In memory of T. A. Stephenson

Organic Chemistry of Dinuclear Metal Centres. Part 9.[1] Diruthenium Complexes of Buta-1,3-diene. *X*-Ray Crystal Structure of $[Ru_2(CO)_2(\mu\text{-}s\text{-}trans\text{-}\eta^2:\eta^{2'}\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ †

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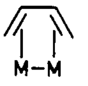
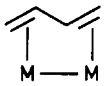
Heating $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ with buta-1,3-diene in toluene gives $[Ru_2(CO)(\mu\text{-}CO)_2(\eta^2\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ which upon photolysis yields $[Ru_2(CO)_2(\mu\text{-}s\text{-}trans\text{-}\eta^2:\eta^{2'}\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\sigma:\eta^3\text{-}CHCHCHCH_3)(\eta\text{-}C_5H_5)_2]$, the latter arising from a new transformation of the diene. These complexes cannot be obtained directly from $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, but photolysis of $[Ru_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ with buta-1,3-diene affords the analogues $[Ru_2(CO)_2(\mu\text{-}s\text{-}trans\text{-}\eta^2:\eta^{2'}\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5Me_5)_2]$ and $[Ru_2(CO)(\mu\text{-}CO)_2(\eta^2\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5Me_5)_2]$. Heating $[Ru_3H_3(CO)_3(\eta\text{-}C_5H_5)_3]$ with buta-1,3-diene in toluene gives $[Ru_2(CO)(\mu\text{-}CO)_2(\eta^2\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)_2(\mu\text{-}s\text{-}trans\text{-}\eta^2:\eta^{2'}\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$, *or* $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\sigma:\eta^3\text{-}CHCHCHCH_3)(\eta\text{-}C_5H_5)_2]$ depending on minor modification of the conditions. The molecular structure of $[Ru_2(CO)_2(\mu\text{-}s\text{-}trans\text{-}\eta^2:\eta^{2'}\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ has been determined by *X*-ray diffraction. The structure was solved by heavy-atom methods and refined by least squares to give a final R 0.038 for 838 unique, observed diffractometer data. Crystals are monoclinic, space group $I2$, with $Z = 2$ in a unit cell of dimensions $a = 11.544(6)$, $b = 7.841(4)$, $c = 8.622(4)$ Å, and $\beta = 103.36(4)°$. The molecule consists of a $(CO)(\eta\text{-}C_5H_5)Ru\text{–}Ru(\eta\text{-}C_5H_5)(CO)$ unit with *trans* CO and $\eta\text{-}C_5H_5$ ligands, symmetrically bridged by a buta-1,3-diene ligand in the *s-trans* conformation so that each Ru atom is η^2 co-ordinated. Compared to unco-ordinated buta-1,3-diene and other complexes with *s-trans*-buta-1,3-diene similarly co-ordinated, the terminal C=C bonds are significantly elongated [1.486(15) Å], consistent with substantial back-donation to the diene lowest unoccupied molecular orbital and depopulation of the diene highest occupied molecular orbital.

The reactions of buta-1,3-diene with transition metal complexes have produced species in which the hydrocarbon bridges a dinuclear metal centre in both *s-cis* (I) and *s-trans* (II) conformations.[2-8] There are other modes (III),[9] (IV),[7] and (V)[10] associated with a pair of non-interacting metal atoms, and rare examples of the diene suffering C–H activation, as in (VI)[11] and (VII).[5] Here we describe the synthesis of diruthenium complexes in which buta-1,3-diene is co-ordinated as $\mu\text{-}s\text{-}trans\text{-}\eta^2:\eta^{2'}\text{-}CH_2CHCHCH_2$, $\eta^2\text{-}CH_2CHCHCH_2$, and, following an unprecedented rearrangement, as $\mu\text{-}\sigma:\eta^3\text{-}CHCHCHCH_3$.



(I)



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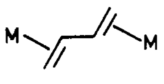

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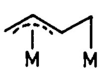

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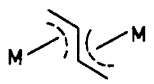

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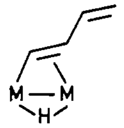
(VI)



(VII)

Results and Discussion

Whereas $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ is generally unreactive towards unsaturated hydrocarbons, its derivative $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (**1**)[12,13] undergoes rapid displacement of diphenylacetylene when heated in their presence.[14] Thus, bubbling ethylene through a boiling toluene solution of (**1**) for 15 min provides a 70% yield of the complex $[Ru_2(CO)(\mu\text{-}CO)_2(C_2H_4)(\eta\text{-}C_5H_5)_2]$ (**2**).[14,15] Similar treatment of (**1**) with buta-1,3-diene for 1 h gave a 56% yield of the analogous η^2-diene complex $[Ru_2(CO)(\mu\text{-}CO)_2(\eta^2\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ (**3**) as yellow air-stable crystals.

The i.r. spectrum of (**3**) indicates that both terminal (1 968m) and bridging (1 777s cm^{-1}) carbonyl groups are present and also shows a weak stretching band at 1 618 cm^{-1} (cyclohexane) characteristic of an unco-ordinated double bond of the diene. This is at higher frequency than that of free buta-1,3-diene (1 605 cm^{-1}, gas phase)[16] and similar to that of $[Ru(PMe_3)_2(\eta^2\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)][PF_6]$ (1 619 cm^{-1}, Nujol).[17] The η^2-co-ordination is confirmed by the n.m.r. spectra, which have signals corresponding to both co-ordinated and unco-ordinated CH and CH_2 groups. In the ^1H n.m.r. spectrum signals due to three unco-ordinated [δ 5.24 (3 H)] and three co-ordinated [δ 1.09 (1 H), 1.97 (1 H), and 3.05 (1 H)] olefinic protons are seen, while the ^{13}C n.m.r. spectrum displays resonances at δ 39.8 (CH_2) and 67.7 (CH) typical of metal-co-ordinated diene carbons and others at δ 112.0 (CH_2) and 140.8 (CH) very close

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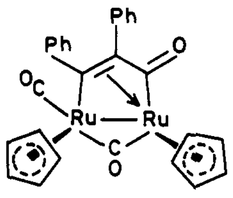
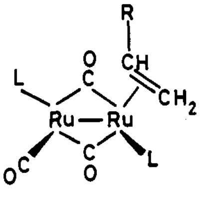
† μ-*s-trans*-1–2-η:3—4-η'-Buta-1,3-diene-bis[carbonyl(η-cyclopentadienyl)ruthenium(I)](*Ru–Ru*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



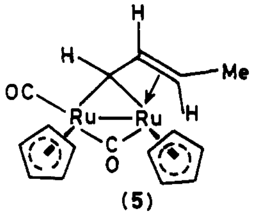
(1)



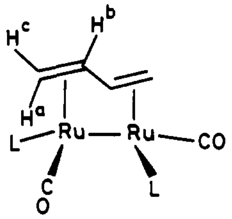
(2) $L = \eta\text{-}C_5H_5, R = H$

(3) $L = \eta\text{-}C_5H_5, R = CHCH_2$

(9) $L = \eta\text{-}C_5Me_5, R = CHCH_2$

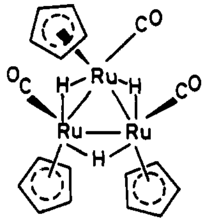


(5)

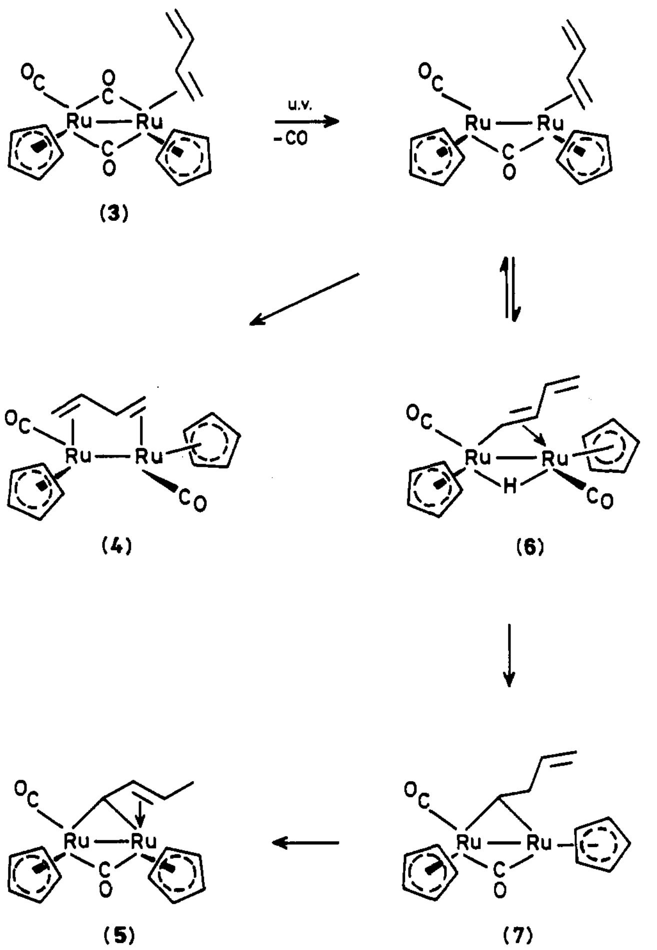


(4) $L = \eta\text{-}C_5H_5$

(8) $L = \eta\text{-}C_5Me_5$



(10)



Scheme.

in shift to those of free buta-1,3-diene (δ 116.3 and 136.9).[18] The shifts of the co-ordinated CH_2 carbons in (2) and (3) are also very similar, at δ 40.3 and 39.8 respectively.

The butadiene ligand can be induced to bridge the diruthenium centre through photolysis of (3) in the presence of an excess of the hydrocarbon (to suppress its dissociation): the complex $[Ru_2(CO)_2(\mu\text{-}s\text{-}trans\text{-}\eta^2{:}\eta^{2'}\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ (4) is formed in 14% yield, in association with an isomer of formulation $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\sigma{:}\eta^3\text{-}CHCHCHCH_3)(\eta\text{-}C_5H_5)_2]$ (5) (10%).

Dark red, air-stable crystalline (4) has a single terminal carbonyl stretching absorption in the i.r. spectrum, at 1 914 cm^{-1}, consistent with a *trans* arrangement of the pairs of CO and $\eta\text{-}C_5H_5$ ligands and co-ordination of the buta-1,3-diene in an *s-trans* conformation. Accordingly, the $\eta\text{-}C_5H_5$ and CO ligands provide single resonances in the ^{13}C n.m.r. spectrum. Signals for the diene ligand, at δ 23.2 and 48.1, are assigned to the CH_2 and CH groups respectively; the corresponding carbon atoms in $[Re_2(CO)_8(\mu\text{-}s\text{-}trans\text{-}\eta^2{:}\eta^{2'}\text{-}CH_2CHCHCH_2)]$ [(II), M = $Re(CO)_4$] are seen at lower field, δ 26.5 and 67.1 respectively.[5] The diene protons of (4) appear at δ 1.69 (H^a), 1.73 (H^b), and 2.63 (H^c) in the ^1H n.m.r. spectrum, again at higher field than the corresponding nuclei in the dirhenium analogue (δ 2.54, 2.73, and 3.06), indicating a substantial transfer of metal electron density to the hydrocarbon. This was confirmed by an *X*-ray diffraction study (see below).

Complex (5) has been prepared previously by a different route, involving combination of ethyne and ethylidene, and was readily characterised by its i.r., ^1H n.m.r., and mass spectra.[19]

The formation of (4) may involve initial dissociation of CO from (3), followed by co-ordination of the free diene double bond to the second ruthenium. Such a scheme has been postulated for the formation of $[Mn_2(CO)_8(\mu\text{-}s\text{-}trans\text{-}\eta^2{:}\eta^{2'}\text{-}CH_2CHCHCH_2)]$ [(II), M = $Mn(CO)_4$] from $[Mn_2(CO)_{10}]$ and buta-1,3-diene, but no intermediate η^2-diene complex was isolated.[7] However, the photochemical reaction of $[Re_2(CO)_{10}]$ with buta-1,3-diene gives a μ-vinyl complex $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}CHCHCHCH_2)]$ [(VII), M = $Re(CO)_4$] which on heating smoothly converts to $[Re_2(CO)_8(\mu\text{-}s\text{-}trans\text{-}\eta^2{:}\eta^{2'}\text{-}CH_2CHCHCH_2)]$ [(II), M = $Re(CO)_4$].[5] The possibility of a reversible C–H activation being associated with the transformation (3) ⟶ (4) therefore cannot be ruled out, especially when a C–H activation is clearly involved in the formation of (5), which arises from a formal 1,4-hydrogen shift rearrangement of the diene. It is attractive to envisage (Scheme) the μ-vinyl complex (6) as being involved in the formation of both (4) and (5), whose evolution then differs only in the course of μ-hydride migration to the $\mu\text{-}CHCHCHCH_2$ ligand. Migration to the α-carbon of the vinyl leads to (4), while migration to the β-carbon gives the co-ordinatively unsaturated $\mu\text{-}CHCH_2CHCH_2$ complex (7) which would be expected to readily undergo a 1,3-hydrogen shift to permit co-ordination of a $\mu\text{-}CHCHCHCH_3$ ligand in (5).

Neither (3), (4), nor (5) is formed when $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ is treated with buta-1,3-diene under thermal or photochemical conditions, paralleling its unreactivity towards ethylene. However, $[Ru_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ is known to react with ethylene under u.v. irradiation to yield $[Ru_2(CO)(\mu\text{-}CO)_2(C_2H_4)(\eta\text{-}C_5Me_5)_2]$,[20] and it behaves likewise with buta-1,3-diene to give $[Ru_2(CO)_2(\mu\text{-}s\text{-}trans\text{-}\eta^2{:}\eta^{2'}\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5Me_5)_2]$ (8). The new complex is not photostable; its yield reached a maximum of 6% after 24 h and diminished thereafter. I.r. and n.m.r. spectra establish the gross structure of (8) to be

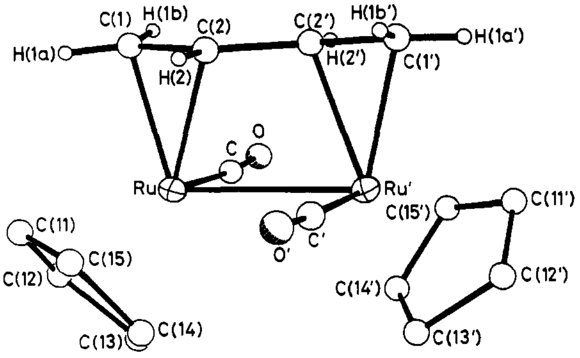


Figure 1. Molecular structure and numbering scheme for $[Ru_2(CO)_2(\mu\text{-}s\text{-}trans\text{-}\eta^2:\eta^{2'}\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ (**4**); cyclopentadienyl group hydrogen atoms are omitted for clarity

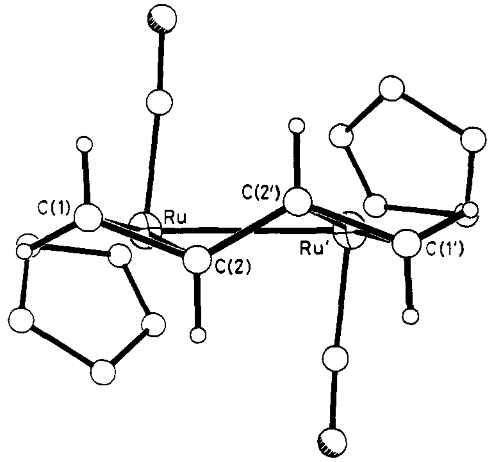


Figure 2. Complex (**4**) viewed along the molecular C_2 axis; cyclopentadienyl group hydrogen atoms are omitted for clarity

analogous to that of (**4**), *i.e.* with the CO and $\eta\text{-}C_5Me_5$ ligands *trans* and the diene co-ordinated in a $\mu\text{-}s\text{-}trans\text{-}\eta^2:\eta^{2'}$ configuration. Thus, like (**4**), (**8**) exhibits a single terminal carbonyl absorption, but at a lower frequency (1 890 cm^{-1}) due to the better electron donation of $\eta\text{-}C_5Me_5$ compared with $\eta\text{-}C_5H_5$. Similarly, the ^1H n.m.r. spectrum shows the diene protons to be comparatively shielded [δ 1.26, 1.61, and 1.98 for (**8**); δ 1.69, 1.73, and 2.63 for (**4**)]. The diene carbons appear in the ^{13}C n.m.r. spectrum at δ 35.2 (CH_2) and 50.2 (CH).

A yellow, oily second product of the reaction was isolated in very low yield and identified on the basis of the i.r. (1 941 and 1 744 cm^{-1}) and mass spectra as $[Ru_2(CO)(\mu\text{-}CO)_2(\eta^2\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5Me_5)_2]$ (**9**), an analogue of (**3**).

The hydride complex $[Ru_3H_3(CO)_3(\eta\text{-}C_5H_5)_3]$ (**10**)[21] has been shown to provide an excellent entry into organotriruthenium chemistry through reactions with alkenes and alkynes.[22,23] We find, however, that its thermal reaction with buta-1,3-diene results in the destruction of the triruthenium unit, leading once again to the diruthenium complexes (**3**), (**4**), and (**5**). The course of the reaction is very sensitive to the conditions. Complexes (**3**) and (**4**) were obtained in 30 and 20% yields, respectively, when the reaction vessel containing (**10**) and an excess of butadiene in toluene was immersed in a hot oil-bath at 105 ± 12 °C for 4.5 h. However, only complex (**5**) was obtained, in 59% yield, when the vessel was immersed at ambient temperature and heated slowly to 130 °C over 4.5 h.

Table 1. Bond lengths (Å) and angles (°) for (**4**)

Ru–C	1.830(9)	Ru–C(1)	2.177(12)
Ru–C(2)	2.215(9)	Ru–C(11)	2.250(17)
Ru–C(12)	2.207(15)	Ru–C(13)	2.232(22)
Ru–C(14)	2.272(16)	Ru–C(15)	2.263(15)
Ru–Ru′	2.870(5)	C–O	1.171(11)
C(1)–C(2)	1.486(15)	C(2)–C(2′)	1.475(23)
C(11)–C(12)	1.368(20)	C(11)–C(15)	1.401(22)
C(12)–C(13)	1.551(25)	C(13)–C(14)	1.243(24)
C(14)–C(15)	1.438(24)		
C–Ru–C(1)	88.3(10)	C–Ru–C(2)	98.3(10)
C(1)–Ru–C(2)	39.5(4)	C–Ru–C(11)	131.3(5)
C(1)–Ru–C(11)	90.2(5)	C(2)–Ru–C(11)	110.7(5)
C–Ru–C(12)	100.6(7)	C(1)–Ru–C(12)	109.6(5)
C(2)–Ru–C(12)	142.9(5)	C(11)–Ru–C(12)	35.7(5)
C–Ru–C(13)	100.6(12)	C(1)–Ru–C(13)	150.1(7)
C(2)–Ru–C(13)	158.8(6)	C(11)–Ru–C(13)	62.5(7)
C(12)–Ru–C(13)	40.9(7)	C–Ru–C(14)	128.1(11)
C(1)–Ru–C(14)	142.4(6)	C(2)–Ru–C(14)	126.8(4)
C(11)–Ru–C(14)	59.9(6)	C(12)–Ru–C(14)	59.9(5)
C(13)–Ru–C(14)	32.0(6)	C–Ru–C(15)	159.4(10)
C(1)–Ru–C(15)	105.4(6)	C(2)–Ru–C(15)	102.0(5)
C(11)–Ru–C(15)	36.2(6)	C(12)–Ru–C(15)	60.7(6)
C(13)–Ru–C(15)	60.0(8)	C(14)–Ru–C(15)	37.0(6)
C–Ru–Ru′	83.7(3)	C(1)–Ru–Ru′	105.5(4)
C(2)–Ru–Ru′	68.8(3)	C(11)–Ru–Ru′	142.7(4)
C(12)–Ru–Ru′	144.7(4)	C(13)–Ru–Ru′	103.8(6)
C(14)–Ru–Ru′	89.6(4)	C(15)–Ru–Ru′	106.5(4)
Ru–C–O	173.9(19)	Ru–C(1)–C(2)	71.6(6)
Ru–C(2)–C(1)	68.8(6)	Ru–C(2)–C(2′)	103.0(4)
C(1)–C(2)–C(2′)	128.0(11)	Ru–C(11)–C(12)	70.4(9)
Ru–C(11)–C(15)	72.4(10)	C(12)–C(11)–C(15)	109.3(14)
Ru–C(12)–C(11)	73.9(9)	Ru–C(12)–C(13)	70.4(10)
C(11)–C(12)–C(13)	105.4(13)	Ru–C(13)–C(12)	68.7(10)
Ru–C(13)–C(14)	75.8(12)	C(12)–C(13)–C(14)	106.0(18)
Ru–C(14)–C(13)	72.2(12)	Ru–C(14)–C(15)	71.2(9)
C(13)–C(14)–C(15)	113.8(16)	Ru–C(15)–C(11)	71.4(9)
Ru–C(15)–C(14)	71.8(9)	C(11)–C(15)–C(14)	105.4(13)

Surprisingly, (**3**) and (**4**) are not here precursors of (**5**); when heated under the conditions used for synthesis of (**5**) neither gave the complex and each was recovered largely unreacted. The pathways followed in this reaction of (**10**) remain obscure.

Molecular Structure of $[Ru_2(CO)_2(\mu\text{-}s\text{-}trans\text{-}\eta^2:\eta^{2'}\text{-}CH_2CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ (**4**).—The molecular structure of (**4**) was determined by *X*-ray diffraction. The structure, which has crystallographic C_2 symmetry, and the numbering scheme are shown in Figure 1, and the results are summarised in Tables 1 and 2. The molecule comprises a diruthenium core with a Ru–Ru single bond distance of 2.870(5) Å, similar to those in $[Ru_2(CO)_6(\mu\text{-}C_8H_8)]$[24] and $[Ru_2(CO)_5(\mu\text{-}C_{16}H_{16})]$.[25] In accord with spectroscopic indications, the CO and $\eta\text{-}C_5H_5$ ligands adopt a *trans* configuration in a $Ru_2(CO)_2(\eta\text{-}C_5H_5)_2$ unit bridged by buta-1,3-diene in the *s-trans* conformation, as clearly shown in Figure 2.

The butadiene ligand is η^2 bound to each ruthenium and nearly planar [torsion angle C(1)–C(2)–C(2′)–C(1′) 174(2)°]. Co-ordination to the $Ru_2(CO)_2(\eta\text{-}C_5H_5)_2$ unit induces marked lengthening in the diene 'double' bonds, to 1.486(15) Å, making them the same length as the central C–C bond [1.475(23) Å]. The C–C–C angles [128.0(11)°] reflect an extended geometry for the diene on co-ordination; in comparison the free diene *trans,trans*-$(2,6\text{-}C_6H_3Cl_2)CHCHCHCHPh$ has C=C 1.346(4) and 1.334(4), C–C 1.456(4) Å, C–C–C 121.2(3) and 123.9(3)°.[26] The implication of the large C–C bond lengths in (**4**) is that the $Ru_2(CO)_2(\eta\text{-}C_5H_5)_2$ unit donates electron density to the diene

Table 2. Atomic co-ordinates ($\times 10^4$) for (**4**)

Atom	*x*	*y*	*z*
Ru	9 761(1)	10 000	6 561(1)
C	11 386(8)	10 040(41)	7 229(9)
O	12 415(6)	9 946(32)	7 749(8)
C(1)	9 808(12)	7 333(14)	7 275(14)
C(2)	9 566(9)	7 410(11)	5 507(11)
C(11)	8 324(13)	10 514(18)	7 874(19)
C(12)	9 259(14)	11 600(18)	8 408(15)
C(13)	9 332(22)	12 719(27)	6 951(23)
C(14)	8 503(14)	12 240(19)	5 844(17)
C(15)	7 842(12)	10 821(25)	6 252(20)
H(2)	8 717(29)	7 452(79)	5 026(69)
H(1a)	9 297(38)	7 387(50)	7 944(46)
H(1b)	10 610(27)	7 135(51)	7 756(48)

lowest unoccupied molecular orbital and depopulates the diene highest occupied molecular orbital very effectively. Less marked bond lengthening was observed for the μ-*s*-*trans*-$\eta^2:\eta^{2'}$-C_4H_6 ligand when bonded to the $Mn_2(CO)_8$ moiety [C–C terminal 1.385(14), 1.388(14), C–C central 1.389(15) Å], but extension of the C–C–C angles as in (**4**) occurred [128.1(10) and 127.9(10)°].[6] The Ru–diene contacts in (**4**) are rather short {Ru–CH_2 2.177(12), Ru–CH 2.215(9) Å, *cf.* Ru–C 2.27–2.31(1) Å in [$Ru_6C(CO)_{15}$(μ-*s*-*trans*-$\eta^2:\eta^{2'}$-MeCHCHCHCHMe)][27]}, in accord with the view that the $Ru_2(CO)_2(\eta\text{-}C_5H_5)_2$ unit binds strongly to the hydrocarbon. It is notable that the extended geometries observed in (**4**) and [$Mn_2(CO)_8$(μ-*s*-*trans*-$\eta^2:\eta^{2'}$-$CH_2CHCHCH_2$)] are associated with longer metal–metal bond lengths [2.870(5) and 3.102(2) Å respectively] than that in the relatively unextended diene of [Co_2(μ-CO)(μ-*s*-*cis*-$\eta^2:\eta^{2'}$-$CH_2CHCHCH_2$)] [Co–Co 2.485(1) Å, diene C–C 1.381(4), 1.438(4), 1.407(4) Å, C–C–C 124.1(3), 123.8(3)°].[8] It seems that when bridging a metal–metal bond buta-1,3-diene exhibits an 'accordion' effect, expanding or contracting in response to electronic and/or steric constraints imposed by its environment.

Experimental

Reactions were performed in a nitrogen atmosphere using standard Schlenk techniques. Toluene (sodium), hexane (sodium), tetrahydrofuran and diethyl ether (sodium–benzophenone), dichloromethane (calcium hydride), and acetone (calcium sulphate) were dried by distillation over the drying agent indicated. Chromatography was on alumina columns (Brockman activity II, *ca.* 3 × 30 cm). The u.v. radiation source was a 500-W medium-pressure Hanovia mercury-vapour lamp, held 20—40 cm from a silica tube. I.r. spectra were obtained with a Nicolet MX-S spectrometer, n.m.r. spectra with JNM FX 90Q and FX 200 instruments, and mass spectra with an AEI MS 902 spectrometer. The complexes [$Ru_2(CO)_4(\eta\text{-}C_5H_5)_2$],[13,28] [$Ru_2$-(CO)(μ-CO){μ-C(O)$C_2Ph_2$}($\eta$-$C_5H_5$)$_2$],[12,13] [$Ru_3H_3(CO)_3(\eta\text{-}C_5H_5)_3$],[26] and [$Ru_2(CO)_4(\eta\text{-}C_5Me_5)_2$][29] were obtained by literature methods.

Reactions of Buta-1,3-*diene*.—With [Ru_2(CO)(μ-CO){μ-C(O)C_2Ph_2}(η-C_5H_5)$_2$] (**1**). Buta-1,3-diene was bubbled vigorously through a boiling toluene (125 cm^3) solution of (**1**) (0.25 g, 0.42 mmol) for 1 h. The solvent was removed under reduced pressure and the residue was chromatographed. Elution with dichloromethane–hexane (1:1) developed two yellow bands. The first yielded a trace of [$Ru_2(CO)_4(\eta\text{-}C_5H_5)_2$], identified by its i.r. spectrum. The second gave 0.11 g (56%) of yellow, crystalline [Ru_2(CO)(μ-CO)$_2$(η^2-$CH_2CHCHCH_2$)(η-C_5H_5)$_2$] (**3**) [ν(CO) (cyclohexane) at 1 968m and 1 777s cm^{-1}, ν(C=C) at 1 618w cm^{-1}; ^{1}H n.m.r. ($CDCl_3$), δ 5.24 (s, 5 H), 5.24 (m, 3 H), 4.98 (s, 5 H), 3.05 (dd, *J* = 1 and 12 Hz, 1 H), 1.97 (m, 1 H), 1.09 (d, *J* = 8 Hz, 1 H); ^{13}C n.m.r. ($CDCl_3$), δ 140.8 (unco-ordinated CH), 112.0 (unco-ordinated CH_2), 91.5 (C_5H_5), 89.8 (C_5H_5), 67.7 (co-ordinated CH), 39.8 (co-ordinated CH_2), CO resonances not observed. Found: C, 43.0; H, 3.5%; *M*, 470. $C_{17}H_{16}O_3Ru_2$ requires C, 43.4; H, 3.4%; *M*, 470]. A third, orange band was eluted with dichloromethane–acetone (9:1) and shown to be unreacted (**1**).

With [$Ru_3H_3(CO)_3(\eta\text{-}C_5H_5)_3$] (**10**). (*a*) Buta-1,3-diene (0.761 g, 14.1 mmol) was condensed (−196 °C) into a Young's tube containing a toluene (55 cm^3) solution of (**10**) (0.24 g, 0.41 mmol). After warming to room temperature, the tube was placed in a hot oil-bath at 105 ± 12 °C for 4.5 h. During this time the solution colour changed from blue to dark yellow. After evaporation of the solvent under reduced pressure, the residue was chromatographed. Elution with dichloromethane–hexane (1:4) developed an orange band which upon solvent evaporation gave 0.056 g (20%) of dark red crystalline [$Ru_2(CO)_2$(μ-*s*-*trans*-$\eta^2:\eta^{2'}$-$CH_2CHCHCH_2$)(η-C_5H_5)$_2$] (**4**) [ν(CO) (in cyclohexane) at 1 914s cm^{-1}; ^{1}H n.m.r. (in $CDCl_3$), δ 5.10 (s, 10 H), 2.63 (m, 2 H), 1.73 (m, 2 H), 1.69 (m, 2 H); ^{13}C n.m.r. (in $CDCl_3$), δ 206.1 (CO), 84.5 (C_5H_5), 48.1 (CH), 23.2 (CH_2). Found: C, 43.4; H, 3.6%; *M*, 442. $C_{16}H_{16}O_2Ru_2$ requires C, 43.4; H, 3.6%; *M*, 442]. Further elution with dichloromethane–hexane (1:1) gave a yellow band which upon solvent evaporation yielded 0.088 g (30%) of yellow crystalline [Ru_2(CO)(μ-CO)$_2$(η^2-$CH_2CHCHCH_2$)(η-C_5H_5)$_2$] (**3**), identified by i.r. and n.m.r. spectroscopy.

(*b*) Buta-1,3-diene (0.523 g, 9.69 mmol) was condensed (−196 °C) into a Young's tube containing (**10**) (0.1 g, 0.17 mmol) in toluene (65 cm^3). After warming to room temperature the tube was placed in an ambient-temperature oil-bath and slowly heated to 130 °C over 4.5 h. During the reaction the solution colour changed from blue to greenish yellow. The solvent was evaporated under reduced pressure and the brown residue was chromatographed. Elution with dichloromethane–hexane (1:1) separated a yellow band which yielded 0.067 g (59%) of orange crystalline [Ru_2(CO)(μ-CO)(μ-σ:η^3-CHCHCHCH$_3$)(η-C_5H_5)$_2$] (**5**), identified by its i.r., n.m.r., and mass spectra.[19]

With [$Ru_2(CO)_4(\eta\text{-}C_5Me_5)_2$]. A suspension of [$Ru_2(CO)_4$-($\eta$-$C_5Me_5$)$_2$] (0.705 g, 1.21 mmol) in tetrahydrofuran (thf) (125 cm^3) was placed in a silica tube and inserted into a Pyrex sleeve (to reduce polymerisation of the diene). The mixture was subjected to u.v. irradiation for 24 h while buta-1,3-diene was bubbled through. After irradiation pentane was added to the now homogeneous solution and the mixture evaporated under reduced pressure, precipitating tan and maroon solids. When no more solids precipitated upon solvent evaporation, the supernatant pentane solution was chromatographed. Elution with hexane gave an orange band which yielded 0.04 g (6%) of red crystalline [$Ru_2(CO)_2$(μ-*s*-*trans*-$\eta^2:\eta^{2'}$-$CH_2CHCHCH_2$)-(η-C_5Me_5)$_2$] (**8**) [ν(CO) (cyclohexane) at 1 890s cm^{-1}; ^{1}H n.m.r. ($CDCl_3$), δ 1.98 (m, 2 H), 1.78 (s, 30 H), 1.61 (m, 2 H), 1.26 (m, 2 H); ^{13}C n.m.r. ($CDCl_3$), δ 95.7 (C_5Me$_5$), 50.2 (CH), 35.2 (CH_2), 10.7 (C_5Me_5), CO resonance not observed. Found: C, 54.0; H, 6.6%; *M*, 583. $C_{26}H_{36}O_2Ru_2$ requires C, 53.6; H, 6.2%; *M*, 583]. The product could be further purified by sublimation [0.01 mmHg (*ca.* 1.3 Pa), 140 °C]. Elution with hexane–diethyl ether (19:1) gave a yellow band which upon solvent evaporation yielded 0.011 g of a yellow oil. The oil was not satisfactorily pure by elemental analysis, but had i.r. [ν(CO) (cyclohexane) at 1 941m and 1 744s cm^{-1}] and mass spectra (M^+ 612) consistent with the formulation [Ru_2(CO)(μ-CO)$_2$(η^2-$CH_2CHCHCH_2$)-(η-C_5Me_5)$_2$] (**9**).

Photolysis of [Ru_2(CO)(μ-CO)$_2$(η^2-$CH_2CHCHCH_2$)(η-C_5H_5)$_2$] (**3**).—Complex (**3**) (0.074 g, 0.16 mmol) was dissolved in thf (110 cm^3) in a silica tube inserted into a Pyrex sleeve. Buta-1,3-diene was bubbled through the solution while it was irradiated (3.5 h). The original yellow solution darkened and a suspension formed. After evaporation of solvent under reduced pressure, chromatography of the residue yielded two bands. Dichloromethane–hexane (1:4) eluted a red band which upon solvent evaporation gave 10 mg (14%) of (**4**), while dichloromethane eluted a yellow band which gave 7 mg (10%) of (**5**), each identified by i.r. and mass spectra.

X-Ray Data Collection and Structure Determination.—Crystals of (**4**) were grown from hexane–thf solution as dark red plates. A single crystal (appproximate dimensions 0.5 × 0.35 × 0.2 mm) was mounted under nitrogen in a thin-walled glass capillary. Diffracted intensities were recorded on a Nicolet P3m four-circle diffractometer at room temperature. Of a total of 2 067 independent measured intensities recorded in the range $3 \leqslant 2\theta \leqslant 60°$, 838 with $F \geqslant 2.0\sigma(F)$ were used in structure solution and refinement. The data were corrected for Lorentz and polarisation effects, but no absorption correction was applied. Check reflections (1,0,−3 and 0,−2,0) were measured every 50 reflections and showed no evidence of decay throughout 114 h of data collection.

Crystal Data.—$C_{16}H_{16}O_2Ru_2$, $M = 442.4$, monoclinic, $a = 11.544(6)$, $b = 7.841(4)$, $c = 8.622(4)$ Å, $\beta = 103.36(4)°$, $U = 759.3(7)$ Å^3, $Z = 2$, $D_c = 1.93$ g cm^{-3}, $F(000) = 432$, space group $I2$ (no. 5); graphite-monochromated Mo-K_α X-radiation, graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 19.5 cm^{-1}.

The structure was solved by conventional Fourier and Patterson heavy-atom methods and refined by full-matrix blocked-cascade least squares. All non-hydrogen atoms were allowed anisotropic thermal parameters. The hydrogen atoms of the buta-1,3-diene ligand were located from difference-Fourier maps and refined with the constraint of C–H *ca.* 0.96 Å; the cyclopentadienyl hydrogen atoms were included at idealised positions (C–H 0.96 Å). Refinement converged at R 0.038 (R' 0.037), $S = 1.32$,* with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$. The final electron-density difference synthesis showed no peaks > 0.9 e Å^{-3}. Calculations were carried out on an Eclipse (Data General) computer in this laboratory using the SHELXTL system of programs.[30] Complex, neutral-atom scattering factors for all atoms were taken from ref. 31. Atomic co-ordinates for complex (**4**) are given in Table 2.

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References

1 Part 8, B. P. Gracey, S. A. R. Knox, K. A. Macpherson, A. G. Orpen, and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 1985, 1935.
2 E. G. Bryan, B. F. G. Johnson, J. W. Kelland, J. Lewis, and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1976, 254.
3 M. Tachikawa, J. R. Shapley, R. C. Haltiwanger, and C. G. Pierpont, *J. Am. Chem. Soc.*, 1976, **98**, 4651.
4 C. G. Pierpont, *Inorg. Chem.*, 1978, **17**, 1976.
5 K-H. Franzreb and C. G. Kreiter, *Z. Naturforsch., Teil B*, 1982, **37**, 1058; *J. Organomet. Chem.*, 1983, **246**, 189.
6 H. E. Sasse and M. L. Ziegler, *Z. Anorg. Allg. Chem.*, 1972, **392**, 167.
7 C. G. Kreiter and W. Lipps, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 201; *Chem. Ber.*, 1982, **115**, 973.
8 J. A. King, jun., and K. P. C. Vollhardt, *Organometallics*, 1983, **2**, 684.
9 M. L. Ziegler, *Z. Anorg. Allg. Chem.*, 1967, **355**, 12.
10 M. D. Fryzuk, W. E. Piers, and S. J. Rettig, *J. Am. Chem. Soc.*, 1985, **107**, 8259.
11 M. D. Fryzuk, T. Jones, and F. W. B. Einstein, *J. Chem. Soc., Chem. Commun.*, 1984, 1556.
12 A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 1297.
13 N. M. Doherty and S. A. R. Knox, *Inorg. Synth.*, in the press.
14 D. L. Davies, A. F. Dyke, S. A. R. Knox, and M. J. Morris, *J. Organomet. Chem.*, 1981, **215**, C30.
15 A. F. Dyke, S. A. R. Knox, and P. J. Naish, *J. Organomet. Chem.*, 1980, **199**, C47.
16 R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, 1947, **15**, 131.
17 M. I. Bruce, T. W. Hambley, J. R. Rodgers, M. R. Snow, and F. S. Wong, *Aust. J. Chem.*, 1982, **35**, 1323.
18 D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, 1971, **36**, 2757.
19 P. Q. Adams, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1983, 222.
20 N. J. Forrow and S. A. R. Knox, *J. Chem. Soc., Chem. Commun.*, 1984, 679.
21 N. J. Forrow, S. A. R. Knox, M. J. Morris, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1983, 234.
22 S. A. R. Knox, *Pure Appl. Chem.*, 1984, **56**, 81.
23 S. A. R. Knox, in 'Homogeneous and Heterogeneous Catalysis,' Proceedings of the Fifth International Symposium on Relations Between Homogeneous and Heterogeneous Catalysis, eds. Yu. Yermakov and V. Likholobov, VNU Science Press, Utrecht, 1986, pp. 847—863.
24 F. A. Cotton and W. T. Edwards, *J. Am. Chem. Soc.*, 1968, **90**, 5412.
25 R. Goddard and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1979, 661.
26 D. Rabinovich and Z. Shakkad, *Acta Crystallogr., Sect. B*, 1975, **31**, 819.
27 P. F. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, G. J. Will, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1980, 1190.
28 A. P. Humphries and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1975, 1710.
29 R. B. King, M. Z. Iqbal, and A. D. King, *J. Organomet. Chem.*, 1979, **171**, 53.
30 G. M. Sheldrick, 'SHELXTL, an Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data,' revision no. 4, Nicolet Instruments Ltd., Warwick, January 1983.
31 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, N_o and N_v = numbers of observations and variables.