Organic Chemistry of Dinuclear Metal Centres. Part 7.[1] Ylides in the Synthesis of Organodiruthenium Complexes: *X*-Ray Crystal Structure of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ †

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Heating $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ with an ylide $Ph_3P{=}CHR$ in toluene at reflux rapidly yields μ-alkylidene complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR)(\eta\text{-}C_5H_5)_2]$ (R = H, 70%; Me, 35%; Et, 28%; or Ph, 57%). A similar reaction with $Ph_3P{=}CHCH{=}CH_2$ gives only a 13% yield of the analogous product $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCHCH_2)(\eta\text{-}C_5H_5)_2]$, the major product (33%) being the isomeric substituted allyl complex $[Ru(CO)\{\eta^3\text{-}C_3H_4[Ru(CO)_2(\eta\text{-}C_5H_5)]\text{-}1\}(\eta\text{-}C_5H_5)]$. Upon u.v. irradiation the latter undergoes rearrangement, with Ru–Ru bond formation, to give the former, believed to proceed *via* a 16-electron σ-allyl species. Further u.v. irradiation of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ releases a CO ligand and brings the alkylidene vinyl substituent into co-ordination, forming $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ in high yield. The two metal atoms in the complex $[Ru(CO)\{\eta^3\text{-}C_3H_4[Ru(CO)_2(\eta\text{-}C_5H_5)]\text{-}1]\}(\eta\text{-}C_5H_5)]$ are also brought into bonding with one another when the allyl is protonated, yielding the methylvinyl cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCHMe)(\eta\text{-}C_5H_5)_2]^+$. Treatment of the cation with $NaBH_4$ results in hydride addition to the β-carbon of the vinyl, producing $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHEt)(\eta\text{-}C_5H_5)_2]$ in good yield. The $\mu\text{-}CH_2$ complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ is not formed when $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ and CH_2N_2 are heated together, but thermally more robust diazoalkanes, $CH(CO_2Et)N_2$ and Ph_2CN_2, afford $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CPh_2)(\eta\text{-}C_5H_5)_2]$ respectively. The latter suffers from steric crowding and readily ejects a CO to give $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CPh_2)(\eta\text{-}C_5H_5)_2]$, in which a double bond of one phenyl ring is co-ordinated to ruthenium. Under CO pressure this transformation is reversed. The complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SO_2)(\eta\text{-}C_5H_5)_2]$ is formed in high yield when SO_2 is bubbled through a boiling toluene solution of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$. Crystals of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell for which $a = 6.771(2)$, $b = 9.315(2)$, $c = 11.864(5)$ Å, $\alpha = 103.12(3)$, $\beta = 100.61(3)$, and $\gamma = 103.40(2)°$. The structure has been solved by heavy-atom methods and refined to R 0.0365 (R' 0.0359) for 2 725 independent intensities. The two $Ru(CO)(\eta\text{-}C_5H_5)$ moieties are held together by a single Ru–Ru bond [2.707(1) Å] which is symmetrically bridged by CO and CH_2 groups. The interplanar angle between the two bridge systems is 161° with the convex side facing the terminal (*cis*) carbonyl groups. The molecule has idealised C_s (*m*) symmetry.

In earlier Parts of this Series we have described several synthetic routes to μ-alkylidene complexes of ruthenium. Thus treatment of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with an organolithium reagent leads to μ-CHR (R = Me or Ph) complexes,[1] while alkynes [2] can be employed to provide μ-CHR (R = Me or Et) or μ-C(Me)R (R = Me, Et, or Ph), and allenes [3] to yield μ-C(Me)R (R = Me or Et). Such complexes are of interest because they may provide an insight into the behaviour of alkylidene groups on a metal surface in catalysis. In this respect the most important alkylidene species is methylene,[4] which is strongly implicated in the carbon chain growth of the Fischer–Tropsch synthesis.[5] However, none of the syntheses mentioned above can yield a $\mu\text{-}CH_2$ diruthenium complex. We now describe the use of the ylide $Ph_3P{=}CH_2$ to prepare $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$, and related studies. Some aspects of this work have appeared in a preliminary communication.[6]

Results and Discussion

Synthesis and Characterisation of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ (1).—The dimetallacycle $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (2) [7] is readily obtained from, and much more reactive than, $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$. It serves as an excellent source of the $Ru_2(CO)_3(\eta\text{-}C_5H_5)_2$ unit in that a molecule of diphenylacetylene is rapidly displaced in boiling toluene by a wide variety of other reagents.[6] These are not conditions under which thermally unstable diazomethane could be expected to introduce CH_2 to the diruthenium centre, and the attempted synthesis of (1) by this method was indeed unsuccessful. However, the thermally more robust ylide $Ph_3P{=}CH_2$ provides (1) smoothly in *ca.* 70% yield when heated with (2). The phosphine complex $[Ru_2(CO)(\mu\text{-}CO)_2(PPh_3)(\eta\text{-}C_5H_5)_2]$ (3) is a co-product, resulting from reaction of liberated PPh_3 with (2), but its yield can be minimised by using an excess of ylide so that (2) is consumed rapidly in the primary reaction.

Yellow crystalline (1) is stable in air apparently indefinitely and also in common organic solvents, in which it is readily soluble. It exists as *cis*-(1a) and *trans*-(1b) isomers which interconvert in solution too rapidly to allow their separation by chromatography. A single crystal selected for an *X*-ray diffraction study (see below) proved to be of the *cis* isomer, and it appears that this is the preferred solid-state configuration; dissolving a mass of crystalline (1) in $[^2H_5]$nitrobenzene gave

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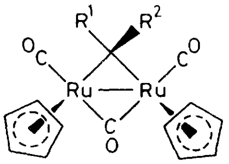
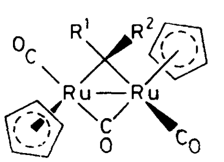
† *cis*-μ-Carbonyl-μ-methylene-bis[carbonyl(η^5-cyclopentadienyl)-ruthenium] (*Ru–Ru*).

Supplementary data available (No. SUP 56028, 8 pp.): H-atom co-ordinates, thermal parameters, full bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: atm = 101 325 N m^{-2}

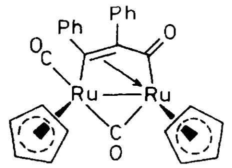


cis-(a)

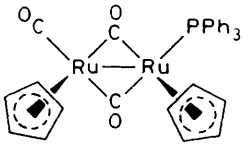


trans-(b)

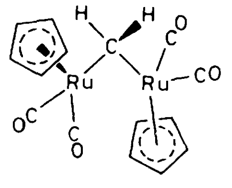
(1a,b) $R^1 = R^2 = H$
(5a,b) $R^1 = Me, R^2 = H$
(6a) $R^1 = Et, R^2 = H$
(7a) $R^1 = Ph, R^2 = H$
(8a,b) $R^1 = CHCH_2, R^2 = H$
(15a,b) $R^1 = CO_2Et, R^2 = H$
(16a) $R^1 = R^2 = Ph$



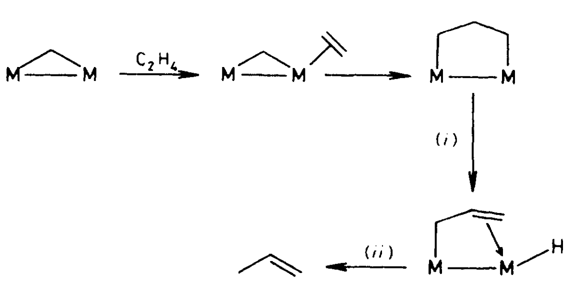
(2)



(3)



(4)



Scheme 1. (*i*) β-elimination, (*ii*) reductive elimination

a solution containing (1a) and (1b) in *ca.* 30 : 1 ratio (determined by n.m.r. spectroscopy), which after several hours equilibrated at a ratio of 4 : 1. In [$^2H_1$]chloroform equilibration occurs more rapidly and within minutes a steady ratio of 1.8 : 1 is attained. However, the *cis* $\rightleftharpoons$ *trans* isomerisation never becomes rapid on the n.m.r. time-scale and even at 150 °C in [$^2H_5$]nitrobenzene distinct sharp proton signals are observed for each of the isomers (present in *ca.* 3 : 1 ratio). This may be contrasted with the behaviour of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$, the *cis* and *trans* isomers of which do interconvert on the n.m.r. time-scale, yielding time-averaged spectra from which a free energy of activation for the isomerisation of *ca.* 85 kJ mol^{-1} was derived.[3] For this μ-CMe_2 complex it was established that *cis* $\rightleftharpoons$ *trans* isomerisation requires a migration of the alkylidene ligand between bridging and terminal sites, and it is likely that the same occurs for the CH_2 ligand in (1). It may therefore be concluded that CH_2 has a stronger preference for a bridging site than does CMe_2, and that the barrier to it adopting a terminal bonding mode exceeds 85 kJ mol^{-1}. On the same basis methylene appears to have a stronger preference for a bridging site when bound to an Fe_2 centre compared with an Ru_2 centre. Thus for $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$, the iron analogue of (1), interconversion of *cis* and *trans* isomers is slow enough to allow their separation by chromatography.[8,9]

We have previously synthesised a range of diruthenium complexes similar to (1), containing μ-CHR and μ-CR_2 ligands,[1] and their n.m.r. spectra display the characteristic [4] low-field shifts for the μ-carbon (δ 140—190 p.p.m.) and μ-C(H) proton (δ 10—11 p.p.m.) of a μ-alkylidene group. The corresponding signals for μ-CH_2 occur at considerably higher field, but still within the expected range; for both (1a) and (1b) the ^{13}C resonance is seen near δ 110 p.p.m., with the ^1H signals observed between δ 7.5 and 9.2 p.p.m. Both (1a) and (1b) have equivalent cyclopentadienyl groups, reflected in their n.m.r. spectra (Experimental section), but the isomers are readily distinguished by the appearance of two CH_2 proton resonances for (1a) and only one for the equivalent CH_2 protons of (1b). The i.r. spectrum (Experimental section) of (1) shows the carbonyl stretching band pattern expected [2] for a mixture of isomers with *cis* and *trans* geometries.

The iron analogue of (1) has been prepared by heating $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $Ph_3P{=}CH_2$ in dioxane,[8] but an attempt to obtain (1) directly from $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ by this method was unsuccessful. Subsequent to our initial report [6] of (1), however, another route to the complex has been devised. Treating dichloromethane with $[Ru(CO)_2(\eta\text{-}C_5H_5)]^-$ yields $[(\eta\text{-}C_5H_5)(CO)_2Ru(\mu\text{-}CH_2)Ru(CO)_2(\eta\text{-}C_5H_5)]$ (4), a compound in which only the methylene holds the two metal atoms together;[10] on u.v. irradiation a molecule of CO is lost from (4) and (1) is formed in high yield. We have discovered that this transformation is irreversible even when (1) is subjected to 150 atm of CO at 100 °C.

Upon thermolysis at 230 °C (1) is decomposed to release methane, but of more interest is the production of propene when (1) is heated in toluene at 210 °C under 0.5 atm of ethene. Similar behaviour has been observed for $[Fe_2(CO)_8(\mu\text{-}CH_2)]$ [11] and $[Co_2(CO)_2(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$,[12] and was interpreted in terms of Scheme 1. Strong support for this path for propene generation was recently obtained when the reaction of $[Os_2(CO)_8(\mu\text{-}CH_2)]$ with ethene led to the isolation of a diosmacyclopentane complex which does indeed decompose to evolve propene.[13] It has been suggested that alkene homologation of this type is involved in the Fischer–Tropsch synthesis.[14,15]

Molecular Structure of cis-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ (1a).—The crystal and molecular structure of (1a) was determined by *X*-ray diffraction methods. The molecular geometry and atomic numbering scheme are shown in Figure 1, and the results are summarised in Tables 1 and 2. It can be seen that the structure comprises two ruthenium atoms bridged symmetrically by a carbonyl and a methylene ligand, with each metal atom also carrying terminal carbonyl and η^5-cyclopentadienyl groups. On the basis of the 18-electron rule a formal metal–metal bond order of one is required and the Ru(1)–Ru(2) distance of 2.707(1) Å conforms with this; it may be compared with distances ranging from 2.69 to 2.72 Å in the structurally related complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}L)(\eta\text{-}C_5H_5)_2]$ (L = CCH_2[1] or CMe_2[3]) and $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2]^+$.[1] The shortening of the bond compared with that [2.735(2) Å] in $[Ru_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ [16] can be traced to a more effective donation of electron density from a metal–metal π* orbital into the low-energy p_π acceptor orbital

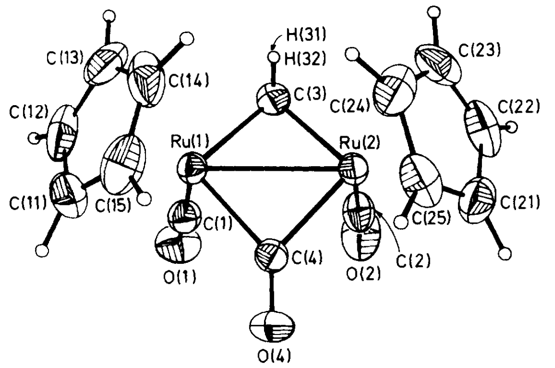


Figure 1. Molecular structure of [Ru$_2$(CO)$_2$(μ-CO)(μ-CH$_2$)(η-C$_5$H$_5$)$_2$] (1)

Table 1. Bond lengths (Å) and selected bond angles (°) for [Ru$_2$(CO)$_2$(μ-CO)(μ-CH$_2$)(η-C$_5$H$_5$)$_2$] (1)

Ru(1)–Ru(2)	2.707(1)		
Ru(1)–C(1)	1.852(6)	Ru(2)–C(2)	1.844(7)
Ru(1)–C(3)	2.077(6)	Ru(2)–C(3)	2.079(5)
Ru(1)–C(4)	2.019(4)	Ru(2)–C(4)	2.035(6)
Ru(1)–C(11)	2.265(8)	Ru(2)–C(21)	2.258(5)
Ru(1)–C(12)	2.219(8)	Ru(2)–C(22)	2.231(8)
Ru(1)–C(13)	2.264(8)	Ru(2)–C(23)	2.276(8)
Ru(1)–C(14)	2.273(9)	Ru(2)–C(24)	2.283(8)
Ru(1)–C(15)	2.276(7)	Ru(2)–C(25)	2.290(6)
C(11)–C(12)	1.380(8)	C(21)–C(22)	1.423(9)
C(12)–C(13)	1.387(12)	C(22)–C(23)	1.355(11)
C(13)–C(14)	1.383(10)	C(23)–C(24)	1.407(11)
C(14)–C(15)	1.389(11)	C(24)–C(25)	1.419(9)
C(15)–C(11)	1.370(11)	C(25)–C(21)	1.394(10)
C(1)–O(1)	1.156(8)	C(2)–O(2)	1 153(9)
C(4)–O(4)	1.179(6)		
C(3)–H(31)	1.02(6)	C(3)–H(32)	0.84(7)
Ru(1)–Ru(2)–C(3)	49.3(2)	Ru(2)–Ru(1)–C(3)	49.4(1)
Ru(1)–C(3)–Ru(2)	81.3(2)	Ru(1)–C(4)–Ru(2)	82.8(3)
Ru(1)–Ru(2)–C(4)	47.9(1)	Ru(2)–Ru(1)–C(4)	48.4(2)
Ru(1)–C(4)–O(4)	139.2(5)	Ru(2)–C(4)–O(4)	136.9(4)
Ru(1)–C(1)–O(1)	177.6(6)	Ru(2)–C(2)–O(2)	178.6(4)
C(1)–Ru(1)–C(3)	89.1(3)	C(2)–Ru(2)–C(3)	85.0(2)
C(1)–Ru(1)–C(4)	87.6(2)	C(2)–Ru(2)–C(4)	88.9(3)
C(1)–Ru(1)–Ru(2)	98.7(2)	C(2)–Ru(2)–Ru(1)	96.5(2)
C(11)–C(12)–C(13)	109.6(6)	C(21)–C(22)–C(23)	108.8(6)
C(12)–C(13)–C(14)	106.3(6)	C(22)–C(23)–C(24)	108.5(6)
C(13)–C(14)–C(15)	108.5(7)	C(23)–C(24)–C(25)	108.0(7)
C(14)–C(15)–C(11)	108.5(6)	C(24)–C(25)–C(21)	107.0(6)
C(15)–C(11)–C(12)	107.1(7)	C(25)–C(21)–C(22)	107.8(6)
H(31)–C(3)–H(32)	126(5)		

Table 2. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for [Ru$_2$(CO)$_2$(μ-CO)(μ-CH$_2$)(η-C$_5$H$_5$)$_2$] (1)

Atom	*x*	*y*	*z*
Ru(1)	0.176 48(6)	0.166 32(4)	0.265 60(4)
Ru(2)	0.234 36(6)	0.426 84(4)	0.195 48(3)
O(1)	0.408 0(8)	−0.001 2(6)	0.113 6(5)
O(2)	0.452 4(9)	0.327 1(6)	0.006 5(5)
O(4)	0.594 7(6)	0.405 2(5)	0.375 0(4)
C(1)	0.318 0(9)	0.064 8(6)	0.170 1(6)
C(2)	0.370 9(10)	0.366 9(7)	0.080 0(5)
C(3)	0.017 8(9)	0.211 8(6)	0.116 5(5)
C(4)	0.425 1(8)	0.354 9(6)	0.310 3(5)
C(11)	0.197 7(12)	0.076 6(9)	0.428 3(7)
C(12)	0.040 5(13)	−0.026 8(7)	0.334 3(7)
C(13)	−0.118 9(11)	0.039 1(9)	0.305 3(7)
C(14)	−0.054 4(13)	0.187 1(9)	0.381 0(8)
C(15)	0.139 9(12)	0.209 3(8)	0.456 3(6)
C(21)	0.342 2(11)	0.686 5(7)	0.257 5(6)
C(22)	0.172 2(13)	0.636 5(8)	0.153 9(6)
C(23)	−0.002 9(11)	0.563 6(7)	0.181 1(7)
C(24)	0.050 8(11)	0.559 8(7)	0.300 4(7)
C(25)	0.267 2(12)	0.638 1(7)	0.348 5(6)
H(31)	0.028(9)	0.147(6)	0.037(5)
H(32)	−0.093(9)	0.225(6)	0.134(5)

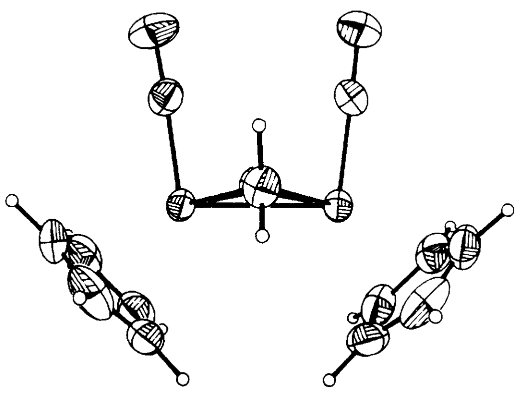
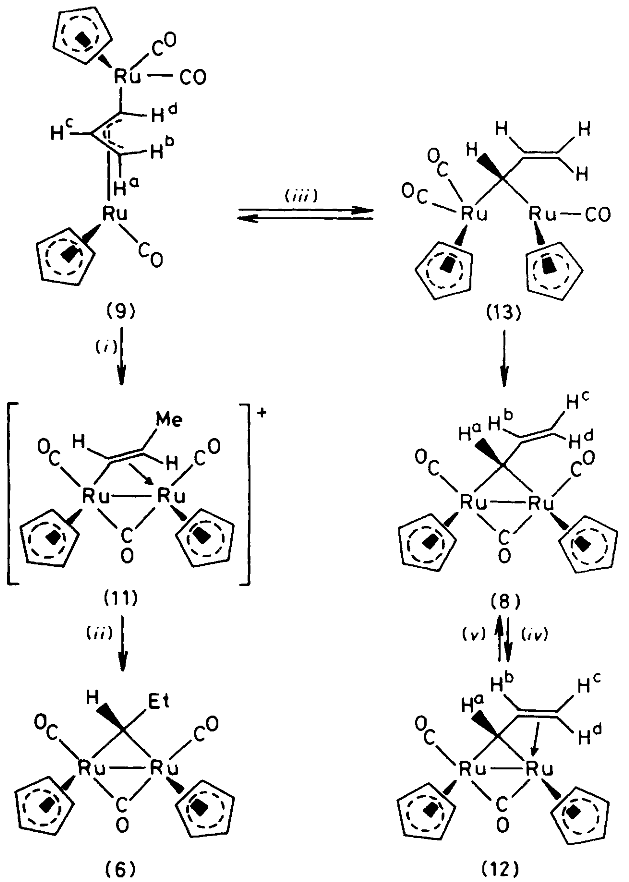


Figure 2. View of the molecular structure of (1) seen in a direction perpendicular to the plane defined by the terminal carbonyl ligands

of methylene than into a π^* orbital of CO, as discussed previously.[1,3]

The terminal carbonyls are arranged *cis* to one another, as are, consequently, the cyclopentadienyl groups. For such a *cis* isomer the central Ru$_2$(μ-C)$_2$ unit is expected to be non-planar, a feature which has been rationalised by molecular-orbital considerations,[17] and this is observed. The dihedral angle between the Ru(1),Ru(2),C(3) and Ru(1),Ru(2),C(4) planes is 19°, with the convex side of the bridge facing the terminal CO ligands, a distortion of similar magnitude to those in [Ru$_2$(CO)$_2$(μ-CO)(μ-L)(η-C$_5$H$_5$)$_2$] [L = CCH$_2$ (22°) [1] or CMe$_2$ (26°) [3]] and [Ru$_2$(CO)$_2$(μ-CO)(μ-CMe)(η-C$_5$H$_5$)$_2$]$^+$ (15°, ref. 1). The distortion is clearly seen from the view of the molecule given in Figure 2, from which also the approximate (non-crystallographic) mirror symmetry of the molecule is apparent.

The bridging methylene lies approximately normal to the Ru(1),Ru(2),C(3) plane (dihedral angle 88.4°) and is characterised by a H(31)–C(3)–H(32) angle of 126(5)° and a Ru(1)–C(3)–Ru(2) angle of 81.3(2)°. Both of these are typical of the μ-CH$_2$ ligand, which in bonding to manganese, iron, cobalt, ruthenium, rhodium, and osmium displays corresponding angles of 105 ± 13 and 81 ± 7° respectively.[4] In contrast, complex (4), in which methylene spans two ruthenium atoms not bonded to one another (Ru $\cdots$ Ru, 3.8 Å), the Ru–C–Ru angle is 123°, a size attributed to steric crowding.[10] The Ru–CH$_2$ distances in (1a) (mean 2.078 Å) are shorter than those in (4) (2.18 Å), reflecting the π-acceptor character of methylene in the former. They are also shorter than the corresponding Ru–C distances [2.113(4) Å] in [Ru$_2$(CO)$_2$(μ-CO)(μ-CMe$_2$)(η-C$_5$H$_5$)$_2$],[3] but longer than those in analogous complexes of powerfully π-accepting μ-C=CH$_2$ [2.030(7) Å] [1] and μ-CMe$^+$ [1.937(4) Å] [1] ligands.

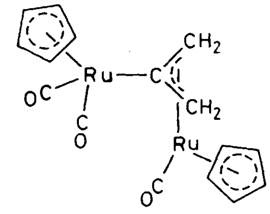


Scheme 2. Reagents: (*i*) $HBF_4\cdot OEt_2$, (*ii*) $NaBH_4$, (*iii*) u.v., (*iv*) u.v., $-CO$, (*v*) CO (200 atm, 100 °C)

The terminal carbonyl ligands of (1a) are almost linear [Ru(1)–C(1)–O(1) 177.6(6) and Ru(2)–C(2)–O(2) 178.6(4)°], and the carbon atoms of the η^5-cyclopentadienyl ligands are co-planar to within 0.01 Å. There are no abnormally short inter- or intra-molecular contacts.

Other Syntheses with Ylides.—Treatment of (2) with the ylides $Ph_3P{=}CHR$ (R = Me, Et, or Ph) under the same conditions employed in the synthesis of (1) gave the known μ-alkylidene complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR)(\eta\text{-}C_5H_5)_2]$ [R = Me (5),[2] Et (6),[2] or Ph (7)[1]] in yields of 30—60%. The previously reported preparations of (5) and (7) are more convenient, but (6), isolated as the *cis* isomer (6a), is better obtained by the ylide route described here. The reactions of $Ph_3P{=}CHCl$ and $Ph_3P{=}CMe_2$ did not afford the corresponding μ-alkylidene complexes; from the former $[RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ [18] was isolated and from the latter only a small yield of (3). Similarly low reactivity of sterically crowded $Ph_3P{=}CMe_2$ has been observed in other reactions with organometallic complexes.[19]

An interesting area of organodiruthenium chemistry, summarised in Scheme 2, is entered through the reaction of (2) with the ylide $Ph_3P{=}CHCHCH_2$. The expected μ-alkylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ (8) was formed in only 13% yield, the major product (33%) being the substituted allyl complex $[Ru(CO)\{\eta^3\text{-}C_3H_4[Ru(CO)_2(\eta\text{-}C_5H_5)]\text{-}1\}(\eta\text{-}C_5H_5)]$ (9). Compared with analogous μ-CHR complexes (R = H, Me, Ph, *etc.*) yellow crystalline (8) is quite insoluble. It exists as *cis* and *trans* isomers which can be partially separated by chromatography, but within minutes in solution the isomers reach an equilibrium *cis* : *trans* ratio of *ca.* 1.5 : 1.



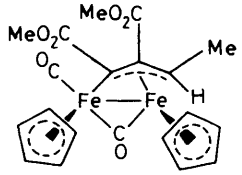
(10)

The characterisation of (8) was straightforward since its spectroscopic properties (Experimental section) are typical of the now wide range of diruthenium μ-alkylidene complexes known.[1-3] The identification of (9) was also facilitated by a close precedent in that the isomeric complex (10), containing a 2-$Ru(CO)_2(\eta\text{-}C_5H_5)$ rather than a 1-$Ru(CO)_2(\eta\text{-}C_5H_5)$ substituent on the η^3-allyl, is formed in the reaction of (2) with allene.[3] The i.r. spectra of (9) and (10) are nearly identical, but whereas (10) displays only two allyl proton resonances in the n.m.r. spectrum, (9) betrays the presence of a σ-bound $Ru(CO)_2(\eta\text{-}C_5H_5)$ substituent in the 1-position by the appearance of four allyl proton signals (see Experimental section). The relatively large H^cH^d coupling of 11 Hz is consistent with the ruthenium substituent being oriented *syn* to H^c rather than *anti;* this is expected on steric grounds.

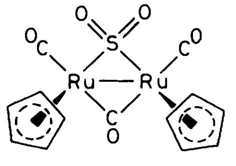
Both (9) and (10), in being formed from (2), are a consequence of Ru–Ru bond cleavage. The Ru–Ru bond was, however, regenerated when (10) was protonated.[3] Addition of $HBF_4\cdot OEt_2$ to the complex effected protonation at a terminal methylene of the allyl to create a methyl group, thereby denuding a ruthenium of an electron, and inducing recovery of an 18-electron configuration through metal–metal bond formation. The product was the μ-vinyl cation $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me){=}CH_2\}(\eta\text{-}C_5H_5)_2]^+$, which upon treatment with $NaBH_4$ suffered hydride addition to the β-vinyl carbon, giving $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$. A similar transformation (see Scheme 2) is effected when $HBF_4\cdot OEt_2$ and $NaBH_4$ are added in succession to (9), the product now being the μ-C(H)Et complex (6) in 63% yield. The known [2] intermediate cation $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CH{=}C(H)Me\}(\eta\text{-}C_5H_5)_2]^+$ (11) was detected by i.r. spectroscopy.

Ruthenium–ruthenium bond formation is also induced (see Scheme 2) when (9) is subjected to u.v. irradiation, resulting in the generation of the new complex $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ (12) in *ca.* 70% yield after 3.5 h. I.r. monitoring of this reaction reveals that it proceeds *via* complex (8), which after 0.75 h is the major species present. As shown in Scheme 2, we envisage the rearrangement of (9) to (8) to occur through a photochemically-induced transformation of the η^3-allyl in (9) to a σ-allyl, forming (13). One ruthenium of this intermediate has a 16-electron configuration, and an 18-electron state can be regained either through reco-ordination of the double bond to regenerate (9) or through metal–metal bond formation, yielding the observed species (8) and subsequently (12). The ejection of CO from (8), allowing co-ordination of the vinyl substituent of the μ-alkylidene, is a reversible process; under 200 atm of CO at 100 °C (12) is converted in good yield to (8).

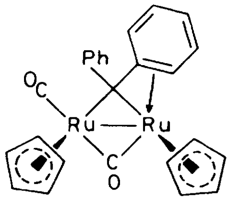
Complex (12) shows in its i.r. spectrum terminal and bridging carbonyl absorptions, and in its n.m.r. spectra signals corresponding to two inequivalent $\eta\text{-}C_5H_5$ groups. The upfield shifts in the resonances of the vinyl group of (8) on becoming co-ordinated in (12) are as expected, but it is interesting to note that one of the methylenic protons of (12) occurs



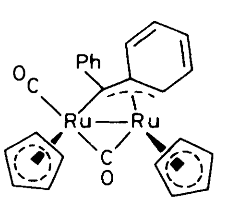
(14)



(18)



(17a)



(17b)

at the surprisingly high-field shift of δ −0.38. From the coupling pattern within the vinyl substituent it is clear that this signal is due to the methylenic proton which lies *trans* to the proton on the central carbon of the C_3 ligand. Complexes analogous to (12) are obtained when diruthenium μ-alkylidene complexes react with alkynes,[20,21] and it has been noted [21] that the site occupied by the hydrogen under discussion here is a very crowded one, towards the interior of the molecule and over the diruthenium centre. This may explain the very high-field shift. Both the ^{1}H (δ 10.3) and ^{13}C (δ 152.8) resonances for the μ-CH group of the C_3 ligand are typical of a μ-alkylidene, suggesting the representation (12). Delocalisation over the C_3 framework is likely, however, as found in an *X*-ray diffraction study [20] of a related di-iron complex $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(CO_2Me)C(CO_2Me)CH(Me)\}(\eta\text{-}C_5H_5)_2]$, consequently depicted in the 'μ-allyl' form (14).

Complex (12) can be prepared from (1) and ethyne under u.v. irradiation, but this and reactions of (1) with other alkynes are to be described in a future Part of this Series. An alternative and unusual synthesis of (12) was reported during the course of this work, involving the simple passing of the η^3-allyl complex $[Ru(CO)(\eta^3\text{-}C_3H_5)(\eta\text{-}C_5H_5)]$ through a deactivated silica-gel column.[22]

Syntheses with Diazoalkanes.—Although the conditions necessary (boiling toluene) for the displacement of diphenylacetylene from complex (2) preclude the synthesis of (1) from diazomethane by this route, other more thermally stable diazoalkanes provide μ-alkylidene complexes smoothly. Thus, within 15 min in boiling toluene ethyl diazoacetate generates a 90% yield of yellow crystalline $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CH(CO_2Et)\}(\eta\text{-}C_5H_5)_2]$ (15) on reaction with (2). Both *cis*-(15a) and *trans*-(15b) isomers of the complex are evident in solution from the ^{1}H and ^{13}C n.m.r. spectra (Experimental section), the *cis* : *trans* ratio being *ca.* 2 : 1 in $CDCl_3$ at room temperature. Interconversion is sufficiently rapid that the isomers could not be separated by chromatography.

The reaction of (2) with diphenyldiazomethane is more interesting, yielding not only the expected $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CPh_2)(\eta\text{-}C_5H_5)_2]$ (16) but also $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CPh_2)(\eta\text{-}C_5H_5)_2]$ (17). On the basis of i.r. and n.m.r. spectra (Experimental section) only the *cis* isomer of (16) appears to be present. This could be in order to minimise steric interactions between the phenyl and $\eta\text{-}C_5H_5$ groups, since in a *cis* isomer one phenyl avoids such contacts entirely. Evidence of crowding in (16) also comes from its decarbonylation to (17), which in boiling toluene is quantitative after 6.5 h. The crowding is clearly severe enough that lessening it by ejection of a CO group takes precedence over the retention of the resonance energy of a phenyl ring. One of the phenyl protons of (17) appears in the n.m.r. spectrum at δ 2.46, and is clearly the one attached to the co-ordinated 'olefinic' bond of the phenyl ring. As with (12), complex (17) can be represented either in the 'vinylalkylidene' (17a) or 'allyl' (17b) form. Although the latter is more likely, the former is useful in understanding the chemistry of (17). Thus, under 100 atm of CO at 100 °C the removal of the phenyl group from co-ordination, in regenerating (16) smoothly, is readily seen as a simple substitution reaction. The interconversion (16) $\rightleftharpoons$ (17) is, in fact, closely related to the interconversion (8) $\rightleftharpoons$ (12). The form of CPh_2 bridging in (17) has been observed recently in other dimetal systems.[23,24]

The bridging sulphur dioxide complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SO_2)(\eta\text{-}C_5H_5)_2]$ (18) is formed in high yield when SO_2 gas is bubbled through a boiling toluene solution of (2). This yellow, crystalline, air-stable compound has i.r. and ^{1}H n.m.r. (+30 to −70 °C) spectra in accord with its existence exclusively as the *cis* isomer indicated.

Experimental

Techniques and instrumentation were as described in Part 1 [7] of this Series. The ylides $Ph_3P{=}CHR$ (R = H, Me, Et, Ph, or $CH{=}CH_2$),[25] Ph_2CN_2,[26] and $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (2) [7] were prepared by literature methods. Ethyl diazoacetate (Aldrich) and SO_2 (B.D.H.) were used as supplied.

Syntheses with Ylides.—The same procedure was followed in each case, exemplified by complex (1).

$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ (1). A toluene (20 cm^3) solution of $Ph_3P{=}CH_2$ (3 mmol) was added to a toluene (100 cm^3) solution of (2) (0.5 g, 0.84 mmol) and the mixture heated at reflux for 0.5 h, during which time a colour change from orange-red to yellow occurred. The solvent was removed at reduced pressure and the residue chromatographed on an alumina column. Elution with dichloromethane–hexane (2 : 3) developed a yellow and an orange band, the former yielding 0.25 g (70%) of a yellow crystalline mixture of *cis*- and *trans*-(1) [m.p. 195—197 °C; ν(CO) (in CH_2Cl_2) at 1 985s, 1 941m, and 1 781m cm^{-1}. ^{1}H N.m.r. (in $CDCl_3$): *cis*-(1a), δ 5.24 (s, 10 H), 7.52 (s, 1 H), and 9.16 (s, 1 H); *trans*-(1b), δ 5.32 (s, 10 H) and 8.44 p.p.m. (s, 2 H). ^{13}C N.m.r. (in $CDCl_3$): *cis*-(1a), δ 88.7 (2 C_5H_5) and 110.3 (CH_2); *trans*-(1b), δ 90.6 (2 C_5H_5) and 111.1 p.p.m. (CH_2). Found: C, 39.1; H, 2.9%; *M*, 431. $C_{14}H_{12}O_3Ru_2$ requires C, 39.1; H, 2.8%; *M*, 431]. The orange band gave 55 mg (10%) of $[Ru_2(CO)(\mu\text{-}CO)_2(PPh_3)(\eta\text{-}C_5H_5)_2]$ (3) as orange crystals [m.p. 202—204 °C (decomp.); ν(CO) (in CH_2Cl_2) at 1 845m and 1 725s cm^{-1}. ^{1}H N.m.r. (in $CDCl_3$): δ 4.73 (s, 5 H), 4.86 (s, 5 H), and 7.40 p.p.m. (m, 15 H). Found: C, 54.7; H, 3.6%; *M*, 679. $C_{31}H_{25}O_3PRu_2$ requires C, 54.9; H, 3.7%; *M*, 679].

In an identical manner the previously uncharacterised complex, $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHEt)(\eta\text{-}C_5H_5)_2]$ (6) was obtained in 28% yield from $Ph_3P{=}CHEt$ as a *cis* isomer [ν(CO) (in

CH_2Cl_2) at 1 975s, 1 937w, and 1 779w cm^{-1}. ^{1}H N.m.r. (in $CDCl_3$): δ 1.24 (t, *J* 7, CH_3), 3.03 (quin, *J* 7, CH_2), 5.02 (s, 10 H, 2 C_5H_5), and 10.64 p.p.m. (t, *J* 7 Hz, μ-CH). ^{13}C N.m.r. (in $CDCl_3$): δ 20.6 (CH_3), 49.0 (CH_2), 89.2 (2 C_5H_5), and 152.4 p.p.m. (μ-C). Found: C, 41.8; H, 3.5%; *M*, 459. $C_{16}H_{16}O_3Ru_2$ requires C, 41.9; H, 3.5%; *M*, 459].

Similar syntheses with Ph_3P=CHMe and Ph_3P=CHPh gave the known complexes (5) (35%) [2] and (7) (57%),[1] respectively. No μ-CMe_2 complex was obtained from Ph_3P=CMe_2, and from Ph_3P=CHCl only [RuCl(CO)(PPh_3)(η-C_5H_5)] (21%) [18] was isolated.

Reaction of (2) *with* Ph_3P=$CHCHCH_2$.—A solution of Ph_3P=$CHCHCH_2$ (5 mmol) in toluene (20 cm^3) was added to a toluene (100 cm^3) solution of (2) (0.59 g, 1 mmol), which upon heating at reflux for 0.5 h became yellow. Chromatography as above gave three bands. The first, eluted with dichloromethane–hexane (1 : 4), gave 0.15 g (33%) of pale yellow powder-like [Ru(CO){η^3-C_3H_4[Ru(CO)$_2$(η-C_5H_5)]-1}(η-C_5H_5)] (9) [m.p. 130—132 °C; ν(CO) (in CH_2Cl_2) at 2 017s, 1 957s, and 1 917s cm^{-1}. ^{1}H N.m.r. (in $CDCl_3$): δ 0.94 (dd, *J* 1 and 9, H^b), 2.62 (d, *J* 11, H^d), 2.68 (dd, *J* 1 and 6, H^a), 4.22 (ddd, *J* 6, 9, and 11 Hz, H^c), 4.98 (s, 5 H, C_5H_5), and 5.33 p.p.m. (s, 5 H, C_5H_5). ^{13}C N.m.r. (in $CDCl_3$): δ 27.7 (CHRu), 43.5 (CH_2), 78.7 (*C*HCH_2), 82.6 (C_5H_5), and 90.8 p.p.m. (C_5H_5). Found: C, 42.0; H, 3.1%; *M*, 457. $C_{16}H_{14}O_3Ru_2$ requires C, 42.1; H, 3.1%; *M*, 457].

The second band was eluted with dichloromethane–hexane (1 : 2) and contained 60 mg (13%) of a yellow crystalline mixture of *cis*- and *trans*-[Ru$_2$(CO)$_2$(μ-CO)(μ-$CHCHCH_2$)(η-C_5H_5)$_2$] (8) [ν(CO) (in CH_2Cl_2) at 1 979s, 1 940w, and 1 784w cm^{-1}. ^{1}H N.m.r.: *cis*-(8a), δ 4.58 (dd, *J* 2 and 9, H^c), 5.04 (dd, *J* 2 and 16, H^d), 5.21 (s, 10 H), 7.12 (ddd, *J* 2, 11, and 16, H^b), and 10.64 (d, *J* 11, H^a); *trans*-(8b), δ 4.59 (dd, *J* 2 and 9, H^c), 5.05 (dd, *J* 2 and 16, H^d), 5.22 (s, 5 H, C_5H_5), 5.25 (s, 5 H, C_5H_5), 7.08 (ddd, *J* 9, 12, and 16, H^b), and 9.79 p.p.m. (d, *J* 12 Hz, H^a). Found: C, 42.6; H, 3.3%; *M*, 457. $C_{16}H_{14}O_3Ru_2$ requires C, 42.1; H, 3.1%; *M*, 457].

The third, orange band was eluted with dichloromethane–hexane (2 : 3) and provided 36 mg (5%) of [Ru$_2$(CO)(μ-CO)$_2$(PPh_3)(η-C_5H_5)$_2$] (3), identified by i.r.

Protonation of [Ru(CO){η^3-C_3H_4[Ru(CO)$_2$(η-C_5H_5)]-1}(η-C_5H_5)] (9).—A diethyl ether (50 cm^3) solution of (9) (55 mg, 0.12 mmol) was treated with an excess of HBF_4·OEt_2, producing an immediate yellow precipitate of the μ-vinyl complex [Ru$_2$(CO)$_2$(μ-CO){μ-CH=C(H)Me}(η-C_5H_5)$_2$][BF_4] (11),[2] identified by i.r. The precipitate was washed with ether and then dissolved in acetone (50 cm^3); to this solution *ca.* 50 mg of $NaBH_4$ was added and the whole stirred for 10 min. Chromatography on alumina, eluting with dichloromethane–hexane (1 : 1), separated 35 mg (63%) of [Ru$_2$(CO)$_2$(μ-CO)(μ-CHEt)(η-C_5H_5)$_2$] (6).

U.v. Irradiation of [Ru(CO){η^3-C_3H_4[Ru(CO)$_2$(η-C_5H_5)]-1}(η-C_5H_5)] (9).—A toluene (80 cm^3) solution of (9) (50 mg, 0.11 mmol) was subjected to u.v. irradiation and the reaction monitored by i.r. spectroscopy. After 0.75 h only a small amount of (9) remained and both [Ru$_2$(CO)$_2$(μ-CO)(μ-$CHCHCH_2$)(η-C_5H_5)$_2$] (8) (mainly) and [Ru$_2$(CO)(μ-CO)(μ-$CHCHCH_2$)(η-C_5H_5)$_2$] (12) were present. After 1.5 h no starting material was left and after 3.5 h almost total conversion to (12) was achieved. Chromatography, eluting with dichloromethane–hexane (2 : 3), developed a yellow band from which 32 mg (68%) of (12) was obtained as a yellow powder [m.p. 195—197 °C; ν(CO) (in CH_2Cl_2) at 1 942s and 1 777m cm^{-1}. ^{1}H N.m.r. (in $CDCl_3$): δ −0.38 (dd, *J* 3 and 9, H^d), 2.63 (dd, *J* 3 and 7, H^c), 4.70 (ddd, *J* 6, 7, and 9, H^b), 4.90 (s, 5 H), and 5.22 (s, 5 H), and 10.34 p.p.m. (d, *J* 6 Hz, H^a). ^{13}C N.m.r. (in $CDCl_3$): δ 39.6 (CH_2), 79.1 (*C*HCH_2), 83.3 (C_5H_5), 88.2 (C_5H_5), and 152.8 p.p.m. (μ-CH). Found: C, 42.0; H, 3.3%; *M*, 429. $C_{15}H_{14}O_2Ru_2$ requires C, 42.1; H, 3.3%; *M*, 429].

Treatment of [Ru$_2$(CO)(μ-CO)(μ-$CHCHCH_2$)(η-C_5H_5)$_2$] (12) *with* CO.—A toluene (30 cm^3) solution of (12) (60 mg, 0.14 mmol) was heated at 100 °C under 200 atm of CO for 17 h. Chromatography gave three yellow bands. The first was eluted with dichloromethane–hexane (1 : 2) and gave 10 mg (16%) of i.r.-identified [Ru$_2$(CO)$_4$(η-C_5H_5)$_2$]. The second was eluted similarly and contained 25 mg (39%) of *cis*- and *trans*-[Ru$_2$(CO)$_2$(μ-CO)(μ-$CHCHCH_2$)(η-C_5H_5)$_2$] (8). The third was eluted with dichloromethane–hexane (1 : 1) and gave *ca.* 10 mg of starting material.

Preparation of [Ru$_2$(CO)$_2$(μ-CO){μ-CH(CO_2Et)}(η-C_5H_5)$_2$] (15).—A mixture of ethyl diazoacetate (0.1 cm^3, 1 mmol) and (2) (0.5 g, 0.85 mmol) was heated in toluene (150 cm^3) at reflux for 15 min, the colour changing from dark red to orange-yellow. After evaporation of the solvent the residue was chromatographed to give, on elution with dichloromethane–hexane (4 : 1), 0.38 g (90%) of yellow crystalline *cis*- and *trans*-(15) [m.p. 187—191 °C; ν(CO) (in CH_2Cl_2) at 1 994s, 1 959m, and 1 792m cm^{-1}. ^{1}H N.m.r. (in $CDCl_3$): *cis*-(15a), δ 9.27 (s, 1 H), 5.28 (s, 10 H), 4.12 (q, *J* 8, 2 H), and 1.22 (t, *J* 8, 3 H); *trans*-(15b), δ 8.44 (s, 1 H), 5.32 (s, 5 H), 5.26 (s, 5 H), 4.20 (q, *J* 8, 2 H), and 1.36 p.p.m. (t, *J* 8 Hz, 3 H). ^{13}C N.m.r. (in $CDCl_3$): *cis*-(15b), δ 14.2 (Me), 60.4 (CH_2), 89.2 (2 C_5H_5), 115.2 (*C*HCO_2Et), 182.9 (*C*O_2Et), 198.1 (2 CO), and 241.9 (μ-CO); *trans*-(15b), δ 14.8 (Me), 60.2 (CH_2), 90.5 (C_5H_5), 92.0 (C_5H_5), 114.2 (*C*HCO_2Et), 183.8 (*C*O_2Et), 197.9 (CO), 198.6 (CO), and 241.7 p.p.m. (μ-CO). Found: C, 40.8; H, 3.3%; *M*, 503. $C_{17}H_{16}O_5Ru_2$ requires C, 40.6; H, 3.2%; *M*, 503].

Preparation of [Ru$_2$(CO)$_n$(μ-CO)(μ-CPh_2)(η-C_5H_5)$_2$] (16, *n* = 2; 17, *n* = 1).—A ten-fold excess of diphenyldiazomethane was heated with (2) (0.6 g, 1 mmol) in toluene (150 cm^3) at reflux for 1 h, then the mixture was chromatographed to yield yellow, orange, and green bands in succession. Elution with dichloromethane–hexane (3 : 1) removed the yellow band, shown to contain a trace of [Ru$_2$(CO)$_4$(η-C_5H_5)$_2$] by i.r., and the orange band. The latter contained 0.71 g of a *ca.* 1 : 1 mixture of yellow (16) and red (17), separated by fractional crystallisation from dichloromethane–hexane [(16): m.p. 224 °C (decomp.); ν(CO) (in CH_2Cl_2) at 1 986s, 1 942m, and 1 798m cm^{-1}. ^{1}H N.m.r. (in CD_2Cl_2): δ 7.65—6.80 (m, 10 H) and 5.10 p.p.m. (s, 10 H). Found: C, 53.1; H, 3.6%; *M*, 555 (*M* − CO). $C_{26}H_{20}O_3Ru_2$ requires C, 53.5; H, 3.4%; *M*, 573. (17): m.p. 190—194 °C; ν(CO) (in CH_2Cl_2) at 1 939s and 1 764m cm^{-1}. ^{1}H N.m.r. (in $CDCl_3$): δ 7.7—6.4 (m, 9 H), 4.86 (s, 5 H), 4.44 (s, 5 H), and 2.46 p.p.m. (dd, *J* 1 and 7 Hz, 1 H). Found: C, 54.6; H, 3.9%; *M*, 555. $C_{25}H_{20}O_2Ru_2$ requires C, 54.1; H, 3.6%; *M*, 555]. The green band was eluted with dichloromethane–hexane (4 : 1) to afford a trace of [Ru$_2$(μ-CO)(μ-C_2Ph_2)(η-C_5H_5)$_2$],[27] identified by i.r.

A sample of complex (16) was converted quantitatively to (17) on heating in toluene at reflux for 6.5 h, and a sample of (17) to (16) on heating in toluene at 100 °C for 17 h under 100 atm of carbon monoxide in an autoclave.

Preparation of [Ru$_2$(CO)$_2$(μ-CO)(μ-SO_2)(η-C_5H_5)$_2$] (18).—After bubbling SO_2 through a boiling toluene (150 cm^3) solution of (2) (0.3 g, 0.5 mmol) for 15 min a colour change from red to orange-yellow was observed. Chromatography on silica gel separated a trace of [Ru$_2$(CO)$_4$(η-C_5H_5)$_2$] on elution with dichloromethane–hexane (1 : 1), and a bright yellow band with dichloromethane–acetone (20 : 1). The latter yielded 0.21 g (88%) of yellow crystalline (18) after recrystallisation from dichloromethane–hexane [m.p. 241—247 °C; ν(CO) (in CH_2Cl_2) at 2 029s, 1 998m, and 1 817m cm^{-1}. ^1H N.m.r. (in [$^2H_6$]acetone): δ 5.72 (s) p.p.m.. Found: C, 32.5; H, 2.0; S, 6.3%; *M*, 481. $C_{13}H_{10}O_5Ru_2S$ requires C, 32.4; H, 2.1; S, 6.7%; *M*, 481].

Reactions of [$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2$] (1).—(a) *Thermolysis*. A sample of complex (1) (25 mg) was heated at 230 °C under vacuum in a sealed glass tube for 2 h. Analysis of the gaseous products by g.l.c. showed only methane to be present.

(b) *With ethylene*. A sample of complex (1) (50 mg) in toluene (3 cm^3) was heated at 210 °C in a sealed glass tube under 0.5 atm of ethylene for 2 h. Analysis as above revealed propene as a product.

X-Ray Data Collection and Structure Determination.—Crystals of [$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2$] (1) grow as yellow lozenge-shaped prisms. A crystal of dimensions 0.17 × 0.12 × 0.06 mm was mounted on a glass fibre and used for the collection of 4 520 independent diffracted intensities in the range $2.9 \leqslant 2\theta \leqslant 60°$ at 292 K on a Nicolet $P2_1m$ four-circle diffractometer. Two check reflections were remeasured every 50 reflections, and analysis of their intensity variation gave no evidence of crystal decay in the 106 h of exposure to *X*-radiation. Only those reflections with $I > 6\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation based on counting statistics only, were considered as observed, a total of 2 725 reflections being used in structure solution and refinement.

Crystal data. $C_{14}H_{12}O_3Ru_2$, $M = 430.4$, triclinic, $a = 6.771(2)$, $b = 9.315(2)$, $c = 11.864(5)$ Å, $\alpha = 103.12(3)$, $\beta = 100.61(3)$, $\gamma = 103.40(2)°$, $U = 685.5(4)$ Å^3, $D_m = 1.94$ (aqueous flotation), $Z = 2$, $D_c = 2.08$ g cm^{-3}, $F(000) = 416$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, and $\mu(\text{Mo-}K_\alpha) = 21.6\ cm^{-1}$.

The metal atomic co-ordinates were located from a sharpened Patterson synthesis, and a subsequent electron-density difference synthesis revealed the location of all the non-hydrogen atoms. All non-hydrogen atoms were allowed to refine with anisotropic thermal parameters. The hydrogen atoms of the cyclopentadienyl ligands were included at calculated positions (C–H, 0.96 Å) and were assigned a fixed isotropic thermal parameter 1.2 times $U_{eq.}$ of the carbon atom to which they were attached. They were allowed to ride [28] on the ring carbon atoms. The methylene hydrogen atoms were located from an electron-density difference synthesis and were refined freely with isotropic thermal parameters. Corrections for Lorentz, polarisation, and *X*-ray absorption effects were carried out. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.0003\ (F_o)^2]^{-1}$, where $\sigma(F)$ is the estimated standard deviation based on counting statistics only, gave a satisfactory weight analysis. Refinement converged at *R* 0.0365 (*R′* 0.0359), and the final electron-density difference synthesis showed no peaks > 0.8 or < −0.9 e Å^{-3}, the largest peaks lying in close proximity to the ruthenium atom positions.

Scattering factors were taken from ref. 29 for all atoms, with corrections for the effects of anomalous dispersion for all atoms. All computations were carried out within the laboratory on an Eclipse (Data General) minicomputer, using the SHELXTL system of programs.[30]

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