—100 mesh), operating at 140—150 °C. Methyl-lithium (Ventron), NaBH$_4$, HBF$_4$·OEt$_2$, 3,3-dimethylallene, dimethyl acetylenedicarboxylate (Aldrich), and ethyne (B.O.C.) were obtained commercially. The complex [Ru$_2$(CO)$_2$(μ-CO)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$] (**1**) was obtained by the literature method.[18,41]

Preparations.—[Ru$_2$(CO)$_2$(μ-CMe)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$][BF$_4$] (**2**). Methyl lithium (2.5 cm^3 of a 1 mol dm^{-3} solution in diethyl ether, 2.5 mmol) was added to a tetrahydrofuran solution (50 cm^3) of [Ru$_2$(CO)$_2$(μ-CO)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$] (**1**) (1.0 g, 2.2 mmol), causing a slight darkening of the originally orange solution. After stirring for 0.75 h the mixture was cooled to −78 °C (solid CO$_2$–ethanol bath) then an excess (*ca.* 1 cm^3) of HBF$_4$·OEt$_2$ was added, provoking precipitation of the product. After warming to room temperature over 0.5 h, solvent was removed under reduced pressure and the residue thoroughly washed with diethyl ether. Recrystallisation from dichloromethane gave 0.86 g (72%) of orange crystalline (**2**) [m.p. 163 °C; (Found: C, 37.4; H, 3.2%. C$_{17}$H$_{19}$BF$_4$O$_2$Ru$_2$ requires C, 37.5; H, 3.5%); ν(CO) (in CH$_2$Cl$_2$) 2 000 cm^{-1}; ^{1}H n.m.r. (in CD$_2$Cl$_2$) δ 3.36 (s, 6 H, CMe$_2$), 4.36 (s, 3 H, CMe), and 5.60 (s, 10 H, 2 C$_5$H$_5$)].

Complex (**2**) may also be obtained in near quantitative yield by adding a few drops of HBF$_4$·OEt$_2$ to a dichloromethane solution of the vinylidene complex (**3**), then evaporating to dryness and washing the product thoroughly with diethyl ether.

[Ru$_2$(CO)$_2$(μ-CCH$_2$)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$] (**3**). A tetrahydrofuran solution of complex (**2**), prepared from 1 g (2.2 mmol) of (**1**) as described above, was evaporated to dryness, the residue washed with diethyl ether to remove HBF$_4$·OEt$_2$, then dissolved in dichloromethane (50 cm^3). The solution was shaken vigorously with water (25 cm^3) in a separating funnel then the organic layer was evaporated and the residue introduced, in the minimum of dichloromethane, to an alumina chromatography column. Elution with dichloromethane gave a single yellow band which yielded 0.66 g (66%) of yellow crystalline (**3**) [m.p. 177 °C (Found: C, 44.9; H, 4.1%, *M* 457. C$_{17}$H$_{18}$O$_2$Ru$_2$ requires C, 44.7; H, 3.9%; *M* 457); ν(CO) (in hexane) 1 945 cm^{-1}; ^{1}H n.m.r. (in CDCl$_3$) δ 2.84 (s, 6 H, CMe$_2$), 5.12 (s, 10 H, 2 C$_5$H$_5$), and 5.88 (s, 2 H, CCH$_3$); ^{13}C n.m.r. (in CDCl$_3$) δ 55.3 (2 Me), 92.8 (2 C$_5$H$_5$), 122.2 (C*C*H$_2$), 175.6 (*C*Me$_2$), 201.0 (2 CO), and 244.5 (*C*CH$_2$) p.p.m.].

[Ru$_2$(CO)$_2$(μ-CHMe)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$] (**4**). To a tetrahydrofuran solution of complex (**2**), prepared from 1 g (2.2 mmol) of (**1**) as described above, an excess of NaBH$_4$ (0.5 g, 13.2 mmol) was added and the mixture stirred for 0.5 h. Solvent was evaporated and the residue extracted with several portions of dichloromethane, which were washed through a short alumina column. The resulting solution was concentrated and chromatographed on alumina. Elution with dichloromethane–hexane (1:1) gave a single yellow band from which 0.76 g (75%) of yellow crystalline (**4**) was obtained. I.r. monitoring of the eluant from the column revealed that the product was almost exclusively the *trans* isomer (**4a**) [m.p. 161 °C (Found: C, 44.9; H, 4.6%; *M* 459. C$_{17}$H$_{20}$O$_2$Ru$_2$ requires C, 44.5; H, 4.4%; *M* 459); ν(CO)(hexane) 1 928 cm^{-1}; ^{1}H n.m.r. (in CDCl$_3$) δ 2.72 (s, 3 H, CMe$_2$), 2.80 (d, *J* 8, 3 H, CH*Me*), 2.80 (s, 3 H, CMe$_2$), 5.1 (s, 10 H, 2 C$_5$H$_5$), 9.40 (q, *J* 8 Hz, 1 H, C*H*Me); ^{13}C n.m.r. (in CDCl$_3$) δ 44.2 (CH*Me*), 55.4 (C*Me$_2$*), 55.5 (C*Me$_2$*), 92.1 (C$_5$H$_5$), 92.5 (C$_5$H$_5$), 135.3 (*C*HMe), 166.8 (*C*Me$_2$), 202.5 (CO), and 202.6 (CO) p.p.m.].

The tail end of the band leaving the column was enriched in the *cis* isomer (**4b**) and recrystallisation of this fraction gave a few mg of this form, as black crystals [ν(CO) (in CH$_2$Cl$_2$) 1 947s and 1 913vs cm^{-1}; ^{1}H n.m.r. (in CDCl$_3$) δ 2.68 (s, 3 H, CMe$_2$), 2.73 (s, 3 H, CMe$_2$), 2.83 (d, *J* 7, 3 H, CH*Me*), 5.11 (s, 10 H, 2 C$_5$H$_5$), and 8.12 (q, *J* 7 Hz, 1 H, C*H*Me)].

Reactions of [Ru$_2$(CO)$_2$(μ-CHMe)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$] (**4**).—(*a*) *With dimethyl acetylenedicarboxylate.* A toluene solution (100 cm^3) of complex (**4**) (0.17 g, 0.36 mmol) and dimethyl acetylenedicarboxylate (0.25 g, 1.8 mmol) was subjected to u.v. irradiation for 17 h, changing from yellow to red. After removal of volatiles at reduced pressure the residue was chromatographed on an alumina column. Elution with dichloromethane developed pink, yellow, and red bands, of which only the latter provided sufficient material for characterisation: 21 mg (10%) of red crystalline [Ru$_2$(CO)(μ-CMe$_2$){μ-C(CO$_2$Me)C(CO$_2$Me)CHMe}(η-C$_5$H$_5$)$_2$] (**17**) [(Found: C, 45.8; H, 4.7%; *M* 573. C$_{22}$H$_{26}$O$_5$Ru$_2$ requires C, 46.2; H, 4.6%; *M* 573); ν(CO) (in CH$_2$Cl$_2$) 1 952s and 1 708m (CO$_2$Me) cm^{-1}; ^{1}H n.m.r. (in CDCl$_3$) δ 0.9 (q, *J* 6, 1 H, C*H*Me), 1.42 (d, *J* 6 Hz, 3 H, CH*Me*), 2.75 (s, 3 H, CMe$_2$), 2.85 (s, 3 H, CMe$_2$), 3.69 (s, 3 H, CO$_2$Me), 3.76 (s, 3 H, CO$_2$Me), 4.64 (s, 5 H, C$_5$H$_5$), and 4.82 (s, 5 H, C$_5$H$_5$)].

(*b*) *With ethyne.* Ethyne was bubbled through a toluene solution (100 cm^3) of complex (**4**) (0.25 g, 0.55 mmol) for 4 h under u.v. irradiation. The mixture was then evaporated to dryness and the residue chromatographed on an alumina column. Elution with dichloromethane–hexane (1:1) removed unreacted (**4**), while dichloromethane eluted a green band from which 40 mg (10%) of dark green crystalline [Ru$_2$(μ-CO)(μ-C$_2$H$_2$)(η-C$_5$H$_5$)$_2$] (**18**) was obtained [m.p. 193 °C (Found: C, 40.3; H, 3.3%; *M* 387. C$_{13}$H$_{12}$ORu$_2$ requires C, 40.3; H, 3.1%; *M* 387); ν(CO) (in CH$_2$Cl$_2$) 1 745 cm^{-1}; ^{1}H n.m.r. (in CDCl$_3$) δ 5.0 (s, 10 H, 2 C$_5$H$_5$) and 9.7 (s, 2 H, C$_2$H$_2$)].

(*c*) *Thermolysis.* Complex (**4**) (50 mg) was heated at 200 °C in a sealed, evacuated Pyrex tube (volume *ca.* 5 cm^3) for 2 h.

Analysis of the volatile hydrocarbon products by g.l.c. revealed a composition $CH_2{=}CH_2$ (20), $CH_2{=}CHMe$ (16), $Me_2C{=}CHMe$ (46), Et(Me)C=CH_2 (14), and $Pr^iCH{=}CH_2$ (4%), identified by comparison with authentic samples.

Thermolysis of complex (**3**) under the same conditions gave a similar result: $CH_2{=}CH_2$ (2), $CH_2{=}CHMe$ (10), $Me_2C{=}CHMe$ (64), Et(Me)C=CH_2 (18), and $Pr^iCH{=}CH_2$ (6%). In neither case was any C_4 or C_6 hydrocarbon product detected.

X-Ray Data Collection and Structure Determination.—Crystals of $[Ru_2(CO)_2(\mu\text{-}CHMe)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (**4a**) grow as yellow prisms with well developed type $\{001\}$, $\{01\bar{1}\}$, and $\{10\bar{1}\}$ faces. A crystal of dimensions *ca.* 0.23 × 0.35 × 0.43 mm was mounted on a glass fibre for *X*-ray structure analysis. Preliminary photography revealed a triclinic lattice. Intensity data were collected on a Nicolet $P2_1$ diffractometer at 220 K in the range $2.9 \leqslant 2\theta \leqslant 60°$ using graphite-monochromated Mo-K_α *X*-radiation (λ = 0.710 69 Å) by θ–2θ scans whose speed varied between 2.93 and 29.3° min^{-1} based on a 2 s prescan.

During the 91 h of data collection the check reflections $\bar{1}\,\bar{2}\,\bar{4}$ and $2\,\bar{4}\,\bar{3}$ showed crystal decay of *ca.* 10%. The data were corrected for Lorentz, polarisation, crystal decay, and *X*-ray absorption effects, the latter assuming the crystal faces to be 001, $00\bar{1}$, $0\bar{1}1$, $01\bar{1}$, $10\bar{1}$, and $\bar{1}01$. Reflections 002, 101, $0\bar{1}1$, $0\bar{1}2$, 011, and $\bar{1}10$ were omitted as their intensities were too large for a counter coincidence correction to be valid. Of the 4 932 measured non-check reflections, 4 448 were unique, with 4 092 satisfying the criterion $I \geqslant 3\sigma(I)$ and being used in structure solution and refinement.

Crystal data. $C_{17}H_{20}O_2Ru_2$, *M* 458.5, triclinic, space group $P\bar{1}$, a = 8.474(2), b = 7.802(3), c = 12.989(5) Å, α = 99.42(3), β = 96.96(3), γ = 107.73(3)°, U = 793.4(4) $Å^3$, Z = 2, D_c = 1.92 g cm^{-3}, $F(000)$ = 452, $\mu(\text{Mo-}K_\alpha)$ = 18.7 cm^{-1}.

The structure was solved using heavy-atom methods and refined by blocked-cascade least squares. The ruthenium atoms were located in a Patterson synthesis and subsequent successive electron density difference syntheses revealed the positions of the remaining non-hydrogen atoms. This model was then refined with all atoms being allowed anisotropic thermal parameters; the hydrogen atoms were thereby located and were allowed to refine freely with isotropic thermal parameters. A weighting scheme of the form $w = [\sigma^2(F) + 0.0002(F)^2]^{-1}$, where $\sigma(F)$ is the estimated standard deviation based on counting statistics only, gave a satisfactory analysis of variance. Refinement converged at *R* 0.026 (*R′* 0.031), *S* = 2.23,* and the final electron-density difference synthesis showed no peaks >0.64 or < −0.67 e $Å^{-3}$. All computations were carried out with programs of the SHELXTL package;[42] complex neutral atom scattering factors were taken from ref. 43. Table 2 lists the atomic positional parameters for the non-hydrogen atoms.

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* Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles. $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}\|F_o| - |F_c\|/\Sigma w^{\frac{1}{2}}|F_o|$; $S = [\Sigma w\|F_o| - F_c\|^2/(N_O - N_V)]^{\frac{1}{2}}$, where N_O and N_V are the numbers of observations and variables, respectively.