Organic Chemistry of Dinuclear Metal Centres. Part 14.[1] Synthesis, *X*-Ray Structure, and Reactivity of the Ruthenium–Ruthenium Double-bonded Complex $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$†

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Ultraviolet irradiation of the metallacycle $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (**1**) in tetrahydrofuran (thf) gives the complex $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ (**2**), shown by *X*-ray diffraction to have a ruthenium–ruthenium double bond [Ru=Ru 2.505(1) Å] bridged transversely by a diphenylacetylene ligand. The loss of two molecules of CO in forming (**2**) is reversible; under 100 atm of CO at 50 °C complex (**2**) is converted into (**1**) in 60% yield. Treatment of unsaturated complex (**2**) with diazoalkanes $RCHN_2$ (R = H, Me, or CO_2Et) results in the corresponding uptake of two alkylidene units to form $[Ru_2(CO)(\mu\text{-}CHR)\{\mu\text{-}C(Ph)C(Ph)CHR\}(\eta\text{-}C_5H_5)_2]$, existing as isomers for R = Me or CO_2Et due to differing orientations of the μ-CHR substituent. The structure of $[Ru_2(CO)(\mu\text{-}CH_2)\{\mu\text{-}C(Ph)C(Ph)CH_2\}(\eta\text{-}C_5H_5)_2]$ (**3**) has been established by *X*-ray diffraction, revealing that one methylene co-ordinates to the dinuclear metal centre while the other links with the alkyne. There are non-bonding C–C distances of 3.07 Å between the two μ-carbons of the complex, but only 2.78 Å separating the μ-CH_2 carbon and the CH_2 carbon of the $C(Ph)C(Ph)CH_2$ ligand. On thermolysis the latter two carbons link, accompanied by other processes, to afford $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(Ph)CHMe\}(\eta\text{-}C_5H_5)_2]$ (**5**). A co-product of the reaction of diazoethane with (**2**) is the di-μ-vinyl complex $[Ru_2(CO)(\mu\text{-}CHCH_2)\{\mu\text{-}C(Ph)CHPh\}(\eta\text{-}C_5H_5)_2]$ (**8**). *X*-Ray diffraction reveals that the two β-carbons of the vinyl groups are 2.99 Å apart and it is these rather than the two μ(α)-carbons (3.06 Å apart) which link on thermolysis, affording complex (**5**) once more. Thermolysis of $[Ru_2(CO)(\mu\text{-}CHCO_2Et)\{\mu\text{-}C(Ph)C(Ph)CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2]$ does not effect carbon–carbon bond formation. Instead, CO is ejected and its site occupied by an oxygen of a carboethoxy group in the complex $[Ru_2(\mu\text{-}CHCO_2Et)\{\mu\text{-}C(Ph)C(Ph)CHC(O)OEt\}(\eta\text{-}C_5H_5)_2]$. Treatment of complex (**1**) with BH_3·thf or LiMe–HBF_4–$NaBH_4$ converts the metallacyclic ketone group into CH_2 or CHMe respectively, yielding $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(Ph)CHR\}(\eta\text{-}C_5H_5)_2]$ (R = H or Me). The nature of the processes observed on thermolysis of complexes (**3**) and (**8**) suggests the importance of least-motion effects in determining the course of carbon–carbon bond formation at a dinuclear metal centre.

The two previous Parts of this Series were concerned with the linking of μ-alkylidene ligands at a diruthenium centre to give an alkene.[1,2] In this Part we describe related studies of carbon–carbon bond formation at a diruthenium centre involving alkylidene and vinylalkylidene ligands which reveal the importance of least-motion effects in determining the course of the process. These studies are based on a μ-alkyne ruthenium–ruthenium double-bonded complex, whose unsaturation allows ready combination of the alkyne with CO and alkylidenes. A preliminary account of some aspects of this work has appeared.[3]

Results and Discussion

The complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (**1**), which is formed by the reaction of diphenylacetylene with $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$,[4] loses two molecules of carbon monoxide on u.v. irradiation in tetrahydrofuran (thf) solution to give air-stable green-black crystalline $[Ru_2(\mu\text{-}CO)(\mu\text{-}C_2Ph_2)(\eta\text{-}C_5H_5)_2]$ (**2**) in *ca.* 50% yield. I.r. (bridging CO) and n.m.r. (equivalent η-C_5H_5 ligands) spectra, and the 18-electron rule, indicated the structure shown in Scheme 1, in which a four-electron alkyne ligand bridges a ruthenium–ruthenium double bond transversely. An *X*-ray diffraction study established that this is indeed the case.

Crystal and Molecular Structure of Complex (**2**).—The crystal structure of complex (**2**) consists of isolated molecules separated by normal van der Waals distances. The molecular structure of (**2**) is illustrated in Figure 1 and selected bond lengths and angles are listed in Table 1. As suggested, the Ru–Ru distance is unusually short, at 2.505(1) Å, and consistent with a bond order of two required by the 18-electron rule. This bond length is similar to that in the 32-electron Ru=Ru species $[Ru_2H_6(N_2)(PPh_3)_4]$[5] [2.556(3) Å] but significantly longer than Ru=Ru distances (2.26—2.29 Å) in tetracarboxylate ruthenium(II) dimers and related complexes.[6,7] The molecule has approximate C_{2v} symmetry with the C_2 axis collinear with the C–O bond. The μ-alkyne shows the usual *cis*-bending back of the phenyl substituents and lengthening of the C≡C bond on co-ordination [C(3)–C(4)–C(41) 141.3(8), C(4)–C(3)–C(31) 139.4(8), C(3)–C(4) 1.336(12), and mean Ru–C 2.106(11) Å]. The transverse orientation of the diphenylacetylene is confirmed, the C(3)–C(4) axis being at 91.0° to the Ru(1)–Ru(2) vector.

Attempts to prepare other μ-alkyne complexes of type (**2**) by

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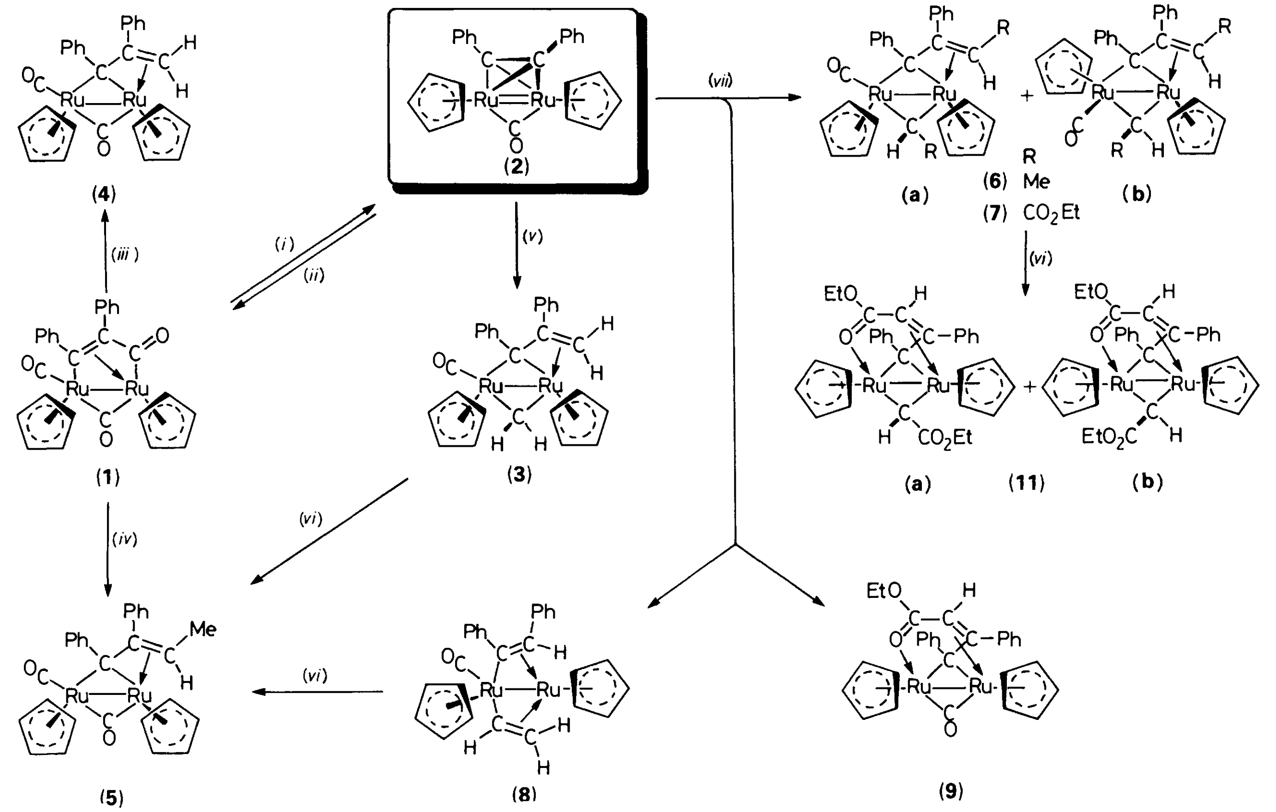
† μ-Carbonyl-μ-diphenylacetylene-bis[(η-cyclopentadienyl)-ruthenium] (*Ru=Ru*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

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



Scheme 1. (*i*) U.v. irradiation; (*ii*) CO (100 atm), 50 °C; (*iii*) BH_3•thf; (*iv*) LiMe, HBF_4, $NaBH_4$; (*v*) CH_2N_2; (*vi*) xylene reflux; (*vii*) $RCHN_2$ (R = Me or CO_2Et)

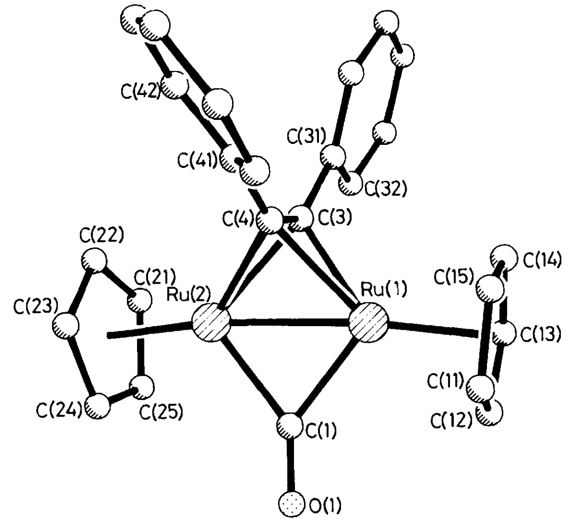


Figure 1. Molecular structure of complex (**2**) showing labelling scheme; all hydrogen atoms have been omitted for clarity

Table 1. Selected bond lengths (Å) and angles (°) for complex (**2**)

Ru(1)–Ru(2)	2.505(1)	Ru(1)–C(1)	2.005(9)
Ru(1)–C(3)	2.091(9)	Ru(1)–C(4)	2.110(8)
Ru(1)–C(11)	2.244(8)	Ru(1)–C(12)	2.209(8)
Ru(1)–C(13)	2.184(8)	Ru(1)–C(14)	2.204(8)
Ru(1)–C(15)	2.241(8)	Ru(2)–C(1)	2.000(9)
Ru(2)–C(3)	2.088(8)	Ru(2)–C(4)	2.135(8)
Ru(2)–C(21)	2.212(14)	Ru(2)–C(22)	2.202(18)
Ru(2)–C(23)	2.200(14)	Ru(2)–C(24)	2.209(14)
Ru(2)–C(25)	2.216(14)	Ru(2)–C(21′)	2.261(22)
Ru(2)–C(22′)	2.247(29)	Ru(2)–C(23′)	2.226(21)
Ru(2)–C(24′)	2.227(22)	Ru(2)–C(25′)	2.249(20)
C(1)–O(1)	1.188(11)	C(3)–C(4)	1.336(12)
C(3)–C(31)	1.471(12)	C(4)–C(41)	1.465(12)
C(31)–C(32)	1.394(12)	C(31)–C(36)	1.370(12)
C(32)–C(33)	1.379(13)	C(33)–C(34)	1.363(15)
C(34)–C(35)	1.385(14)	C(35)–C(36)	1.379(14)
C(41)–C(42)	1.384(13)	C(41)–C(46)	1.374(12)
C(42)–C(43)	1.390(15)	C(43)–C(44)	1.362(16)
C(44)–C(45)	1.366(18)	C(45)–C(46)	1.374(15)
Ru(2)–Ru(1)–C(1)	51.2(3)	Ru(2)–Ru(1)–C(3)	53.1(2)
C(1)–Ru(1)–C(3)	102.2(3)	Ru(2)–Ru(1)–C(4)	54.3(2)
C(1)–Ru(1)–C(4)	101.4(3)	C(3)–Ru(1)–C(4)	37.1(3)
Ru(1)–Ru(2)–C(1)	51.4(3)	Ru(1)–Ru(2)–C(3)	53.2(2)
C(1)–Ru(2)–C(3)	102.5(3)	Ru(1)–Ru(2)–C(4)	53.4(2)
C(1)–Ru(2)–C(4)	100.7(3)	C(3)–Ru(2)–C(4)	36.9(3)
Ru(1)–C(1)–Ru(2)	77.5(3)	Ru(1)–C(1)–O(1)	141.4(7)
Ru(2)–C(1)–O(1)	141.0(7)	Ru(1)–C(3)–Ru(2)	73.7(3)
Ru(1)–C(3)–C(4)	72.2(5)	Ru(2)–C(3)–C(4)	73.5(5)
Ru(1)–C(3)–C(31)	129.6(6)	Ru(2)–C(3)–C(31)	139.8(6)
C(4)–C(3)–C(31)	139.4(8)	Ru(1)–C(4)–Ru(2)	72.3(3)
Ru(1)–C(4)–C(3)	70.7(5)	Ru(2)–C(4)–C(3)	69.7(5)
Ru(1)–C(4)–C(41)	138.8(6)	Ru(2)–C(4)–C(41)	133.5(6)
C(3)–C(4)–C(41)	141.3(8)		

the same route were unsuccessful. Photolysis of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2R_2\}(\eta\text{-}C_5H_5)_2]$ (R = Me or CO_2Me)[4] gave no identifiable products, while the ethyne and phenylethyne analogues of complex (**1**) yielded only traces of the corresponding μ-vinylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CHR)(\eta\text{-}C_5H_5)_2]$ (R = H or Ph).[8] This was surprising in view of the fact that the ethyne analogue of (**2**) is known, obtained in low yield when $[Ru_2(CO)_2(\mu\text{-}CHMe)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ is photolysed in the presence of ethyne.[2] Other complexes in which an alkyne transversely bridges a metal–

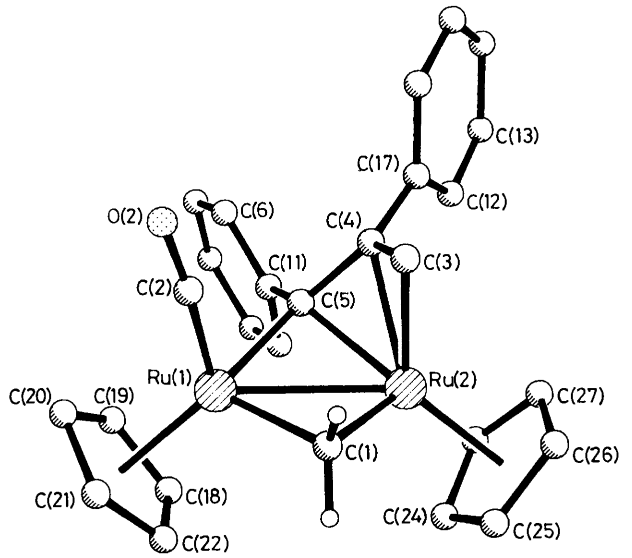
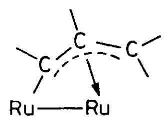


Figure 2. Molecular structure of complex (3) showing labelling scheme for the first of the two independent molecules present in the crystal structure; all hydrogen atoms except those on C(1) have been omitted for clarity. The hydrogens on C(3) were not located

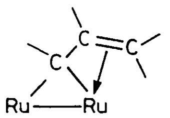
metal double bond are known, *e.g.* $[Fe_2(CO)_6(\mu-C_2R_2)]$ (R = Ph or Bu^t)[9] and $[Co_2(\mu-C_2R_2)(\eta-C_5Me_5)_2]$ (R = Ph or $SiMe_3$).[10]

The decarbonylation of complex (1) is reversible; treatment of (2) with 100 atm of CO at 50 °C regenerates (1) in *ca.* 60% yield. Reaction with methylene occurs in similar fashion to CO, but much more readily. Thus, addition of diazomethane to a thf solution of complex (2) at 0 °C results in the rapid incorporation of two methylene groups, forming orange crystalline $[Ru_2(CO)(\mu-CH_2)\{\mu-C(Ph)C(Ph)CH_2\}(\eta-C_5H_5)_2]$ (3) in *ca.* 75% yield. The i.r. spectrum of (3) clearly showed that the bridging carbonyl ligand of (1) was now terminally bonded, while the ^1H n.m.r. spectrum revealed that the bridging site was occupied by a methylene (low-field signals at δ 7.03 and 9.00), and that a second methylene had combined with the alkyne to form a co-ordinated vinylalkylidene ligand $\mu-\sigma:\eta^3-C(Ph)C(Ph)CH_2$ (methylene signals at δ 3.12 and −0.30) of known type.[11–13] This same ligand is present in $[Ru_2(CO)(\mu-CO)\{\mu-C(Ph)C(Ph)CH_2\}(\eta-C_5H_5)_2]$ (4) (CH_2 protons at δ 3.05 and 0.10), obtained in 64% yield upon $BH_3\cdot$thf reduction of the ketone group in (1). Complex (4) is also formed when $[Ru_2(CO)_2(\mu-CO)(\mu-CH_2)(\eta-C_5H_5)_2]$ is photolysed in the presence of diphenylacetylene,[14] showing that the vinylalkylidene ligand can be produced either by reaction of a pre-co-ordinated alkyne with an alkylidene or *vice versa.* This is confirmed in striking fashion by the treatment of $[Ir_2(\mu-CH_2)_2(cod)_2]$ (cod = cyclo-octa-1,5-diene) with diphenylacetylene, which yields $[Ir_2(\mu-CH_2)\{\mu-C(Ph)C(Ph)CH_2\}(cod)_2]$, structurally closely related to complex (3).[15] Alkylidene–alkyne linking *via* reaction of a diazoalkane with a $\mu-C_2(CF_3)_2$ ligand has been observed by Dickson *et al.*[16] The addition of a CH_2 group to a metal–metal double bond, as in the formation of (3), has wide precedent in the work of Herrmann and others,[17] but double addition of the type described here was unknown at the time it was first reported,[3] and remains rare. Stone and co-workers[18] have subsequently observed double methylene addition to a μ-alkylidyne system. The molecular structure of complex (3) was established by *X*-ray diffraction study of its hexane solvate, providing details of the molecular geometry which help to explain the nature of the products formed upon thermolysis of the complex.

Crystal and Molecular Structure of Complex $(3)\cdot 0.25C_6H_{14}$.—Crystals of this complex consist of isolated molecules of (3) (two independent molecules per asymmetric unit of the unit cell) and hexane, the latter being disordered around a site of two-fold symmetry. The two independent molecules of (3) are very similar in bond lengths and angles, but are of opposite chirality, the crystal therefore consisting of a racemic mixture of D- and L-(3). One of these molecules is illustrated in Figure 2, and selected bond lengths and bond angles for this structure are listed in Table 2. In the discussion below molecular dimensions given are averaged over the two molecules, with atom labels referring to those in Figure 2. Molecules of (3) contain a diruthenium unit in which the Ru–Ru bond order is unity [Ru(1)–Ru(2) 2.713(1) Å]. Each ruthenium carries an $\eta^5-C_5H_5$ ligand and there is a terminal carbonyl ligand bound to Ru(1). The Ru–Ru vector is bridged symmetrically by a methylene ligand [Ru(1)–C(1) 2.072(7) and Ru(2)–C(1) 2.069(7) Å] and asymmetrically by a 1,2-diphenylallylidene ligand $[C(Ph)C(Ph)CH_2]$ which results from formal addition of a methylene group to the co-ordinated diphenylacetylene group of complex (2). The allylidene ligand binds to the Ru_2 unit by σ [to Ru(1)] and η^3 [to Ru(2)], π-allyl-like interactions. The C–C bond lengths [C(5)–C(4) 1.431(10) and C(4)–C(3) 1.439(11) Å] serve to emphasise the delocalised, allyl-like nature of the ligand [see structure (**A**) below]. However, the equality of the Ru–C(5) distances [Ru(1)–C(5) 2.081(7) and Ru(2)–C(5) 2.089(7) Å], and the longer Ru(2)–C(4) 2.152(7) and Ru(2)–C(3) 2.142(8) Å bond lengths suggest this ligand may also be described as a vinyl-substituted μ-alkylidene [see structure (**B**) below].



(A)



(B)

The structure determination shows that (3) can be regarded as a di-μ-alkylidene complex. Such complexes have been shown[2] to undergo linking of the μ-carbons on thermolysis, to evolve an alkene, and were this process to occur for (3) the product would be 2,3-diphenylbuta-1,3-diene. The prospect of constructing a diene in this way at a dinuclear metal centre led us to decompose (3) under vacuum at 200 °C. In the event, this yielded no diene and only a variety of low-yield unidentified organic products. Examination of the molecular structure of complex (3) provided a plausible reason for this failure, in that while the bridging carbon atoms C(1) and C(5) are separated by 3.07(2) Å, the methylene carbons C(1) and C(3) are only 2.78(2) Å apart. This feature is clearly shown in Figure 3, which presents the central portion of (3) viewed along the Ru–Ru axis. If least-motion effects are significant these distances would suggest that C(1)–C(3) linking is favoured over C(1)–C(5) linking. This appears to be the case. Heating complex (3) in xylene (b.p. 148 °C) for 40 h gave a 30% yield of orange crystalline $[Ru_2(CO)(\mu-CO)\{\mu-C(Ph)C(Ph)CHMe\}(\eta-C_5H_5)_2]$ (5), a complex previously obtained by reaction of $[Ru_2(CO)_2(\mu-CO)(\mu-CHMe)(\eta-C_5H_5)_2]$ with diphenylacetylene.[11,12] Interestingly, we have discovered in this work that the sequence of reagents which converts a μ-CO group into μ-CHMe at a diruthenium centre,[8] namely LiMe, HBF_4, and $NaBH_4$, also converts the ketonic CO of (1) into CHMe, affording (5) in 50% yield.

A possible mechanism for the conversion of complex (3) into (5) is shown in Scheme 2. In the first step carbon–carbon bond formation occurs *via* reductive elimination, creating a 16-electron ruthenium centre. A subsequent 1,2-hydrogen shift (perhaps through β-hydrogen elimination at the 16-electron centre and then transfer to the adjacent carbon by another

Table 2. Selected bond lengths (Å) and angles (°) for complex (**3**)$\cdot 0.25C_6H_{14}$

Ru(1)–Ru(2)	2.715(1)	Ru(1)–C(1)	2.074(7)	C(10)–C(11)	1.382(12)	C(12)–C(13)	1.374(13)
Ru(1)–C(2)	1.801(10)	Ru(1)–C(5)	2.076(7)	C(12)–C(17)	1.397(12)	C(13)–C(14)	1.397(16)
Ru(1)–C(18)	2.309(11)	Ru(1)–C(19)	2.306(11)	C(14)–C(15)	1.360(15)	C(15)–C(16)	1.389(14)
Ru(1)–C(20)	2.238(12)	Ru(1)–C(21)	2.201(13)	C(16)–C(17)	1.397(13)	C(18)–C(19)	1.334(16)
Ru(1)–C(22)	2.282(12)	Ru(2)–C(1)	2.061(7)	C(18)–C(22)	1.323(16)	C(19)–C(20)	1.349(16)
Ru(2)–C(3)	2.139(9)	Ru(2)–C(4)	2.156(7)	C(20)–C(21)	1.470(19)	C(21)–C(22)	1.414(19)
Ru(2)–C(5)	2.090(7)	Ru(2)–C(23)	2.264(9)	C(23)–C(24)	1.383(13)	C(23)–C(27)	1.398(13)
Ru(2)–C(24)	2.287(10)	Ru(2)–C(25)	2.264(10)	C(24)–C(25)	1.449(14)	C(25)–C(26)	1.391(15)
Ru(2)–C(26)	2.229(9)	Ru(2)–C(27)	2.231(9)	C(26)–C(27)	1.444(12)	O(32)–C(32)	1.167(13)
Ru(3)–Ru(4)	2.711(1)	Ru(3)–C(31)	2.069(7)	C(33)–C(34)	1.446(11)	C(34)–C(35)	1.418(10)
Ru(3)–C(32)	1.797(10)	Ru(3)–C(35)	2.086(7)	C(34)–C(42)	1.520(10)	C(35)–C(41)	1.498(10)
Ru(3)–C(48)	2.261(13)	Ru(3)–C(49)	2.292(14)	C(36)–C(37)	1.399(14)	C(36)–C(41)	1.396(13)
Ru(3)–C(50)	2.316(13)	Ru(3)–C(51)	2.309(16)	C(37)–C(38)	1.389(17)	C(38)–C(39)	1.366(23)
Ru(3)–C(52)	2.254(17)	Ru(4)–C(31)	2.077(7)	C(39)–C(40)	1.368(14)	C(40)–C(41)	1.398(12)
Ru(4)–C(33)	2.144(9)	Ru(4)–C(34)	2.148(7)	C(42)–C(43)	1.385(11)	C(42)–C(47)	1.398(12)
Ru(4)–C(35)	2.089(7)	Ru(4)–C(53)	2.258(9)	C(43)–C(44)	1.382(12)	C(44)–C(45)	1.381(16)
Ru(4)–C(54)	2.299(10)	Ru(4)–C(55)	2.253(10)	C(45)–C(46)	1.366(14)	C(46)–C(47)	1.370(12)
Ru(4)–C(56)	2.221(8)	Ru(4)–C(57)	2.218(9)	C(48)–C(49)	1.342(20)	C(48)–C(52)	1.421(23)
C(2)–O(2)	1.161(12)	C(3)–C(4)	1.432(11)	C(49)–C(50)	1.368(19)	C(50)–C(51)	1.337(22)
C(4)–C(5)	1.444(10)	C(4)–C(17)	1.497(11)	C(51)–C(52)	1.446(28)	C(53)–C(54)	1.368(14)
C(5)–C(11)	1.510(10)	C(6)–C(7)	1.395(12)	C(53)–C(57)	1.385(14)	C(54)–C(55)	1.436(14)
C(6)–C(11)	1.375(11)	C(7)–C(8)	1.370(19)	C(55)–C(56)	1.420(14)	C(56)–C(57)	1.446(13)
C(8)–C(9)	1.376(13)	C(9)–C(10)	1.373(11)	C(60)–C(62)	1.271(48)	C(61)–C(62)	1.309(52)
				C(61)–C(63)	1.654(34)		

Ru(2)–Ru(1)–C(2)	104.6(3)	Ru(2)–Ru(1)–C(1)	48.7(2)	Ru(1)–C(2)–O(2)	174.3(8)	Ru(2)–C(3)–C(4)	71.2(5)
Ru(2)–Ru(1)–C(5)	49.6(2)	C(1)–Ru(1)–C(2)	92.1(4)	Ru(2)–C(4)–C(3)	69.8(5)	Ru(2)–C(4)–C(5)	67.7(4)
C(2)–Ru(1)–C(5)	89.0(3)	C(1)–Ru(1)–C(5)	95.3(3)	C(3)–C(4)–C(5)	117.6(7)	Ru(2)–C(4)–C(17)	127.7(5)
Ru(1)–Ru(2)–C(3)	84.3(2)	Ru(1)–Ru(2)–C(1)	49.2(2)	C(3)–C(4)–C(17)	120.5(7)	C(5)–C(4)–C(17)	121.4(6)
Ru(1)–Ru(2)–C(4)	78.1(2)	C(1)–Ru(2)–C(3)	82.9(3)	Ru(1)–C(5)–Ru(2)	81.3(2)	Ru(1)–C(5)–C(4)	122.5(5)
C(3)–Ru(2)–C(4)	39.0(3)	C(1)–Ru(2)–C(4)	106.5(3)	Ru(2)–C(5)–C(4)	72.6(4)	Ru(1)–C(5)–C(11)	115.6(5)
C(1)–Ru(2)–C(5)	95.3(3)	Ru(1)–Ru(2)–C(5)	49.1(2)	Ru(2)–C(5)–C(11)	133.1(5)	C(4)–C(5)–C(11)	119.7(6)
C(4)–Ru(2)–C(5)	39.7(3)	C(3)–Ru(2)–C(5)	71.1(3)	Ru(3)–C(31)–Ru(4)	81.7(2)	Ru(3)–C(32)–O(32)	173.2(9)
Ru(4)–Ru(3)–C(32)	103.3(3)	Ru(4)–Ru(3)–C(31)	49.3(2)	Ru(4)–C(33)–C(34)	70.5(4)	Ru(4)–C(34)–C(33)	70.2(4)
Ru(4)–Ru(3)–C(35)	49.5(2)	C(31)–Ru(3)–C(32)	89.3(4)	Ru(4)–C(34)–C(35)	68.2(4)	C(33)–C(34)–C(35)	119.2(6)
C(32)–Ru(3)–C(35)	89.0(3)	C(31)–Ru(3)–C(35)	95.5(3)	Ru(4)–C(34)–C(42)	127.9(5)	C(33)–C(34)–C(42)	118.5(7)
Ru(3)–Ru(4)–C(33)	85.1(2)	Ru(3)–Ru(4)–C(31)	49.0(2)	C(35)–C(34)–C(42)	121.8(5)	Ru(3)–C(35)–Ru(4)	81.0(2)
Ru(3)–Ru(4)–C(34)	77.9(2)	C(31)–Ru(4)–C(33)	82.7(3)	Ru(3)–C(35)–C(34)	122.5(5)	Ru(4)–C(35)–C(34)	72.7(4)
C(33)–Ru(4)–C(34)	39.4(3)	C(31)–Ru(4)–C(34)	105.9(3)	Ru(3)–C(35)–C(41)	114.5(5)	Ru(4)–C(35)–C(41)	134.1(5)
C(31)–Ru(4)–C(35)	95.2(3)	Ru(3)–Ru(4)–C(35)	49.5(2)	C(34)–C(35)–C(41)	120.7(6)		
C(34)–Ru(4)–C(35)	39.1(3)	C(33)–Ru(4)–C(35)	71.4(3)				
		Ru(1)–C(1)–Ru(2)	82.1(3)				

reductive elimination) gives the μ-σ:η^3-C(Ph)C(Ph)CHMe ligand, co-ordinated at an unsaturated 32-electron diruthenium centre. Uptake of a molecule of CO, compensating for the effective loss of two electrons from the diruthenium centre in the formation of the new carbon–carbon bond, completes the transformation to (**5**). The additional CO present in (**5**) is evidently scavenged from the decomposition of molecules of (**3**). The observed 30% yield of (**5**) indicates a very efficient CO transfer process, perhaps of bimolecular character. Support for this proposition comes from the failure to increase the yield of (**5**) significantly when the thermolysis of (**3**) is carried out under 1—10 atm of carbon monoxide. A related carbon–carbon bond formation process has been observed at a triosmium centre; when $[Os_3(CO)_9(\mu\text{-}CH_2)(\mu_3\text{-}C_2Ph_2)]$ was heated acetylenic and methylene carbons 2.86 Å apart combined to afford $[Os_3(\mu\text{-}H)(CO)_9(\mu\text{-}CHCPhCPh)]$.[19]

It is important to note that the conversion of complex (**3**) into (**5**) is in effect an alkene homologation process involving combination of co-ordinated alkene and methylene groups. It has been suggested[20,21] that such a process is responsible for the carbon-chain growth which occurs on a metal surface in the Fischer–Tropsch synthesis, either in place of or in addition to the currently popular alkyl homologation mechanism.

Trimethylsilyldiazomethane does not react with complex (**2**), perhaps for steric reasons, but diazoethane and ethyl diazoacetate (*i.e.* $RCHN_2$, R = Me or CO_2Et) also effect double alkylidene addition, to give the appropriate analogue of (**3**). Both $[Ru_2(CO)(\mu\text{-}CHMe)\{\mu\text{-}C(Ph)(CPh)CHMe\}(\eta\text{-}C_5H_5)_2]$ (**6**) and $[Ru_2(CO)(\mu\text{-}CHCO_2Et)\{\mu\text{-}C(Ph)C(Ph)CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2]$ (**7**) exist, however, as inseparable isomers [(**a**) and (**b**)] arising from the asymmetry introduced by the substituent on the μ-CHR ligand. In each case one isomer (**a**) shows a ^1H n.m.r. signal for the μ-C*H*R proton at substantially lower field (*ca.* δ 2.5 lower) than that for isomer (**b**). Previous experience[22] of this situation indicates that isomer (**a**) has a *cis* configuration for the η-cyclopentadienyl ligands, with the μ-CHR ligand oriented so that the proton lies between the rings, and that isomer (**b**) has the η-cyclopentadienyl ligands *trans*. The (**a**):(**b**) ratio for complex (**6**) is near 1:1, and that for (**7**) about 1:2.

Thermolysis of complex (**6**) yielded no analogues of (**5**), indicating that carbon–carbon bond formation between the alkylidene groups is hindered by the presence of methyl substituents.

The major product from the reaction of diazoethane with complex (**2**) was not (**6**) (15%) but red-purple $[Ru_2(CO)(\mu\text{-}CHCH_2)\{\mu\text{-}C(Ph)CHPh\}(\eta\text{-}C_5H_5)_2]$ (**8**), isolated in *ca.* 20% yield and readily characterised by ^1H n.m.r. spectroscopy as a di-μ-vinyl complex. A likely mechanism for the formation of (**8**) is laid out in Scheme 3. Addition of an ethylidene group to the Ru=Ru double bond of (**2**), probably *via* initial complexation of

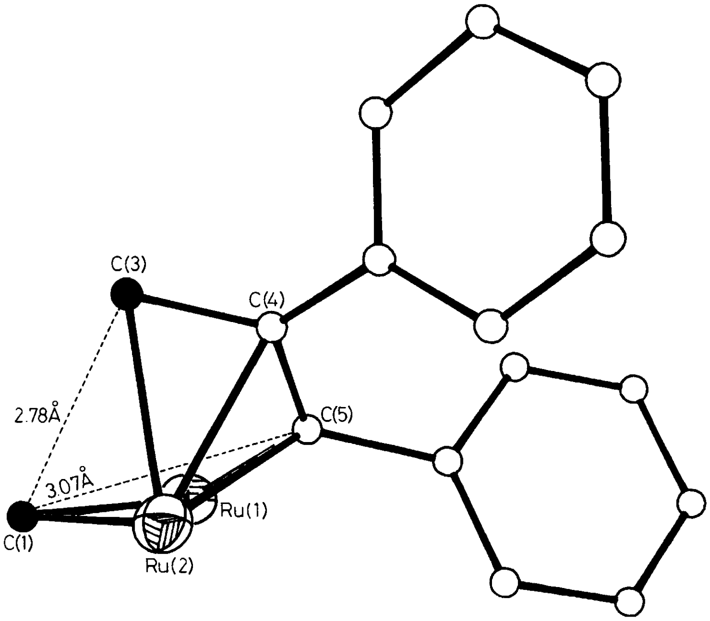
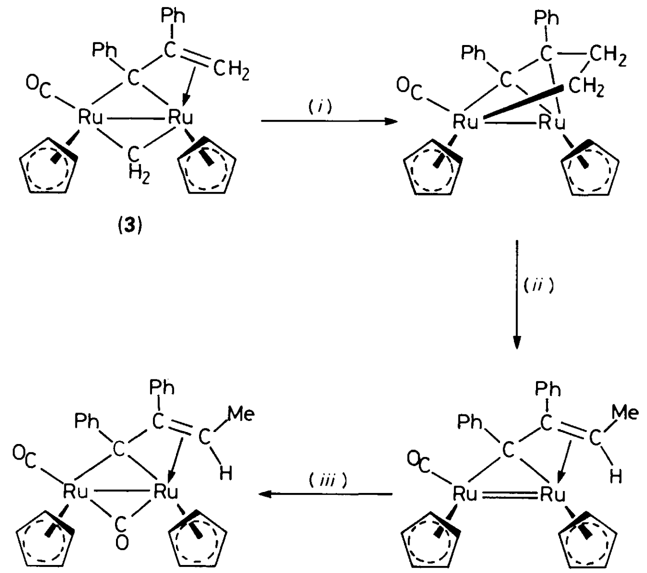
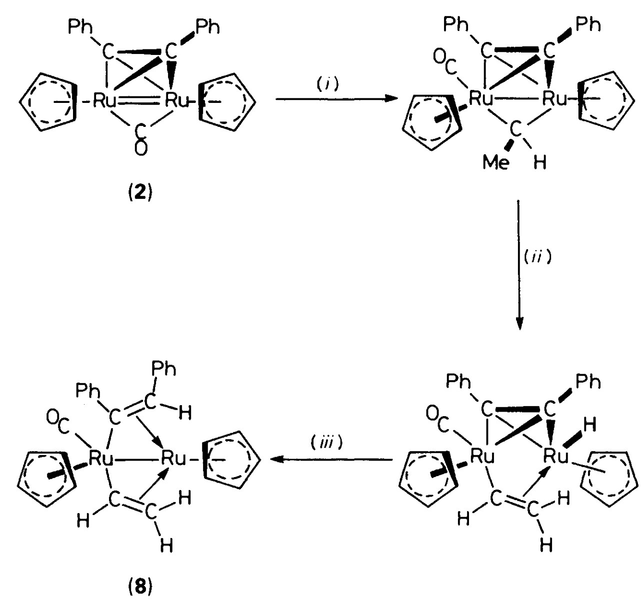


Figure 3. The central portion of complex (**3**), viewed along the metal–metal axis, illustrating non-bonding carbon–carbon distances



Scheme 2. (*i*) C–C bond formation; (*ii*) hydrogen shift; (*iii*) +CO



Scheme 3. (*i*) $MeCHN_2$; (*ii*) β-hydrogen elimination; (*iii*) reductive elimination

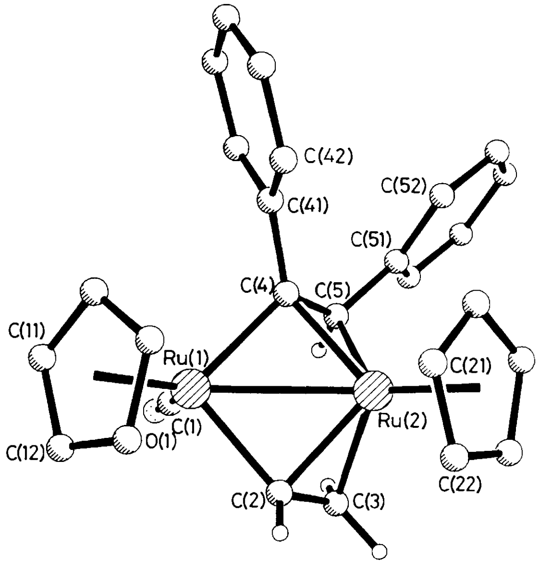
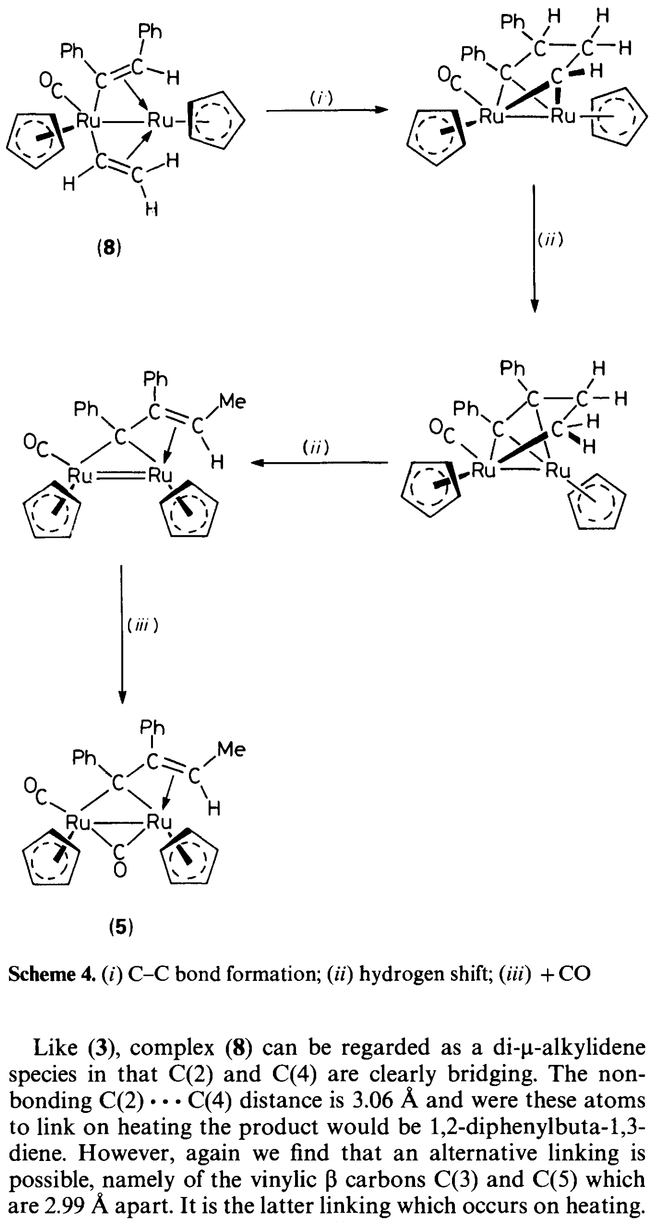


Figure 4. Molecular structure of complex (**8**) showing labelling scheme; all phenyl and cyclopentadienyl group hydrogen atoms have been omitted for clarity

the diazoalkane, is envisaged to be followed by β-hydrogen elimination and then hydrogen transfer from ruthenium to diphenylacetylene in a reductive-elimination step. In view of the yields of complexes (**8**) and (**6**), *i.e.* 20 and 15% respectively, the β-elimination step appears to occur at roughly the same rate as the co-ordination of a second ethylidene. The structure of (**8**) was firmly established by a single-crystal *X*-ray diffraction study.

Crystal and Molecular Structure of Complex (**8**).—The molecular structure of complex (**8**) is illustrated in Figure 4 and selected bond lengths and angles are listed in Table 3. Molecules of (**8**) consist of a diruthenium unit in which a Ru–Ru single bond [2.720(1) Å] is doubly bridged by vinyl ligands. Each ruthenium carries an η^5-C_5H_5 ligand and Ru(1) a terminal carbonyl ligand. The vinyl ligands are co-ordinated in the usual σ,π fashion with *both* being σ bonded to Ru(1) and π bonded to Ru(2). The resulting molecular structure has approximate mirror symmetry if the phenyl substituents are discounted. The Ru–C σ-bond distances for the two vinyl ligands are significantly different, with that for the 1,2-diphenylvinyl ligand longer than for the unsubstituted vinyl [Ru(1)–C(4) 2.132(4), Ru(1)–C(2) 2.049(4) Å]. In contrast, the Ru–C π-bonded distances are similar for the two ligands, each showing characteristic asymmetry, with the bridging carbon more strongly bound than the terminal vinyl carbon [Ru(2)–C(2) 2.089(4), Ru(2)–C(3) 2.212(3); Ru(2)–C(4) 2.077(3), Ru(2)–C(5) 2.213(3) Å]. The C–C bonds in the vinyl ligands are significantly longer than true double bonds [C(2)–C(3) 1.396(5) and C(4)–C(5) 1.429(4) Å] as a consequence of co-ordination. In addition the disubstituted vinyl shows substantial rehybridisation (from sp^2 towards sp^3) as reflected in the twisting about the C(4)–C(5) bond [torsion angle C(41)–C(4)–C(5)–C(51) is 19.0°].



Scheme 4. (*i*) C–C bond formation; (*ii*) hydrogen shift; (*iii*) +CO

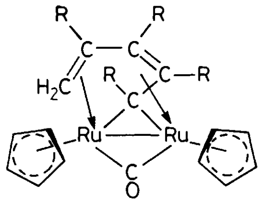
Like (3), complex (**8**) can be regarded as a di-μ-alkylidene species in that C(2) and C(4) are clearly bridging. The non-bonding C(2) ··· C(4) distance is 3.06 Å and were these atoms to link on heating the product would be 1,2-diphenylbuta-1,3-diene. However, again we find that an alternative linking is possible, namely of the vinylic β carbons C(3) and C(5) which are 2.99 Å apart. It is the latter linking which occurs on heating. Refluxing (**8**) in xylene for 60 h affords complex (**5**) in 22% yield, only slightly lower than the yield of (**5**) obtained when (**3**) is thermolysed. Scheme 4 shows a plausible pathway for the transformation of (**8**) to (**5**), involving C(3)–C(5) bond formation followed by two hydrogen shifts and, again, the scavenging of a molecule of carbon monoxide.

This first observation of the combination of two vinyl groups at a dinuclear metal centre should be seen in relation to the recent suggestion[23] that surface vinyl groups may play an important role in the carbon–carbon bond-formation process of the Fischer–Tropsch synthesis. Complexes related to (**8**) have been obtained recently by the reaction of ethylene with $[Ru_2(\mu\text{-}H)_4(\eta\text{-}C_5Me_5)_2]$.[24]

A minor product of the reaction of (**2**) with ethyl diazoacetate, orange crystalline $[Ru_2(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(Ph)CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2]$ (**9**), was assigned the structure shown (Scheme 1), by comparison with the complex (**10**) whose structure has been established by *X*-ray diffraction.[12] Only one alkylidene unit has been added to (**2**) in forming (**9**), but the unsaturation of the dimetal centre has been fully erased by the *O*-co-ordination of the ethoxycarbonyl group. This is reflected in the shift to lower frequency of the ν(C=O) stretch of the CO_2Et group, which is seen at 1 595 cm^{-1} for (**9**) compared with1 678 cm^{-1} for the isomers of (**7**), where the group is unco-ordinated.

Table 3. Selected bond lengths (Å) and angles (°) for complex (**8**)

Ru(2)–Ru(1)	2.720(1)	Ru(2)–C(2)	2.089(4)
Ru(2)–C(3)	2.212(3)	Ru(2)–C(4)	2.077(3)
Ru(2)–C(5)	2.213(3)	Ru(2)–C(21)	2.249(3)
Ru(2)–C(22)	2.237(4)	Ru(2)–C(23)	2.230(5)
Ru(2)–C(24)	2.237(5)	Ru(2)–C(25)	2.235(4)
Ru(1)–C(1)	1.840(3)	Ru(1)–C(2)	2.049(4)
Ru(1)–C(4)	2.132(4)	Ru(1)–C(11)	2.262(5)
Ru(1)–C(12)	2.265(5)	Ru(1)–C(13)	2.289(4)
Ru(1)–C(14)	2.302(3)	Ru(1)–C(15)	2.292(3)
O(1)–C(1)	1.162(4)	C(2)–C(3)	1.396(5)
C(4)–C(5)	1.429(4)	C(4)–C(41)	1.494(4)
C(5)–C(51)	1.497(5)	C(21)–C(22)	1.401(5)
C(21)–C(25)	1.408(6)	C(22)–C(23)	1.412(6)
C(23)–C(24)	1.415(7)	C(24)–C(25)	1.411(5)
C(11)–C(12)	1.418(6)	C(11)–C(15)	1.400(6)
C(12)–C(13)	1.409(6)	C(13)–C(14)	1.416(5)
C(14)–C(15)	1.420(6)	C(41)–C(42)	1.396(3)
C(41)–C(46)	1.400(5)	C(42)–C(43)	1.392(4)
C(43)–C(44)	1.377(6)	C(44)–C(45)	1.380(4)
C(45)–C(46)	1.387(5)	C(51)–C(52)	1.404(4)
C(51)–C(56)	1.396(4)	C(52)–C(53)	1.396(6)
C(53)–C(54)	1.382(4)	C(54)–C(55)	1.386(5)
C(55)–C(56)	1.393(6)		
Ru(1)–Ru(2)–C(2)	48.3(1)	Ru(1)–Ru(2)–C(3)	76.4(1)
C(2)–Ru(2)–C(3)	37.7(1)	Ru(1)–Ru(2)–C(4)	50.6(1)
C(2)–Ru(2)–C(4)	94.6(2)	C(3)–Ru(2)–C(4)	103.9(1)
Ru(1)–Ru(2)–C(5)	76.3(1)	C(2)–Ru(2)–C(5)	100.1(1)
C(3)–Ru(2)–C(5)	85.2(1)	C(4)–Ru(2)–C(5)	38.8(1)
Ru(2)–Ru(1)–C(1)	103.2(2)	Ru(2)–Ru(1)–C(2)	49.5(1)
C(1)–Ru(1)–C(2)	88.8(2)	Ru(2)–Ru(1)–C(4)	48.9(1)
C(1)–Ru(1)–C(4)	86.8(2)	C(2)–Ru(1)–C(4)	94.1(1)
Ru(1)–C(1)–O(1)	177.9(5)	Ru(2)–C(2)–Ru(1)	82.2(1)
Ru(2)–C(2)–C(3)	75.9(2)	Ru(1)–C(2)–C(3)	125.3(3)
Ru(2)–C(3)–C(2)	66.3(2)	Ru(2)–C(4)–Ru(1)	80.5(1)
Ru(2)–C(4)–C(5)	75.8(2)	Ru(1)–C(4)–C(5)	117.9(2)
Ru(2)–C(4)–C(41)	132.2(2)	Ru(1)–C(4)–C(41)	116.3(2)
C(5)–C(4)–C(41)	122.2(3)	Ru(2)–C(5)–C(4)	65.5(2)
Ru(2)–C(5)–C(51)	121.1(2)	C(4)–C(5)–C(51)	125.6(2)



(**10**) R = CO_2Me

Similar *O*-co-ordination is achieved by heating the isomers of (**7**) in xylene for a day. The terminal carbonyl is eliminated and its site occupied by the *O*-co-ordinated ethoxycarbonyl, in an entropy-driven chelation reaction. The isomers (**7a**) and (**7b**) give rise to corresponding isomers of the product (**11a**) and (**11b**), again with ν(C=O) of the CO_2Et group at 1 595 cm^{-1}, and distinguished by the ^1H n.m.r. shift of the μ-CH groups. Unlike (**7**), the isomers of (**11**) are separable by chromatography. No evidence was obtained for carbon–carbon bond formation upon thermolysis of (**7**), presumably because of steric inhibition by the ethoxycarbonyl substituents on the carbons in question.

Table 4. Structure analyses

Compounds	(2)	(3)·0.25C_6H_{14}	(8)
(*a*) Crystal data			
Formula	$C_{25}H_{20}ORu_2$	$C_{27}H_{24}ORu_2 \cdot C_{1.5}H_{3.5}$	$C_{27}H_{24}ORu_2$
M	538.6	588.2	566.7
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca* (no. 61)	*I*2 (no. 5)	$P\bar{1}$ (no. 2)
a/Å	24.585(6)	20.386(9)	8.876(2)
b/Å	9.279(2)	8.202(3)	9.381(2)
c/Å	17.621(4)	28.710(11)	15.896(2)
α/°	90	90	114.30(2)
β/°	90	90.51(4)	94.29(3)
γ/°	90	90	109.57(3)
U/Å^3	4 020(2)	4 800(3)	1 101.3(4)
T/K	295	295	295
Z	8	8	2
D_c/g cm^{-3}	1.78	1.62	1.71
F(000)	2 128	2 256	564
μ(Mo-K_α)/cm^{-1}	14.9	12.5	13.6
(*b*) Data collection and reduction			
Crystal dimensions/mm	*ca.* 0.3 (diameter)	0.11 × 0.11 × 0.5	0.35 × 0.2 × 0.15
Wavelength/Å	0.710 69	0.710 69	0.710 69
2θ range/°	4—50	3—50	3—60
Scan method	ω—2θ	Wyckoff ω	ω—2θ
Scan width (ω°)	$1.0 + \Delta_{\alpha_1\alpha_2}$	1.0	$1.0 + \Delta_{\alpha_1\alpha_2}$
Total data	2 761	4 907	7 156
Unique data	2 133	4 555	6 367
'Observed' data, N_o	1 673	3 916	4 350
n in observation criterion [$F^2 > n\sigma(F^2)$]	2	2	3
Crystal faces [distance from origin (mm)]		(010)[0.25], $(0\bar{1}0)$[0.25] (101)[0.055], $(\bar{1}0\bar{1})$[0.055] $(10\bar{1})$[0.053], $(\bar{1}01)$[0.053]	
No. azimuthal scan data used			398
Minimum, maximum transmission coefficients		0.676, 0.826	0.819, 0.956
(*c*) Refinement *			
Disordered atoms	C_5H_5 on Ru(2)	Hexane	None
Least-squares variables, N_v	208	554	367
R	0.039	0.033	0.028
R'	0.040	0.041	0.028
S	1.25	1.36	1.24
g	0.000 22	0.0002	0.000 07
Final difference map features (e Å^{-3})	+0.8, −0.5	+0.65, −0.33	+0.41, −0.46

* $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$; $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$; $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics.

Conclusion

The thermolysis of the 'di-μ-alkylidene' complexes (**3**) and (**8**) results in carbon–carbon bond formation not between the μ-carbons, but in each case between two carbons which are closer together. This indicates that least-motion effects are important in determining the course of carbon–carbon bond-formation processes at a dinuclear metal centre. The carbon–carbon bond formation on heating (**3**) involves the combination of co-ordinated alkene and methylene and points to the viability of such a process for carbon-chain growth on a metal surface in the Fischer–Tropsch synthesis. The involvement of surface vinyl groups is also given support by the first observation, in the thermolysis of (**8**), of vinyl linking at a dinuclear metal centre.

Experimental

Techniques and instrumentation were as described in Part 9 of this series.[25] Methyl-lithium (Ventron), $HBF_4 \cdot OEt_2$, $NaBH_4$, $BH_3 \cdot$thf, diphenylacetylene, and ethyl diazoacetate (Aldrich) were used as supplied. Diazomethane,[26] diazoethane,[27] and [Ru_2(CO)(μ-CO){μ-C(O)C_2Ph_2}(η-C_5H_5)$_2$][4] were prepared by the literature methods.

Preparation of [Ru_2(μ-CO)(μ-C_2Ph_2)(η-C_5H_5)$_2$] (**2**).—A thf solution (200 cm^3) of complex (**1**) (0.69 g, 1.2 mmol) in a silica tube was subjected to u.v. irradiation for 20 h while purging with a slow stream of nitrogen. The colour changed from orange to dark green. Solvent was removed at reduced pressure and the residue was chromatographed on an alumina column. Elution with dichloromethane–hexane (4:1) gave a green band which afforded 0.295 g (47%) of black crystalline complex (**2**) [m.p. 205—209 °C (Found: C, 55.1; H, 4.2%; *M* 539. $C_{25}H_{20}ORu_2$ requires C, 55.6; H, 3.7%; *M* 539); ν(CO) (in cyclohexane) at 1 771s cm^{-1}; ^{1}H n.m.r. (in $CDCl_3$) δ 4.89 (s, 10 H, 2 C_5H_5) and 7.40 (m, br, 10 H, 2 Ph); ^{13}C n.m.r. (in $CDCl_3$) δ 83.1 (2 C_5H_5), 127.2, 128.2, 128.4, 134.9 (2 Ph), and 144.8 (CPh) p.p.m.].

Reactions of [Ru$_2$(μ-CO)(μ-C$_2$Ph$_2$)(η-C$_5$H$_5$)$_2$] (**2**).—(*a*) *With carbon monoxide.* An acetone (100 cm^3) solution of complex (**2**) (0.15 g, 0.28 mmol) was treated with CO (100 atm) at 50 °C in an autoclave for 17 h, resulting in a colour change from dark brown to orange-green, and the deposition of orange crystals on the wall of the glass reaction vessel. I.r. spectroscopy identified these as [Ru$_2$(CO)(μ-CO){μ-C(O)C$_2$Ph$_2$}(η-C$_5$H$_5$)$_2$] (**1**). The remaining solution was evaporated to dryness and the residue was chromatographed on alumina. Elution with dichloromethane–hexane (4:1) removed a yellow band which yielded a few mg of [Ru$_2$(CO)$_4$(η-C$_5$H$_5$){η-C$_5$H$_4$–Ru(CO)$_2$(η-C$_4$H$_5$)}],[28] also identified by i.r. spectroscopy, then dichloromethane–acetone (19:1) developed an orange band due to (**1**). The combined yield of (**1**) from the solution and deposited on the walls was 0.11 g (66%).

(*b*) *With diazomethane.* An excess of diazomethane (0.32 g, 7.62 mmol) was distilled into a thf solution (100 cm^3) of complex (**2**) (0.2 g, 0.37 mmol) at 0 °C and the mixture was allowed to stir for 15 min, the colour changing from dark brown to orange. Removal of solvent at reduced pressure and chromatography of the residue on alumina gave one major orange band on elution with dichloromethane–hexane (3:7), which afforded 0.16 g (75%) of orange crystalline [Ru$_2$(CO)(μ-CH$_2$){μ-C(Ph)C(Ph)-CH$_2$}(η-C$_5$H$_5$)$_2$] (**3**) [m.p. 172—174 °C (Found: C, 57.5; H, 4.6%; *M* 567. $C_{27}H_{24}ORu_2$ requires C, 57.2; H, 4.2%; *M* 567); ν(CO) (in CH_2Cl_2) at 1 934s cm^{-1}; ^{1}H n.m.r. (in $CDCl_3$) δ −0.30 (d, *J* 2, 1 H, CPhCH_2), 3.12 (d, *J* 2 Hz, 1 H, CPhCH_2), 4.81 (s, 5 H, C_5H_5), 4.90 (s, 5 H, C_5H_5), 6.95 (br, 10 H, 2 Ph), 7.03 (s, 1 H, μ-CH$_2$), and 9.00 (s, 1 H, μ-CH$_2$); ^{13}C n.m.r. (in $CDCl_3$) δ 48.5 (CPhCH$_2$), 83.7, 90.7 (2 C_5H_5), 96.2 (CPh), 123.9, 125.7, 126.2, 126.8, 127.3, 129.3, 129.6, 131.5, 143.5, 155.9 (2 Ph and μ-CH$_2$), 179.0 (μ-CPh), and 206.4 (CO) p.p.m.]. Two minor yellow bands were also eluted but yielded only traces of unidentified material.

(*c*) *With diazoethane.* Complex (**2**) (0.2 g, 0.37 mmol) was treated with a 10-fold excess of diazoethane, exactly as outlined for diazomethane in (*b*). Chromatography gave three bands: (*i*) orange, eluted with dichloromethane–hexane (1:5), which yielded 33 mg (15%) of orange crystalline [Ru$_2$(CO)(μ-CHMe)-{μ-C(Ph)C(Ph)CHMe}(η-C$_5$H$_5$)$_2$] (**6**) [(Found: C, 58.1; H, 5.1%; *M* 595. $C_{29}H_{28}ORu_2$ requires C, 58.6; H, 4.8%; *M* 595); ν(CO) (in CH_2Cl_2) at 1 919s cm^{-1}; ^{1}H n.m.r. (in $CDCl_3$) (two isomers) δ 10.90 (q, *J* 7, μ-CHMe), 8.48 (q, *J* 7, μ-CHMe), 7.6—6.8 (m, Ph), 4.92, 4.81, 4.77, 4.75 (s, C_5H_5), 2.82 (d, *J* 7, μ-CHMe), 2.78 (d, *J* 7 Hz, μ-CHMe), 1.37 (s, CPhCHMe), 1.29 (s, CPhCHMe), 0.70 (s, CPhCHMe), and 0.63 (s, CPhCHMe); ^{13}C n.m.r. (in $CDCl_3$) (two isomers) δ 207.9, 207.3 (CO), 177.5, 176.1 (μ-CPh), 157.4, 148.3 (μ-CHMe), 156.0, 155.9, 140.8, 140.6, 131.8, 130.2, 129.5, 129.2, 126.9, 126.8, 126.3, 125.4, 123.5, 123.4 (Ph), 100.3, 98.0 (CPh), 92.4, 91.1, 85.6, 84.5 (C_5H_5), 64.0, 58.0 (CPhCHMe), 46.9, 34.5 (μ-CHMe), 22.7, 21.6 (CPhCHMe) p.p.m.]; (*ii*) red-orange, eluted with dichloromethane–hexane (1:3), which gave 44 mg (21%) of red-purple crystalline [Ru$_2$-(CO)(μ-CHCH$_2$){μ-C(Ph)CHPh}(η-C$_5$H$_5$)$_2$] (**8**) [(Found: C, 57.4; H, 4.3%; *M* 567. $C_{27}H_{24}ORu_2$ requires C, 57.2; H, 4.3%; *M* 567); ν(CO) (in CH_2Cl_2) at 1 949s cm^{-1}; ^{1}H n.m.r. (in $CDCl_3$) δ 10.34 (dd, *J* 6.8 and 9.8, 1 H, μ-CH), 7.2—6.7 (m, 10 H, 2 Ph), 4.99 (s, 5 H, C_5H_5), 4.65 (s, 5 H, C_5H_5), 4.31 (dd, *J* 1.5 and 6.8, 1 H, CHCH_2), 2.77 (s, 1 H, CPhCHPh), and 2.00 (dd, *J* 1.5 and 9.8 Hz, 1 H, CHCH_2); ^{13}C n.m.r. (in $CDCl_3$) δ 205.0 (CO), 180.1 (μ-CPh), 158.0 (μ-CH), 156.1, 149.4, 129.4, 127.4, 124.7, 122.8 (Ph), 91.2, 83.9 (C_5H_5), 65.1 (CHPh), and 49.6 (CH$_2$) p.p.m.]; (*iii*) yellow, eluted with dichloromethane–hexane (4:1), containing a small amount of starting material (**2**).

Table 5. Atomic co-ordinates (× 10^4) for complex (**2**)

Atom*	*x*	*y*	*z*
Ru(1)	1 368(1)	728(1)	802(1)
Ru(2)	449(1)	1 753(1)	1 100(1)
C(1)	694(1)	−302(10)	1 142(5)
C(3)	1 061(3)	2 727(9)	458(5)
C(4)	1 212(3)	2 844(9)	1 184(5)
O(1)	522(3)	−1 479(7)	1 252(4)
C(11)	2 027(3)	−836(9)	1 113(4)
C(12)	1 733	−1 356	475
C(13)	1 796	−347	−124
C(14)	2 129	796	142
C(15)	2 272	494	907
C(21)	−306(5)	2 624(23)	594(6)
C(22)	−145	3 515	1 210
C(23)	−157	2 669	1 881
C(24)	−324	1 255	1 680
C(25)	−416	1 227	885
C(21′)	−129(8)	3 389(19)	1 602(21)
C(22′)	−207	2 047	1 973
C(23′)	−382	1 030	1 423
C(24′)	−413	1 745	711
C(25′)	−256	3 203	822
C(31)	1 131(3)	3 493(10)	−266(4)
C(32)	869(4)	3 012(10)	−920(5)
C(33)	969(4)	3 642(11)	−1 615(5)
C(34)	1 328(4)	4 757(12)	−1 673(6)
C(35)	1 585(4)	5 264(12)	−1 026(6)
C(36)	1 484(4)	4 629(10)	−333(6)
C(41)	1 436(3)	3 885(9)	1 725(5)
C(42)	1 263(4)	5 304(10)	1 721(5)
C(43)	1 470(5)	6 302(12)	2 233(6)
C(44)	1 847(5)	5 878(13)	2 754(6)
C(45)	2 016(4)	4 476(15)	2 768(5)
C(46)	1 806(4)	3 484(10)	2 269(5)

* Atoms C(21)–C(25) have site occupancy 0.62(1); C(21′)–C(25′) have site occupancy 0.38(1).

(*d*) *With ethyl diazoacetate.* A thf solution (120 cm^3) of complex (**2**) (0.15 g, 0.28 mmol) and an excess of ethyl diazoacetate (0.2 g, 2.32 mmol) was refluxed for 1.5 h, during which time the colour changed from dark brown to orange. Chromatography on alumina, eluting with dichloromethane–hexane (4:1), gave two orange bands. The first yielded 33 mg (19%) of orange crystalline [Ru$_2$(μ-CO){μ-C(Ph)C(Ph)CH-(CO$_2$Et)}(η-C$_5$H$_5$)$_2$] (**9**) [m.p. 145—148 °C (Found: C, 55.7; H, 4.2%; *M* 625. $C_{29}H_{26}O_3Ru_2$ requires C, 55.8; H, 4.2%; *M* 625); ν(CO) (in CH_2Cl_2) at 1 746s and 1 595s cm^{-1}; ^{1}H n.m.r. (in $CDCl_3$) δ 6.89 (m, br, 10 H, 2 Ph), 4.54 (s, 5 H, C_5H_5), 4.38 (s, 5 H, C_5H_5), 3.82 (q, *J* 6, 2 H, CH$_2$), 3.54 (s, 1 H, CHCO$_2$Et), and 1.15 (t, *J* 7 Hz, 3 H, CH$_3$)] and the second 88 mg (44%) of orange crystalline [Ru$_2$(CO)(μ-CHCO$_2$Et){μ-C(Ph)C(Ph)CH-(CO$_2$Et)}(η-C$_5$H$_5$)$_2$] (**7**) [m.p. 192—193 °C (Found: C, 55.7; H, 4.5%; *M* 711. $C_{33}H_{32}O_5Ru_2$ requires C, 55.8; H, 4.5%; *M* 711); ν(CO) (in CH_2Cl_2) at 1 955s and 1 678 (br) cm^{-1}; ^{1}H n.m.r. (in $CDCl_3$), major isomer (**7b**), δ 7.33 (s, 1 H, μ-CH), 6.90 (m, br, 10 H, 2 Ph), 5.03 (s, 5 H, C_5H_5), 4.86 (s, 5 H, C_5H_5), 4.17 (q, *J* 7, 2 H, CH$_2$), 3.84 (m, 2 H, CH$_2$), 1.39 (t, *J* 7, 3 H, CH$_3$), and 0.96 (t, *J* 7 Hz, 3 H, CH$_3$); minor isomer (**7a**), δ 9.78 (s, 1 H, μ-CH), 5.16 (s, 5 H, C_5H_5), and 4.87 (s, 5 H, C_5H_5); ^{13}C n.m.r. (in $CDCl_3$), major isomer, δ 204.1 (CO), 184.4 (CO$_2$Et), 183.8 (CO$_2$Et), 174.9 (μ-CPh), 154.7, 140.1, 132.1, 131.2, 129.5, 129.0, 127.2, 126.9, 126.4, 126.1, 124.4 (Ph and μ-CH), 102.7 (CPh),

Table 6. Atomic co-ordinates (× 10^4) for complex (**3**)·$0.25C_6H_{14}$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	3 032(1)	5 000	1 547(1)	C(31)	2 997(4)	−161(11)	286(2)
Ru(2)	4 265(1)	5 167(1)	1 201(1)	O(32)	1 769(5)	−3 376(10)	187(3)
Ru(3)	2 055(1)	115(1)	25(1)	C(32)	1 918(5)	−2 028(12)	112(3)
Ru(4)	3 230(1)	209(1)	−408(1)	C(33)	3 141(4)	−2 392(11)	−438(2)
C(1)	3 375(4)	4 820(11)	871(3)	C(34)	2 724(4)	−1 664(9)	−791(2)
C(2)	2 852(4)	2 852(12)	1 570(3)	C(35)	2 298(3)	−373(9)	−665(2)
O(2)	2 699(4)	1 498(9)	1 614(3)	C(36)	1 906(4)	2 000(12)	−1 166(3)
C(3)	4 241(4)	2 567(11)	1 255(3)	C(37)	1 453(5)	2 656(16)	−1 483(4)
C(4)	4 361(4)	3 242(9)	1 708(3)	C(38)	931(5)	1 734(19)	−1 651(4)
C(5)	3 932(4)	4 530(9)	1 863(2)	C(39)	869(5)	167(22)	−1 497(3)
C(6)	3 932(4)	4 318(11)	2 728(3)	C(40)	1 321(4)	−513(13)	−1 200(3)
C(7)	3 994(5)	4 970(19)	3 175(3)	C(41)	1 848(4)	384(11)	−1 019(2)
C(8)	4 160(5)	6 574(14)	3 238(3)	C(42)	2 820(4)	−2 160(10)	−1 296(3)
C(9)	4 265(4)	7 521(12)	2 850(3)	C(43)	2 902(4)	−1 098(11)	−1 666(3)
C(10)	4 189(4)	6 888(10)	2 411(3)	C(44)	2 955(5)	−1 694(13)	−2 114(3)
C(11)	4 030(3)	5 268(11)	2 340(2)	C(45)	2 910(6)	−3 344(14)	−2 204(3)
C(12)	5 440(4)	3 813(11)	2 162(3)	C(46)	2 832(5)	−4 403(12)	−1 841(3)
C(13)	5 939(4)	3 228(14)	2 441(3)	C(47)	2 791(5)	−3 827(11)	−1 394(3)
C(14)	5 986(5)	1 564(14)	2 540(4)	C(48)	1 614(7)	1 442(19)	637(4)
C(15)	5 526(5)	541(13)	2 357(3)	C(49)	1 914(6)	2 587(16)	382(5)
C(16)	5 013(5)	1 108(11)	2 080(3)	C(50)	1 617(8)	2 710(15)	−45(4)
C(17)	4 960(4)	2 770(10)	1 982(3)	C(51)	1 117(7)	1 658(23)	−76(6)
C(18)	2 816(5)	7 635(13)	1 783(4)	C(52)	1 096(8)	784(19)	361(8)
C(19)	2 589(5)	6 646(14)	2 114(4)	C(53)	3 620(4)	2 229(11)	−863(3)
C(20)	2 122(6)	5 662(15)	1 934(5)	C(54)	3 616(5)	2 843(12)	−420(4)
C(21)	2 057(6)	6 097(19)	1 439(4)	C(55)	4 037(5)	1 840(13)	−136(3)
C(22)	2 508(6)	7 392(15)	1 382(4)	C(56)	4 306(4)	623(13)	−429(3)
C(23)	4 998(4)	7 212(12)	1 303(3)	C(57)	4 031(4)	887(13)	−889(4)
C(24)	4 503(5)	7 816(12)	1 019(3)	C(60)*	93(12)	6 008(33)	1 293(9)
C(25)	4 504(5)	6 841(13)	599(3)	C(61)	5(15)	6 178(41)	558(10)
C(26)	4 989(5)	5 656(14)	641(3)	C(62)	78(16)	5 201(61)	915(12)
C(27)	5 306(4)	5 895(12)	1 087(3)	C(63)*	0	5 671(76)	0

* Atomic site occupancy 0.5.

93.6, 87.3 (C_5H_5), 59.6, 59.3 (CH_2), 56.2 (*C*HCO_2Et), 14.9, and 14.2 (Me); minor isomer, δ 90.7, 86.7 (C_5H_5), 62.2 (*C*HCO_2Et), 60.4, 60.1 (CH_2), and 14.6 (Me) p.p.m.].

Thermolysis Reactions.—(*a*) [$Ru_2(CO)(\mu\text{-}CH_2)\{\mu\text{-}C(Ph)C(Ph)CH_2\}(\eta\text{-}C_5H_5)_2$] (**3**). Complex (**3**) (0.2 g, 0.35 mmol) was heated in xylene (100 cm^3) at reflux for 40 h, then the reaction mixture was chromatographed on alumina. Elution with dichloromethane–hexane (2:3) developed two yellow bands. The first contained a trace of starting material, identified by i.r. spectroscopy, and the second gave 62 mg (30%) of orange crystalline [$Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(Ph)CHMe\}(\eta\text{-}C_5H_5)_2$] (**5**), identified by mass, i.r., and ^1H n.m.r. spectroscopy.

(*b*) [$Ru_2(CO)(\mu\text{-}CHCH_2)\{\mu\text{-}C(Ph)CHPh\}(\eta\text{-}C_5H_5)_2$] (**8**). Complex (**8**) (85 mg, 0.16 mmol) was heated in xylene (100 cm^3) at reflux for 60 h, then the mixture was chromatographed on alumina. Elution with dichloromethane–hexane (3:2) gave two orange bands. The first gave 10 mg of unreacted starting material (**8**), and the second 21 mg (22%) of orange crystalline (**5**), identified by the i.r. and ^1H n.m.r. spectra as in (*a*).

(*c*) [$Ru_2(CO)(\mu\text{-}CHCO_2Et)\{\mu\text{-}C(Ph)C(Ph)CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2$] (**7**). A mixture of isomers (**7a**) and (**7b**) (0.25 g, 0.4 mmol) was heated in xylene (100 cm^3) at reflux for 25 h, resulting in a colour change from orange to red. Chromatography on alumina gave three bands. The first, brown, was eluted with dichloromethane–hexane (2:3) and yielded 71 mg (26%) of red crystalline [$Ru_2(\mu\text{-}CHCO_2Et)\{\mu\text{-}C(Ph)C(Ph)CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2$] (**11a**) [(Found: C, 55.5; H, 4.4%; *M* 683. $C_{32}H_{32}O_4Ru_2$ requires C, 56.3; H, 4.7%; *M* 683); ν(CO) (in CH_2Cl_2) at 1 674, 1 637, and 1 595 cm^{-1}; ^1H n.m.r. (in $CDCl_3$) δ 7.02 (br, 10 H, 2 Ph), 6.89 (s, 1 H, μ-CH), 4.70 (s, 5 H, C_5H_5), 4.38 (s, 5 H, C_5H_5), 4.06 (q, *J* 7, 2 H, CH_2), 3.77 (m, 2 H, CH_2), 3.51 (s, 1 H, CPhC*H*), 1.30 (t, *J* 3 H, Me), and 1.21 (t, *J* 7 Hz, 3 H, Me)]. The second, orange band was also eluted with dichloromethane–hexane (2:3) and afforded 125 mg (46%) of orange crystalline (**11b**) [(Found: C, 56.1; 4.8%; *M* 683. $C_{32}H_{32}O_4Ru_2$ requires C, 56.3; H, 4.7%; *M* 683); ν(CO) (in CH_2Cl_2) at 1 684 and 1 595 cm^{-1}; ^1H n.m.r. (in $CDCl_3$) δ 10.90 (s, 1 H, μ-CH), 7.01 (br, 10 H, 2 Ph), 4.65 (s, 5 H, C_5H_5), 4.34 (s, 5 H, C_5H_5), 4.27 (q, *J* 7, 2 H, CH_2), 3.97 (m, 2 H, CH_2), 3.44 (s, 1 H, CPhC*H*), 1.43 (t, *J* 7, 3 H, Me), and 1.22 (t, *J* 7 Hz, 3 H, Me)]. The third, orange band was eluted with dichloromethane–hexane (4:1) and was identified by i.r. spectroscopy as containing unreacted (**7**).

Preparation of [$Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(Ph)CHMe\}(\eta\text{-}C_5H_5)_2$] (**5**).—Methyl-lithium (2 cm^3 of a 1 mol dm^{-3} solution in diethyl ether) was added to a thf (100 cm^3) solution of complex (**1**) (0.53 g, 0.9 mmol). The mixture was stirred for 0.5 h, after which time i.r. spectroscopy revealed the disappearance of the ketonic carbonyl stretch of (**1**), then cooled to −78 °C (ethanol–solid CO_2). An excess of $HBF_4\cdot OEt_2$ (*ca.* 2 cm^3) was added followed, after stirring for 15 min, by $NaBH_4$ (0.5 g, 13.2 mmol). The mixture was allowed to warm to room temperature over 0.5 h and evaporated to dryness. Chromatography on alumina, eluting with dichloromethane–hexane (2:3) then gave an orange band from which 0.26 g (49%) of orange crystalline complex (**5**) was obtained [m.p. 162–163 °C (Found: C, 56.3; H, 4.1%; *M* 595. $C_{28}H_{24}O_2Ru_2$ requires C, 56.5; H, 4.1%; *M* 595); ν(CO) (in CH_2Cl_2) at 1 946s and 1 768m cm^{-1}; ^1H n.m.r. (in $CDCl_3$) δ 7.5—6.6 (br, 10 H, 2 Ph), 5.05 (s, 5 H, C_5H_5), 4.84 (s, 5 H, C_5H_5), 1.24 (d, *J* 6, 3 H, CH*Me*), and 0.71 (q, *J* 6 Hz, 1 H, C*H*Me); ^{13}C n.m.r. (in $CDCl_3$) δ 204.8 (μ-CO), 175.4 (μ-C), 155.4, 139.0, 131.8, 130.1, 128.6, 127.1, 126.8, 125.9, 123.7 (Ph), 90.8 (C_5H_5), 86.9 (*C*Ph), 86.5 (C_5H_5), 58.4 (*C*HMe, and 22.2

Table 7. Atomic co-ordinates (× 10^4) for complex (**8**)

Atom	*x*	*y*	*z*
Ru(2)	766(1)	1 638(1)	3 025(1)
Ru(1)	2 068(1)	−292(1)	3 458(1)
O(1)	5 495(4)	2 184(4)	4 644(2)
C(1)	4 164(4)	1 250(5)	4 183(2)
C(2)	1 174(4)	1 428(4)	4 272(2)
C(3)	1 883(5)	3 184(4)	4 576(2)
C(4)	2 519(3)	752(4)	2 492(2)
C(5)	3 328(4)	2 566(4)	2 882(2)
C(21)	−1 779(4)	−66(4)	2 058(3)
C(22)	−1 919(4)	1 045(5)	2 935(3)
C(23)	−1 117(5)	2 740(5)	3 085(3)
C(24)	−477(5)	2 677(5)	2 288(3)
C(25)	−886(4)	941(4)	1 661(2)
C(11)	2 524(4)	−2 588(4)	3 346(3)
C(12)	1 484(4)	−2 288(4)	3 975(2)
C(13)	−15(4)	−2 553(4)	3 442(2)
C(14)	97(4)	−3 006(4)	2 490(2)
C(15)	1 678(5)	−3 034(4)	2 437(2)
C(41)	2 518(4)	−438(4)	1 514(2)
C(42)	1 110(4)	−1 764(4)	820(2)
C(43)	1 215(5)	−2 883(4)	−57(2)
C(44)	2 733(5)	−2 704(5)	−255(2)
C(45)	4 144(4)	−1 413(5)	423(3)
C(46)	4 044(4)	−282(4)	1 294(2)
C(51)	3 810(4)	3 522(4)	2 321(2)
C(52)	3 025(4)	2 935(4)	1 371(2)
C(53)	3 512(4)	3 927(4)	905(2)
C(54)	4 795(4)	5 525(4)	1 373(3)
C(55)	5 609(4)	6 115(4)	2 305(3)
C(56)	5 124(4)	5 125(4)	2 771(2)

(CH*Me*) p.p.m.] after recrystallisation from dichloromethane–hexane.

Preparation of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Ph)C(Ph)CH_2\}(\eta\text{-}C_5H_5)_2]$ (**4**).—An excess of BH_3•thf (0.26 g, 3 mmol) was added to a thf (100 cm^3) solution of complex (**1**) (0.2 g, 0.34 mmol) and the mixture was stirred for 1 h. After evaporation to dryness, chromatography of the residue, eluting with dichloromethane–hexane (2:3), gave 125 mg (64%) of orange crystalline complex (**4**) [m.p. 213—215 °C (Found: C, 53.0; H, 4.1%; *M* 581. $C_{27}H_{22}O_2Ru_2$ requires C, 53.0; H, 3.7%; *M* 581); ν(CO) (in CH_2Cl_2) at 1 948s and 1 775m cm^{-1}; ^1H n.m.r. (in $CDCl_3$) δ 7.30 (m, 10 H, 2 Ph), 5.07 (s, 5 H, C_5H_5), 4.89 (s, 5 H, C_5H_5), 3.05 (d, *J* 3, 1 H, CH_2), and 0.10 (d, *J* 3 Hz, 1 H, CH_2); ^{13}C n.m.r. (in $CDCl_3$) δ 243.9 (μ-CO), 204.2 (CO), 175.4 (μ-*C*Ph), 155.6, 141.6, 131.7, 130.2, 128.5, 127.4, 127.0, 126.4, 126.2, 124.0 (Ph), 98.1 (*C*PhCH$_2$), 91.0, 85.8 (C_5H_5), and 43.0 (CH_2) p.p.m.].

Structure Determinations for Complexes (**2**), (**3**)•$0.25C_6H_{14}$, *and* (**8**).—Many of the details of the structure analyses carried out on these three complexes are listed in Table 4. *X*-Ray diffraction measurements were made using Nicolet four-circle *P*3*m* diffractometers on single crystals mounted in thin-walled glass capillaries at room temperature. Cell dimensions for each analysis were determined from the setting angle values of 15 centred reflections.

For each structure analysis, intensity data were collected for unique portions of reciprocal space and corrected for Lorentz, polarisation, crystal decay (negligible in each case), and long-term intensity fluctuations, on the basis of the intensities of three check reflections repeatedly measured during data collection. For complex (**2**) only reflections with intensity above a low threshold were recorded (>12 counts s^{-1} for $2\theta < 40°$, >8 counts s^{-1} for $40 < 2\theta < 50°$). Corrections for *X*-ray absorption effects were applied for (**3**)•$0.25C_6H_{14}$ on the basis of the indexed crystal faces and dimensions, and for (**8**) by an empirical correction derived from azimuthal scan data. The structures were solved by heavy-atom (Patterson and difference Fourier) methods, and refined by blocked-cascade least squares against *F*. For complex (**2**) one cyclopentadienyl ring [on Ru(2)] showed a two-site disorder. In complex (**3**)•$0.25C_6H_{14}$ there are two crystallographically distinct molecules of (**3**) present and the hexane solvent is disordered about a site of two-fold symmetry.

All non-hydrogen atoms were assigned anisotropic displacement parameters with the exception of the disordered carbons C(21′)–C(25′) of (**2**), and the disordered hexane carbons of (**3**)•$0.25C_6H_{14}$. All hydrogen atoms in complexes (**2**) and (**3**)•$0.25C_6H_{14}$ were constrained to ideal geometries (with C–H 0.96 Å). All hydrogen atoms were assigned isotropic displacement parameters [fixed for (**3**)•$0.25C_6H_{14}$ and (**2**), excepting the phenyl hydrogens which had a common refined isotropic U_{iso}]. Positional constraints were applied to the disordered cyclopentadienyl carbons of (**2**) (C–C 1.42 Å). The chirality of the crystal of (**3**)•$0.25C_6H_{14}$ used could not be determined unambiguously from the diffraction data.

Final difference syntheses showed no chemically significant features, the largest being close to the metal or solvent atoms. Refinements converged smoothly to residuals given in Table 4. Tables 5—7 report the positional parameters for these structure determinations. All calculations were made with programs of the SHELXTL[29] system as implemented on a Nicolet R3m/E structure determination system. Complex neutral-atom scattering factors were taken from ref. 30.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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