Organic Chemistry of Dinuclear Metal Centres. Part 1. Combination of Alkynes with Carbon Monoxide at Di-iron and Diruthenium Centres: Crystal Structure of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ †

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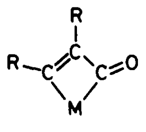
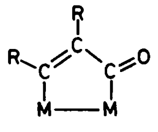
Under u.v. radiation a variety of alkynes (HC_2H, MeC_2Me, PhC_2Ph, $MeO_2CC_2CO_2Me$, MeC_2H, PhC_2H, and PhC_2Me) reacts with $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ to form complexes $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2R_2\}(\eta\text{-}C_5H_5)_2]$ in 10—90% yields. Only PhC_2Ph produces an analogous complex with $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, but $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ undergoes alkyne exchange on heating in toluene with HC_2H, MeC_2Me, MeC_2H, PhC_2H, or PhC_2Me to afford the appropriate $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2R_2\}(\eta\text{-}C_5H_5)_2]$ in near quantitative yield. The linking of alkyne and CO to produce a dimetallacyclopentenone ring was established through an *X*-ray diffraction study of the title compound. Crystals are orthorhombic, space group *Pbca*, with $Z = 8$ in a unit cell of dimensions $a = 14.797(3)$, $b = 17.805(8)$, and $c = 16.739(8)$ Å. The structure was solved by heavy-atom methods and refined by least squares to *R* 0.033 for 3 726 diffractometer-measured reflection intensities. The molecule contains a dimetallacyclopentenone ring in which the ethylenic bond is η^2-bound to ruthenium, so that the bridging C(O)C(Ph)C(Ph) ligand is σ-co-ordinated to one ruthenium and η^3-co-ordinated to the other. Compounds $[M_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C(R^1)C(R^2)\}(\eta\text{-}C_5H_5)_2]$ (M = Fe or Ru) in which $R^1 \neq R^2$ exist as isomers as a result of linking of either end of the alkyne with CO. Steric factors appear to determine the relative stability of the isomers when one of R is H, but electronic factors are influential when neither is H. The dimetallacyclopentenones are fluxional, undergoing synchronous carbonyl 'insertion' into, and elimination from, the dimetallacycle. Free energies of activation appear dependent upon the size of the 'alkyne' substituents. In boiling toluene, carbonyl elimination from the dimetallacycle in $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ becomes irreversible, and the dimetallacyclobutene complex $[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ is formed quantitatively as *cis* and *trans* isomers. Only *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ is generated when $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ is heated with $MeO_2CC_2CO_2Me$. The ease with which carbon–carbon bond-making and -breaking occurs at the di-iron and diruthenium centres is recognised.

THE organic chemistry of mononuclear metal centres is now well established, but in comparison little attention has been paid to dinuclear metal centres. However, in seeking to understand the catalysis of organic reactions by metal surfaces or by metal clusters it is clearly important to consider the dinuclear metal centre and particularly the nature and reactivity of organic species co-ordinated at (bridging) the centre. The premise that the study of polynuclear metal compounds may shed light on metal surface phenomena has been discussed elsewhere.[1] This paper is the first in a Series which will describe an investigation of the organic chemistry of dinuclear metal centres in complexes.


(1)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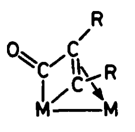
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The combination of carbon monoxide with alkynes in the presence (often catalytic) of transition-metal carbonyls has attracted study for 40 years. Much of the chemistry remains obscure mechanistically but there has been speculation that metallacycles (1) are involved with monometal carbonyls and dimetallacycles (2) and (3) with dimetal carbonyls.[2] These are regarded as intermediates in the formation of, for example, esters, lactones, quinones, and cyclopentadienones in such reactions. Stable examples of (1) are known, as in $[\overline{Ru\{C(O)C(CF_3)C}(CF_3)\}(CO)_2\{P(OMe)_3\}_2]$,[3] and now in this paper we describe the chemistry of di-iron and diruthenium complexes containing the unit (2). In a previous article a ditungsten compound based on (3) was reported.[4] Since this work was first communicated [5] a dirhodium species containing the arrangement (2) has arisen.[6]

RESULTS AND DISCUSSION

A wide range of alkynes RC_2R reacts with the cyclopentadienyliron dicarbonyl dimer $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ under u.v. irradiation to provide complexes $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2R_2\}(\eta\text{-}C_5H_5)_2]$ (4)—(12). Yields vary from 10 to 86%, depending on the alkyne, and the optimum length of irradiation from 16 h to 28 d. The products are isolated as green to brown crystals or powders and are air- and solution-stable save for that derived from diphenylacetylene, which decomposes readily to release the alkyne. In contrast diphenylacetylene is the only alkyne which generates an analogous complex (13) in reaction with $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$. However, on heating this complex in toluene with other alkynes an exchange of alkyne occurs rapidly (<1 h) to produce (14)—(21) in high yields as stable orange crystalline compounds. Employment of alkynes $R^1C_2R^2$ ($R^1 \neq R^2$) in the above syntheses gives the products as

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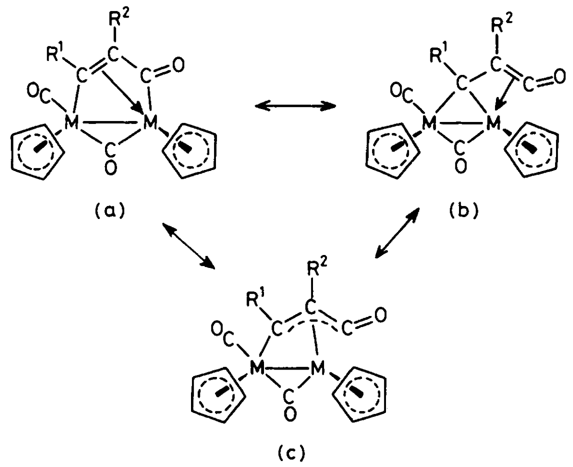
† μ-Carbonyl-1-carbonyl-1,2-bis(η-cyclopentadienyl)-μ-[σ : 1′—3′-η-3′-oxo-1′,2′-diphenylpropen-1′,3′-diyl-$C^{1'}$(Ru¹)-$C^{1'-3'}$(Ru²)]diruthenium(*Ru–Ru*).



M = Fe	M = Ru
(4) $R^1 = R^2 = H$	(13) $R^1 = R^2 = Ph$
(5) $R^1 = R^2 = Me$	(14) $R^1 = R^2 = H$
(6) $R^1 = R^2 = Ph$	(15) $R^1 = R^2 = Me$
(7) $R^1 = R^2 = CO_2Me$	(16) $R^1 = H$, $R^2 = Me$
(8) $R^1 = H$, $R^2 = Me$	(17) $R^1 = Me$, $R^2 = H$
(9) $R^1 = Me$, $R^2 = H$	(18) $R^1 = H$, $R^2 = Ph$
(10) $R^1 = H$, $R^2 = Ph$	(19) $R^1 = Ph$, $R^2 = H$
(11) $R^1 = Ph$, $R^2 = Me$	(20) $R^1 = Ph$, $R^2 = Me$
(12) $R^1 = Me$, $R^2 = Ph$	(21) $R^1 = Me$, $R^2 = Ph$

mixtures of isomers, *e.g.* (8) and (9), inseparable by chromatography or crystallisation.

Elemental analyses and mass spectra (see Table 1) of (4)—(21) revealed that the complexes were derived by replacement of one CO in $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ by one molecule of alkyne. However, i.r. spectra clearly indicated that a more complicated reaction than simple ligand exchange had occurred. Bands were observed characteristic of terminal and bridging carbon monoxide, but also others at frequencies more typical of ketonic CO (see Table 2). For example, the complex (13) has absorptions at 1 978s, 1 803s, and 1 731m cm^{-1}. This indication that alkyne and CO had combined was confirmed by an *X*-ray diffraction study of (13).

The structure of (13) is displayed in Figure 1, which also shows the atom-numbering scheme, while Figure 2 presents a stereodrawing of the molecule. Interatomic distances and interbond angles are given in Tables 3 and 4. The molecule is based on two ruthenium atoms at a

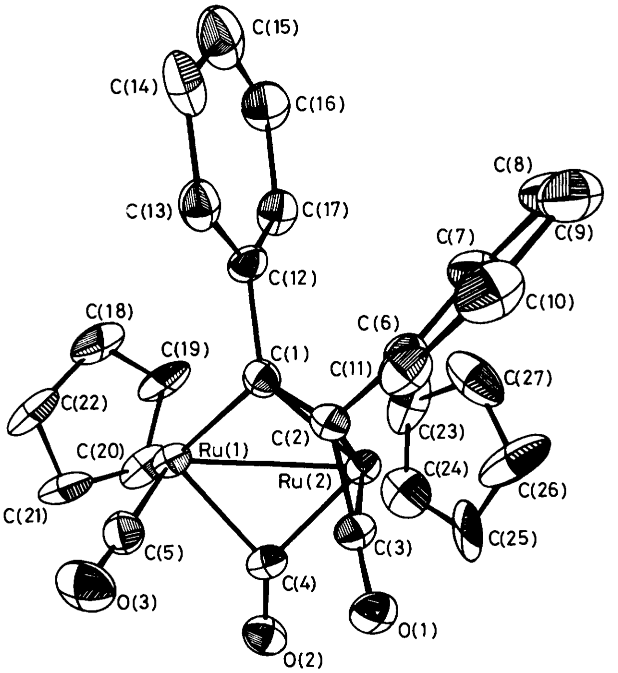


FIGURE 1 Molecular structure of (13), with atomic numbering scheme. Thermal ellipsoids are constructed at the 50% probability level

TABLE 1

Physical and analytical data for new compounds

Compound	Colour	M.p. (°C)	Analysis (%) [a] C	Analysis (%) [a] H	*M* [a, b]
(4)	Green	>200 [c]	50.9 (51.1)	3.4 (3.4)	352 (352)
(5)	Olive green	172—178 [c]	53.6 (53.7)	3.3 (4.2)	380 (380) [d]
(6)	Brown	129—131 [c]	64.0 (64.2)	4.3 (3.9)	448 [e] (504)
(7)	Dark brown	151 [f]	49.0 (48.7)	3.5 (3.4)	444 (444)
(8)/(9)	Olive green	175—180 [c]	59.0 (58.9)	3.8 (3.8)	366 (366)
(10)	Brown	189—191 [c]	58.4 (58.9)	3.6 (3.7)	428 (428)
(11)/(12)	Dark green	154	59.5 (59.7)	3.8 (3.6)	442 (442) [d]
(13)	Red	170—172	54.0 (54.5)	3.4 (3.4)	595 (595)
(14)	Brown	164—166 [f]	40.6 (40.7)	2.7 (2.7)	443 (443)
(15)	Orange	178—180 [f]	43.7 (43.4)	3.7 (3.4)	471 (471)
(16)/(17)	Orange	190—195	42.1 (42.1)	3.1 (3.2)	457 (457)
(18)/(19)	Orange	193—195 [f]	48.8 (48.7)	3.5 (3.1)	519 (519)
(20)/(21)	Orange	195	49.1 (49.5)	3.6 (3.4)	533 (533)
(28) *cis*	Orange	206—209 [c]	48.9 (48.7)	3.5 (3.4)	468 (468)
trans	Purple	206—209 [c]	48.6 (48.7)	3.6 (3.4)	468 (468)
(29)	Yellow	190—192 [c]	40.8 (40.7)	2.9 (2.9)	559 (559)
(30)	Green	150—154 [c]	55.8 (55.9)	4.2 (4.3)	322 (322)
(31)	Green	180—182 [c]	49.2 (49.5)	3.7 (3.8)	582 (582)
(35)	Orange	159—163	37.9 (37.9)	2.5 (2.1)	667 (667)

[a] Calculated values in parentheses. [b] By mass spectrometry with electron-impact ionisation. [c] Melts with decomposition. [d] By mass spectrometry with field-desorption ionisation. [e] Heaviest ion $(M - 2CO)^+$. [f] Isomerises on melting.

TABLE 2

I.r. and n.m.r. data for new compounds

Compound	Carbonyl bands (cm^{-1}) [a]	^{1}H N.m.r. (δ/p.p.m.) [b]	^{13}C N.m.r. (δ/p.p.m.) [c]
(4)	1 977s, 1 820 (sh), 1 806 (sh), 1 789m, 1 751m	2.44 (d, *J* 7.5, 1 H), 4.78 (s, 5 H), 5.09 (s, 5 H), 12.45 (d, *J* 7.5, 1 H)	13.2 (CH), 86.8 (C_5H_5), 88.2 (C_5H_5), 181.0 (CH), 212.9 (CO), 234.3 (C=O), 261.3 (μ-CO)
(5)	1 969s, 1 790s, 1 745m	1.55 (s, 3 H), 3.78 (s, 3 H), 4.78 (s, 5 H), 5.14 (s, 5 H) [d]	
(6)	1 977s, 1 797s, 1 751m	4.75 (s, 5 H), 4.86 (s, 5 H), 7.24 (m, 10 H) [d]	
(7)	1 992s, 1 816s, 1 767m, 1 700m (CO_2Me)	3.73 (s, 3 H), 4.20 (s, 3 H), 4.93 (s, 5 H), 5.05 (s, 5 H)	52.4 (CO_2*Me*), 52.5 (CO_2*Me*), 89.6 (C_5H_5), 90.1 (C_5H_5), 211.3 (CO), 222.3 (C=O), 257.1 (μ-CO)
(8)/(9)	1 974s, 1 773s, 1 754m, 1 734m	1.60 (s, 3 H), 3.89 (s),[e] 4.65 (s, 5 H), 4.95 (s, 5 H), 11.78 (s, 1 H)	
(10)	1 977s, 1 794s, 1 746m	4.59 (s, 5 H), 5.13 (s, 5 H), 7.38 (m, 3 H), 7.80 (m, 2 H), 12.83 (s, 1 H)	
(11)/(12)	1 973s, 1 800s, 1 754m	1.32 (s, 3 H), 4.00 (s),[e] 4.82 (s, 5 H), 5.05 (s, 5 H), 7.42 (m, 3 H), 8.08 (m, 2 H) [c]	
(13)	1 978s, 1 803s, 1 731m	5.28 (s, 5 H), 5.56 (s, 5 H), 7.30 (m, 10 H) [c]	4.53 (*C*Ph), 89.7 (C_5H_5), 92.5 (C_5H_5), 127.3 (Ph), 128.0 (Ph), 129.3 (Ph), 129.9 (Ph), 131.1 (Ph), 179.2 (*C*Ph), 201.5 (CO), 217.8 (C=O), 238.2 (μ-CO) [f]
(14)	1 974s, 1 805m, 1 794m, 1753m	3.42 (d, *J* 7, 1 H), 5.16 (s, 5 H), 5.40 (s, 5 H), 10.94 (d, *J* 7, 1 H)	24.0 (CH), 87.7 (C_5H_5), 89.7 (C_5H_5), 156.7 (CH), 199.6 (CO), 222.4 (C=O), 236.0 (μ-CO) [g]
(15)	1 974s, 1 799s, 1 749m	1.72 (s, 3 H), 3.47 (s, 3 H), 5.20 (s, 5 H), 5.52 (s, 5 H) [c]	16.9 (Me), 36.8 (Me), 41.6 (*C*Me), 88.4 (C_5H_5), 90.7 (C_5H_5), 178.0 (*C*Me) [g,h]
(16)/(17)	1 975s, 1 801s, 1 753m, 1 732m	1.74 (s, 3 H), 5.25 (s, 5 H), 5.51 (s, 5 H), 10.50 (s, 1 H), [3.16 (s, 1 H), 3.49 (s, 3 H), 5.23 (s, 5 H), 5.55 (s, 5 H)] [c,i]	21.4 (Me), 41.3 (*C*Me), 87.5 (C_5H_5), 89.0 (C_5H_5), 155.4 (CH), 211.9 (CO), [87.9 (C_5H_5), 89.7 (C_5H_5)] [b,h,i]
(18)/(19)	1 977s, 1 803s, 1 746m	5.16 (s, 5 H), 5.62 (s, 5 H), 7.35 (m, 5 H), 11.33 (s, 1 H), [3.43 (s, 1 H), 5.30 (s, 5 H), 5.43 (s, 5 H), 7.35 (m, 5 H)] [c,i]	43.7 (*C*Ph), 89.0 (C_5H_5), 90.2 (C_5H_5), 127.5 (Ph), 127.9 (Ph), 129.0 (Ph), 139.6 (Ph), 152.1 (CH), 200.5 (CO), 221.2 (C=O) [j]
(20)/(21)	1 976s, 1 802s, 1 748m	1.42 (s, 3 H), 3.59 (s),[e] 5.00 (s, 5 H), 5.30 (s, 5 H), 7.34 (m, 5 H)	
(28) *cis*	2 010s, 1 976m, 1 805s, 1 698m (CO_2Me)	3.95 (s, 6 H), 4.95 (s, 10 H)	51.6 (CO_2*Me*), 89.5 (C_5H_5), 165.9 (*C*O_2Me), 211.1 (CO), 266.1 (μ-CO) [g]
trans	1 975m, 1 805s, 1 698m (CO_2Me)	3.95 (s, 6 H), 4.86 (s, 10 H)	54.9 (CO_2*Me*), 91.5 (C_5H_5), 166.1 (*C*O_2Me) [g,h]
(29)	2 005s, 1 971m, 1 784m, 1 685m (CO_2Me)	3.80 (s, 6 H), 5.39 (s, 10 H)	52.1 (CO_2*Me*), 91.2 (C_5H_5), 122.4 (*C*CO_2Me), 170.1 (*C*O_2Me), 198.4 (CO), 235.4 (μ-CO) [g]
(30)	1 978s	4.34 (s, 5 H), 4.70 (s, 5 H), 5.30 (m, 2 H), 8.99 (m, 2 H)	
(31)	1 982s	3.73 (s, 3 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 3.95 (s, 3 H), 4.92 (s, 5 H), 4.97 (s, 5 H)	
(35)	2 079s, 2 038s, 2 025s, 2 001s, 1 992s, 1 988s, 1 972s, 1 954w, 1 809m, 1 779 (sh), 1 769m, 1 751w [k]	4.98 (d, *J* 2, 2 H), 5.04 (d, *J* 2, 2 H), 5.25 (s, 5 H), 5.46 (s, 5 H)	

[a] In CH_2Cl_2 solution. [b] In $CDCl_3$ solution, coupling constants in Hz. [c] In C_5D_5N solution. [d] In CD_3CN solution. [e] Methyl signal of minor isomer. [f] At −30 °C. [g] In CD_2Cl_2 solution. [h] CO signals unobserved. [i] Data for minor isomer in square brackets. [j] Minor isomer unobserved. [k] In cyclohexane solution.

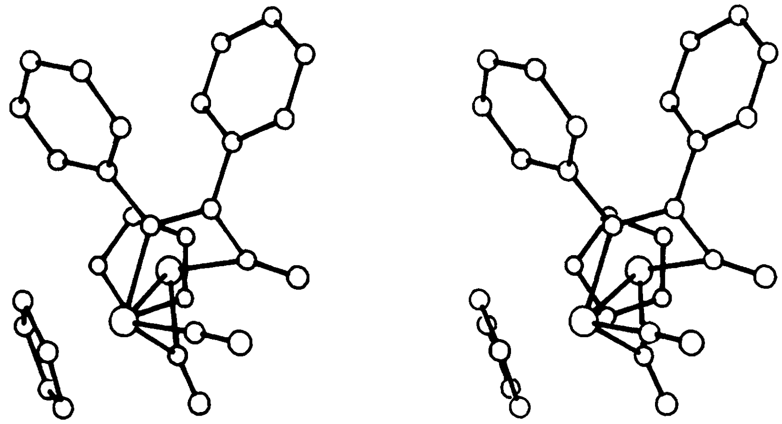


FIGURE 2 Stereoscopic view of (13)

single bond distance [2.729(1) Å], bridged symmetrically by a carbonyl group; ruthenium Ru(1) also carries a terminal carbonyl, and each metal atom has a cyclopentadienyl ligand bound in an η^5 fashion. Also bridging the diruthenium centre is a species derived from the linking of a diphenylacetylene molecule and carbon monoxide. The bonding of this ligand can be formalised in two ways. In the first, shown as (13a), it is represented as a dimetallacyclopentenone ring Ru(1)–C(1)–C(2)–C(3)–Ru(2) in which the ethylenic bond C(1)–C(2) is itself η^2-bound to Ru(2). In the second formalism (13b) the atom C(1) is regarded as a μ-carbene with a ketenic substituent [C(2)=C(3)=O(1)] which is η^2-bonded through C(2)–C(3) to Ru(2). The available geometric evidence suggests that the actual bonding situation lies somewhere between these two extremes, *i.e.* the ' allylic ' form (13c) has some validity, but is considerably closer to (13a) than (13b). The bond C(1)–C(2) shows only a little rotation, such that the dihedral angle between the planes formed by C(1), C(2), and C(12) and by C(1), C(2), C(3), and C(6) is 5.6°. In contrast, the plane formed by atoms C(2), C(3), O(1), and Ru(2) makes an angle of 128.4° with the ' ethylenic ' plane, indicating considerable rotation about C(2)–C(3). The bond length C(1)–C(2) [1.423(6) Å] is within the range for a co-ordinated double bond; for example, in $K[PtCl_3(C_2H_4)]$ [7] C–C is 1.375(4) Å and in $[Ni\{P(OC_6H_4Me\text{-}o)_3\}_2(C_2H_4)]$ [8] 1.46(2) Å. It is also close to the 1.41 Å expected for an allyl group. However, the bond length C(2)–C(3) [1.461(5) Å] is only fractionally shorter than that found [9] in studies of a range of 2-propen-1-ones (1.47—1.50 Å) and cannot be seen as conclusive evidence of some π character in this bond.

TABLE 3

Important interatomic distances (Å) for $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$ (13) *

Ru(1)–Ru(2)	2.729(1)	Ru(2)–C(23)	2.323(3)
Ru(1)–C(1)	2.080(4)	Ru(2)–C(24)	2.253(4)
Ru(1)–C(4)	2.039(4)	Ru(2)–C(25)	2.191(4)
Ru(1)–C(5)	1.865(5)	Ru(2)–C(26)	2.223(4)
Ru(1)–C(18)	2.284(3)	Ru(2)–C(27)	2.305(4)
Ru(1)–C(19)	2.289(4)	C(12)–C(1)	1.499(5)
Ru(1)–C(20)	2.268(4)	C(1)–C(2)	1.423(6)
Ru(1)–C(21)	2.249(3)	C(2)–C(3)	1.461(5)
Ru(1)–C(22)	2.259(4)	C(2)–C(6)	1.497(5)
Ru(2)–C(1)	2.158(4)	C(3)–O(1)	1.198(5)
Ru(2)–C(2)	2.219(4)	C(4)–O(2)	1.179(5)
Ru(2)–C(3)	2.011(4)	C(5)–O(3)	1.138(5)
Ru(2)–C(4)	2.005(4)		

* Throughout the tables of crystallographic data estimated standard deviations are given in parentheses.

TABLE 4

Important bond angles (°) for (13)

Ru(1)–C(1)–C(2)	122.9(3)	C(1)–Ru(1)–C(5)	89.3(2)
Ru(1)–C(1)–Ru(2)	80.1(1)	Ru(2)–Ru(1)–C(5)	103.8(2)
Ru(1)–C(1)–C(12)	118.3(3)	C(4)–Ru(1)–C(5)	85.3(2)
C(12)–C(1)–C(2)	117.3(4)	C(1)–Ru(1)–Ru(2)	51.2(1)
C(12)–C(1)–Ru(2)	131.1(3)	C(4)–Ru(1)–Ru(2)	47.0(1)
C(1)–C(2)–C(6)	124.2(4)	C(1)–Ru(1)–C(4)	93.0(2)
C(1)–C(2)–C(3)	116.1(4)	Ru(1)–Ru(2)–C(1)	48.7(1)
C(1)–C(2)–Ru(2)	68.7(2)	Ru(1)–Ru(2)–C(2)	76.6(1)
C(6)–C(2)–C(3)	117.3(4)	Ru(1)–Ru(2)–C(3)	86.4(1)
C(6)–C(2)–Ru(2)	126.3(3)	Ru(1)–Ru(2)–C(4)	48.1(1)
C(3)–C(2)–Ru(2)	62.3(3)	C(1)–Ru(2)–C(2)	37.9(2)
C(2)–C(3)–O(1)	138.1(5)	C(1)–Ru(2)–C(3)	71.8(2)
C(2)–C(3)–Ru(2)	77.7(4)	C(1)–Ru(2)–C(4)	91.7(2)
O(1)–C(3)–Ru(2)	143.6(4)	C(2)–Ru(2)–C(3)	40.1(2)
Ru(1)–C(4)–Ru(2)	84.9(2)	C(2)–Ru(2)–C(4)	100.6(2)
Ru(1)–C(4)–O(2)	136.8(4)	C(3)–Ru(2)–C(4)	79.1(2)
Ru(2)–C(4)–O(2)	138.2(4)		
Ru(1)–C(5)–O(3)	176.7(5)		

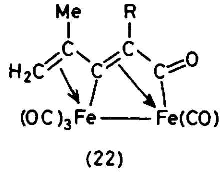
The co-ordinated ' ethylenic ' fragment rests at distances Ru(2)–C(1) 2.158(4) and Ru(2)–C(2) 2.219(4) Å. The longer of these is identical to that found in the unsubstituted ethylene complex $[RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2]$.[10] The slightly shorter Ru(2)–C(1) distance indicates some involvement of (13b) in the bonding. The distances Ru(2)–C(3) [2.011(4) Å] and Ru(1)–C(1) [2.080(4) Å] are more typical of σ bonding.

The bond length C(3)–O(1) [1.198(5) Å] of the metallacyclic carbonyl group is entirely typical of propenones.[9] The angle O(1)–C(3)–C(2) of 138.1(5)° is, however, problematical. In the metallacyclic ketonic complex $[Mo\{C(O)CH_2CH_2NH\}(CO)_2(\eta\text{-}C_5H_5)]$ [11] the angle O–C–C at the ketonic carbon atom is 119.6(2.0)° and in a related ' allylic ketone ' $[\overline{Mo\{C(O)C_4Me_4C(CF_3)_2O}\}(CO)(\eta\text{-}C_5H_5)]$ [12] the corresponding angle is 130.8(1.2)°. This deviation from the ideal geometry in complex (13) can be rationalised as due to a contribution of (13b), with *sp* carbon C(3), to the overall structure but may be more subtle as there are considerable distortions at C(3) arising from the bonding requirements of other parts of the molecule.

The cyclopentadienyl ligands on the two metal atoms are mutually *cis* with respect to the metal–metal axis, such that the angle between the normals to the planes of the rings is 90.9°. There is an asymmetry in the bonding of the C_5H_5 ring attached to Ru(2), and this is consistent with the expected *trans* effects of the groups in the three co-ordination positions opposite. The shortest approach of the ring is *trans* to the Ru–Ru bond and the ' ethylenic ' portion of the bridge; the longest distance is *trans* to the carbonyl and ketonic carbon atoms.

The interactions of the metal atoms with terminal and bridging carbonyl groups are unremarkable and the metal–metal bond length is quite normal. There are no intermolecular contacts less than 3.0 Å.

The compounds (22), derived from the reactions of 1-en-3-ynes with $[Fe_2(CO)_9]$, have been shown to contain a bridging unit very related to that in (4)—(21).[13] Here also *X*-ray data were indicative of a large contribution from a dimetallacyclopentenone form to an allylic representation.

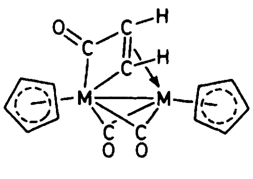


(22)

There is substantial n.m.r. evidence to suggest that the ' bridging ' carbon C(R^1) in the complexes (4)—(21)

may be likened to a μ-carbene. Carbon-13 and proton n.m.r. data thus reveal large shift differences between the CR^1 and CR^2 fragments of the ' alkyne ' portion of the dimetallacyclopentenone ring, with the CR^1 unit having low-field values typical of a μ-carbene. For example, for each of those compounds for which ^{13}C spectra have been obtained one ' alkyne ' carbon resonates in the range δ 152—181 and the other at 13—45 p.p.m. The latter is characteristic of co-ordinated olefinic carbon and can be assigned with confidence to $C(R^2)$, while the former, due to $C(R^1)$, may be compared with the μ-carbene carbon shifts in *cis*-$[Fe_2(CO)_3(\mu\text{-CHMe})(\eta\text{-}C_5H_5)_2]$ [14] and $[Rh_2(\mu\text{-}CPh_2)_2(\eta\text{-}C_5H_5)_2]$,[15] observed at 172.9 and 188.2 p.p.m. respectively. Proton n.m.r. spectra also indicate that the CR^1 group has μ-carbene character, in that the complexes (4), (8), (10), (14), (16), and (18) derived from HC_2H or HC_2R exhibit a signal at the very low field (δ 10—13) to be expected of a μ-CHR proton, such as that in *cis*-$[Fe_2(CO)_3(\mu\text{-CHMe})(\eta\text{-}C_5H_5)_2]$ [14] which occurs at δ 11.6. Protons present as R^2, in (4), (9), (14), (17), and (19), are seen in the range δ 2.4—3.4 characteristic of co-ordinated olefinic CR^2. Methyl groups also show large differences in proton shifts according to their position of substitution in the dimetallacyclopentenone ring. This is exemplified by (5) and (15), derived from but-2-yne, where an R^1 methyl resonates at δ 3.4—3.8 and an R^2 methyl at δ 1.5—1.7. Recognising the implication of such shifts has proved invaluable in identifying isomers like (8) and (9) or (16) and (17).

The i.r. spectra of the complexes (4) and (14) require some comment. Each shows a pattern of carbonyl bands characteristic of the group of compounds (4)—(21) in general, and in accord with the results of the structural study of (13). However, there are additional bands in the bridging carbonyl region, at 1 820(sh) and 1 806(sh) cm^{-1} for (4), and at 1 805m cm^{-1} for (14). The presence in solution of an isomer with only bridging carbonyls is indicated, perhaps with structure (23). Such an arrangement of alkyne and linked CO, η^2-bound to each metal atom, is known in the complex $[W_2(CO)_4\{\mu\text{-}\eta^2:\eta^2\text{-}C(O)C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (24).[4] Carbon-13 and proton n.m.r. spectra provide no additional evidence for the existence of this second isomer, from which it is concluded that rapid interconversion occurs with the established form. The i.r. spectrum of (4) does contain a weak band at *ca.* 1 600 cm^{-1} which could be attributed to a metallacyclic CO in (23), by comparison with (24) where the appropriate band is seen at 1 601 cm^{-1}. These effects are seen only with (4) and (14), which are derived from HC_2H, suggesting that an isomer of form (23) is disfavoured when more sterically demanding substituents are present.



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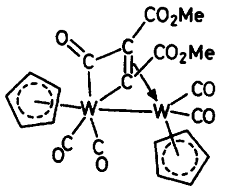


(24)

Steric effects also appear to be significant in determining the ratios of the isomers which arise in the dimetallacyclopentenones prepared from unsymmetrical alkynes $R^1C_2R^2$. Where at least one substituent is H identification of the isomers is readily achieved on the basis that a very low field proton shift in the n.m.r. spectrum is due to H residing on the bridging carbon of the dimetallacycle, for reasons discussed earlier. As a result, it is evident that from $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and propyne an (8) : (9) ratio of *ca.* 20 : 1 is obtained at ambient temperature, while from phenylacetylene only isomer (10) is present in detectable concentration. Clearly, the preferred isomer is the one in which the least bulky substituent is attached to the μ-C of the dimetallacyclopentenones, *i.e.* as R^1 in the diagrams. The corresponding ratios of isomers for the ruthenium analogues (16) : (17) and (18) : (19) are *ca.* 7 : 1 and 10 : 1 respectively, lower ratios which show that steric factors, although still controlling, are as expected less significant for the larger metal. Inspection of Figure 2 does show that a substituent R^1 is held on the same side of the metal–metal axis as, and between, the two *cis*-oriented C_5H_5 ligands and that the R^2 substituent is in a more open site. When neither R^1 nor R^2 is hydrogen, electronic influences appear to be dominant in selecting the more stable isomer. Thus, from PhC_2Me, (11) : (12) and (20) : (21) ratios of *ca.* 25 : 1 are produced when steric arguments alone might have predicted the reverse situation; it is concluded that in such systems the most electron-withdrawing substituent is seen as R^1 in preference to R^2.

Steric factors appear also to be important in the fluxional behaviour which is exhibited by each of the complexes (4)—(21). The fluxionality involves an unprecedented low-energy carbon–carbon bond-making and -breaking, and is best discussed separately for the cases where $R^1 = R^2$ and where $R^1 \neq R^2$. In the first instance, each complex of a symmetrically disubstituted alkyne displays, at room temperature or below, ^1H and ^{13}C n.m.r. spectra (Table 2) in accord with the solid-state structure determined for (13), *i.e.* inequivalent C_5H_5 ligands, inequivalent R groups, and three CO environments. On warming, spectral changes characteristic of fluxional motion follow, leading to the eventual time-average equivalence of the C_5H_5 ligands, the R groups, and two of the CO groups. This is exemplified by complex (7), whose n.m.r. spectra are shown in Figures 3 and 4. It is clear that the substituents R^1 and R^2 can only become equivalent on the n.m.r. time scale if there is a rapid breaking and regeneration of the ' alkyne–CO ' link, involving *both* ends of the ' alkyne.' Moreover, the ^{13}C n.m.r. spectrum (Figure 4) of a ^{13}CO-enriched sample of (7) reveals that an exchange only of terminal and metallacyclic ketonic CO occurs in the fluxional process, and that the bridging CO remains immobile. At −30 °C (7) shows ^{13}CO signals at 257.1, 222.3, and 211.3 p.p.m., that at lowest field being characteristic of a bridging CO group on iron. Thus, for [$Fe_2(CO)_4(\eta$-$C_5H_5)_2$] (in CD_2Cl_2 at −100 °C) the bridging and terminal CO signals are observed at 272.9 and 210.9 p.p.m., respectively. Although the individual assignment of terminal or metallacyclic CO to a particular 222.3 or 211.3 p.p.m. signal cannot be made with complete confidence on this basis, it is the recognition of their environmental exchange which is important. At 90 °C this pair of signals has collapsed into coalescence while that of the bridging CO remains sharp. Isomerisation of (7) to a dimetallacyclobutene complex at higher temperatures (see below) prevented the high-temperature-limiting spectrum being achieved.

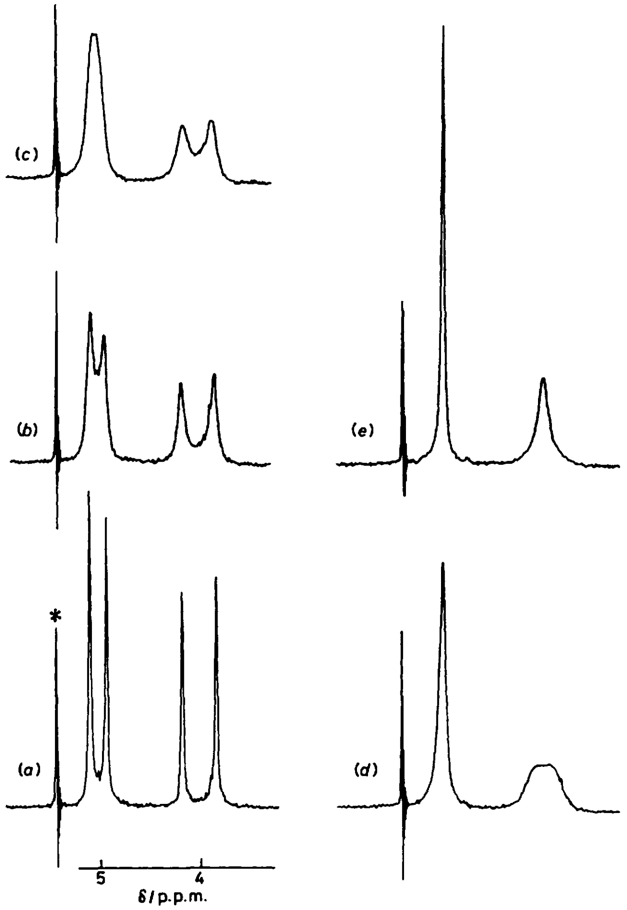


FIGURE 3 Proton n.m.r. spectrum of (7) at (a) 25, (b) 45, (c) 56, (d) 67, and (e) 76 °C in [$^2H_3$]acetonitrile solution. The asterisk denotes CH_2Cl_2

This spectroscopic behaviour is accounted for by the occurrence of the fluxional process illustrated as (25) $\rightleftharpoons$ (26). This involves an unprecedented reversible ejection of CO from the dimetallacycle to become a terminal ligand, and migration of the other end of the ' alkyne' to the existing terminal CO. Alternatively, this can be considered as synchronous carbonyl insertion (strictly alkyl migration) into, and elimination from, the dimetallacycle. Reference to the structure of (13) (Figure 1) allows the fluxionality to be seen as the creation of a new bond C(1)–C(5) at the same time as the bond C(2)–C(3) is cleaved; C(2) moves into the bridging position occupied by C(1), which loses co-ordination to Ru(2) in its shift towards C(5). The small movement required of the CO groups is striking. We believe that the process is best viewed as this concerted molecular rearrangement rather than one in which there is a distinct transient-μ-alkyne species such as (27) or (28). Both these latter can, in fact, be ruled out. A study of the ^1H n.m.r. spectra of the complexes (16)/(17) and (18)/(19), for which $R^1 \neq R^2$, reveals four cyclopentadienyl signals at low temperatures due to the presence of

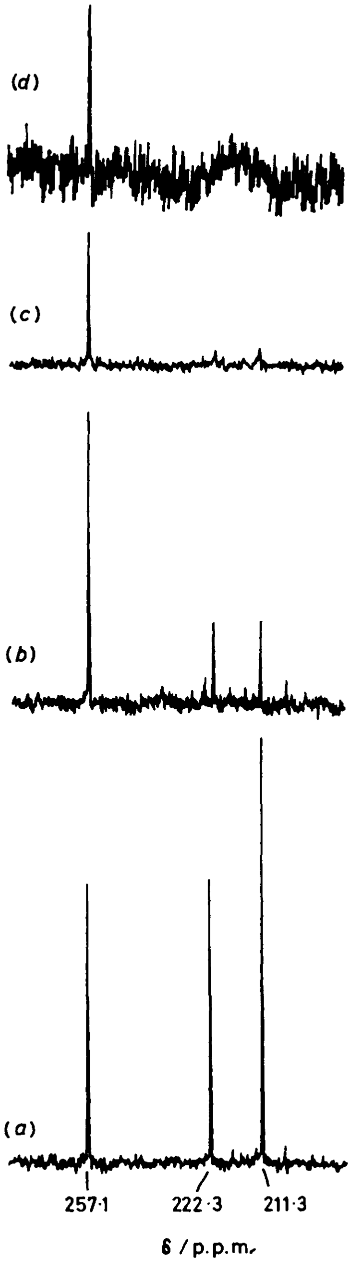
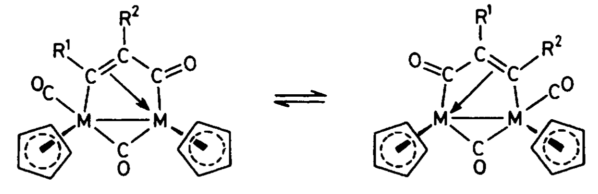


FIGURE 4 Carbon-13 n.m.r. spectrum of ^{13}CO-enriched (7) at (a) −30, (b) 30, (c) 60, and (d) 90 °C in [$^2H_5$]pyridine solution

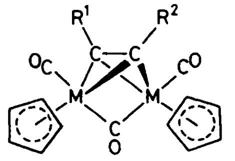
two non-degenerate isomers (25) and (26). On raising the temperature, coalescence is induced and at the high-temperature limit two sharp C_5H_5 signals are observed, as expected for a (25) $\rightleftharpoons$ (26) interconversion. This is illustrated for complexes (18)/(19) in Figure 5. Any involvement of a species (27), with a laterally bridging



(25) (26)

alkyne, would allow the cyclopentadienyl ligands to become *equivalent*.

The possibility of a complex like (28) as an intermediate in the fluxional process is eliminated by the actual isolation of such species as stable complexes. Thus, while (7) is fluxional at temperatures up to 100 °C, at toluene reflux temperature (111 °C) or on heating above the melting point an irreversible ejection of CO from the dimetallacycle occurs to give $[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (28) in high yield as a



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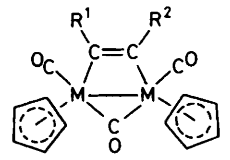


(28) M = Fe, $R^1 = R^2 = CO_2Me$
(29) M = Ru, $R^1 = R^2 = CO_2Me$

mixture of two isomers with *cis* and *trans* arrangements of the C_5H_5 and CO ligands. The nature of the isomers is readily shown by their i.r. spectra, the *cis* having two terminal CO bands and the *trans* one, as predicted on symmetry grounds.

Activation-energy data have been obtained for those complexes (4)—(21) which survived heating sufficiently for coalescence temperatures to be achieved and measured, and are collected in Table 5. It may first be noted, by reference to the data for compound (7), that the activation energy is the same for C_5H_5, R group, and CO averaging, confirming that a single fluxional process is responsible for each coalescence. The consistency of the values for this compound, and for (15), also suggest that whatever the worth of $\Delta G^‡$ in absolute terms when calculated in this way, it is valid to discuss trends in $\Delta G^‡$. In fact, the barriers generally appear to be higher for iron than for ruthenium compounds, but within each group both electron-releasing (Me) and -withdrawing (Ph or CO_2Me) substituents give rise to lower values of $\Delta G^‡$ than does H. This suggests (*a*) that steric factors are important in determining the size of the barrier, and (*b*) that there is less crowding in the transition state of the fluxional process than in the ground-state molecules. The greater size of ruthenium over iron would be expected to ease steric interactions and lower $\Delta G^‡$, as observed. The importance of steric factors in determining the relative stability of isomers (25) and (26) when $R^1 \neq R^2$ was recognised and discussed earlier.

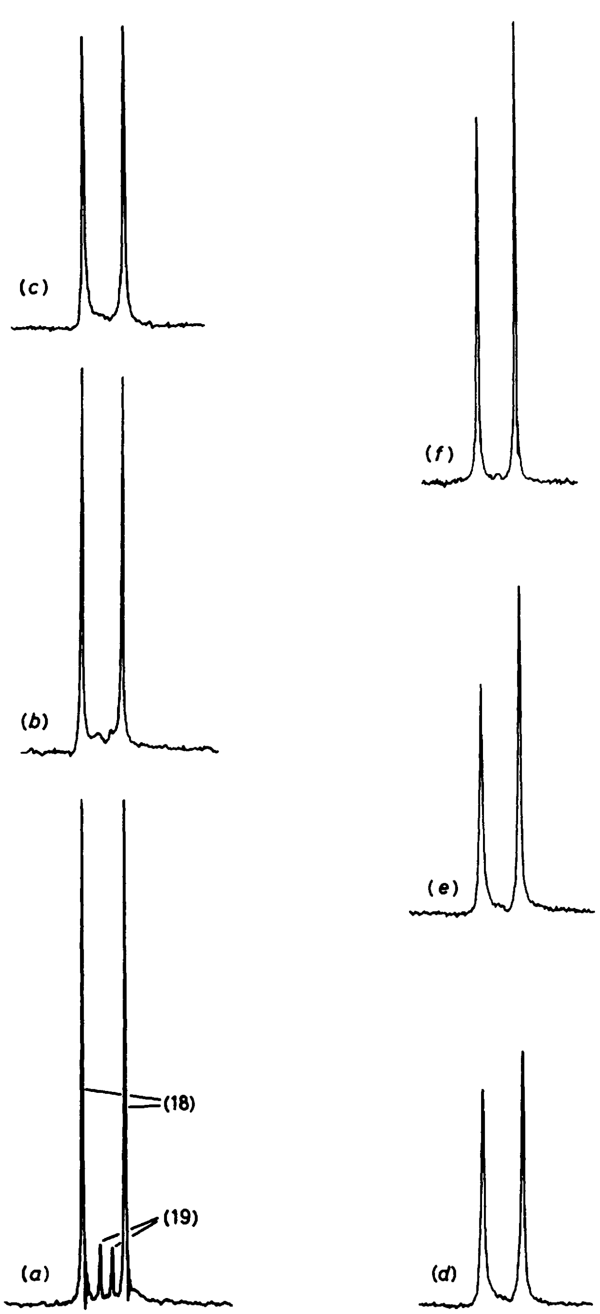


FIGURE 5 Proton n.m.r. spectrum (η-C_5H_5 signals) of (18)/(19) at (*a*) 30, (*b*) 50, (*c*) 60, (*d*) 70, (*e*) 80, and (*f*) 100 °C in $[^2H_5]$-pyridine solution

Like the fluxionality, the rapid and essentially quantitative alkyne-exchange reaction employed in the synthesis of (14)—(21) from (13) in boiling toluene is extraordinary for the ease with which a carbon–carbon

TABLE 5

Free energies of activation for the fluxional process

Compound	Solvent	Coalescing signals	$\Delta\nu$/Hz	T_c/K	$\Delta G^‡_{T_c}$/kJ mol^{-1} *
(4)	o-Dichlorobenzene	η-C_5H_5 (^1H)	29	399	84.8
(5)	[$^2H_5$]Pyridine	η-C_5H_5 (^1H)	36	368	77.3
(7)	[$^2H_3$]Acetonitrile	CO_2Me (^1H)	38	340	71.0
	[$^2H_3$]Acetonitrile	η-C_5H_5 (^1H)	18	329	70.1
	[$^2H_5$]Pyridine	CO (^{13}C)	276	363	70.1
(13)	[$^2H_5$]Pyridine	η-C_5H_5 (^1H)	30	317	66 7
(14)	[$^2H_5$]Pyridine	η-C_5H_5 (^1H)	23	371	79.4
(15)	[$^2H_5$]Pyridine	Me (^1H)	175	354	69.6
	[$^2H_5$]Pyridine	η-C_5H_5 (^1H)	32	330	69.4

* Calculated using the expression $\Delta G^‡_{T_c} = -RT \ln(\pi\Delta\nu h/\sqrt{2}kT_c)$, where T_c = coalescence temperature and $\Delta\nu$ = chemical shift separation of exchanging nuclei (D. Kost, E. H. Coulson, and M. Raban, *Chem. Commun.*, 1971, 656).

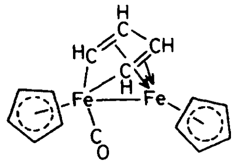
bond [C(2)–C(3) of (13)] is broken and another re-formed at the dinuclear metal centre. Displacement of PhC_2Ph appears equally fast whatever the incoming alkyne (or other reagent [16]), suggesting that a dissociative mechanism is in operation and that very reactive co-ordinatively unsaturated ' $Ru_2(CO)_3(\eta$-$C_5H_5)_2$ ' is involved. Such an intermediate, which would contain formally a double metal–metal bond, could be expected to co-ordinate an incoming alkyne at the diruthenium centre prior to alkyne–CO combination. Alkyne exchange in a metallacyclobutene has recently also been observed, with diphenylacetylene replacing bis(trimethylsilyl)acetylene in $[Ti\{CH_2C(SiMe_3)C(SiMe_3)\}(\eta$-$C_5H_5)_2]$.[17] While in the latter there is involved in all probability a transient terminal methylene ligand, in (13) it is a CO which fulfils this role.

The ruthenium analogue of (7) was not obtained upon treatment of (13) with dimethyl acetylenedicarboxylate. In boiling toluene (29) was formed, no doubt *via* the dimetallacyclopentenone which at this temperature rearranges to the dimetallacyclobutene in the same manner as (7). The alkyne-exchange reaction is useful only in synthesising ruthenium complexes. The diphenylacetylene complex of iron (6) is very unstable thermally and yields $[Fe_2(CO)_4(\eta$-$C_5H_5)_2]$ in attempted exchange reactions, while (4) reacts only with $MeO_2CC_2CO_2Me$, to yield (28).

Only a *cis* isomer of (29) was detected, contrasting with a 6 : 1 ratio of *cis* and *trans* (28) formed on heating of solid (7). Although separable by chromatography the *trans* isomer of (28) converts into the thermodynamically more stable *cis* form within 3 h at 25 °C in dichloromethane or 1.5 h in boiling toluene. This transformation is instantaneous if a drop of HBF_4 is added to an acetone solution of the *trans* isomer, probably occurring *via* a transient cationic μ-vinyl species $[Fe_2(CO)_2(\mu$-$CO)\{\mu$-$C(CO_2Me)CH(CO_2Me)\}(\eta$-$C_5H_5)_2]^+$.

Thermolysis of a dimetallacyclopentenone complex provides a dimetallacyclobutene only when $R^1 = R^2 = CO_2Me$. For other R groups either decomposition occurs or, when one or both is hydrogen, a quite different rearrangement to afford a μ-vinylidene complex, to be described in a subsequent paper in this series.

The reactions of alkynes with $[M_2(CO)_4(\eta$-$C_5H_5)_2]$ produce small amounts of products other than (4)—(21). Several of the $[Fe_2(CO)_4(\eta$-$C_5H_5)_2]$ reactions gave evidence of complexes with a single CO band in the i.r., but these were usually oily and unstable and not thoroughly characterised. Two of this number were, however, isolated as dark green crystalline substances and identified as $[Fe_2(CO)(\mu$-$C_4H_4)(\eta$-$C_5H_5)_2]$ (30) and $[Fe_2(CO)\{\mu$-$C_4(CO_2Me)_4CO\}(\eta$-$C_5H_5)_2]$ (31) (Tables 1 and 2). These are not new structural types, such metallacyclopentadiene and metallacyclohexadienone species being common issue of reactions of metal carbonyl with alkynes.[18,19] The presence of four methyl-group signals in the ^1H n.m.r. spectrum of (31) requires that there be no mirror plane of molecular symmetry, unlike (30). The isolation of (31) was not unexpected in view of the production of the analogous (32) when $[Fe_2(CO)_4(\eta$-$C_5H_5)_2]$ is subjected to u.v. irradiation in the presence of hexafluorobut-2-yne.[20] No complex of the type (4)—(21) was observed in this latter reaction, but such species are surely intermediates in the formation of both (31) and (32).



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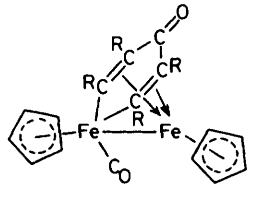
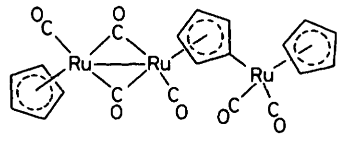


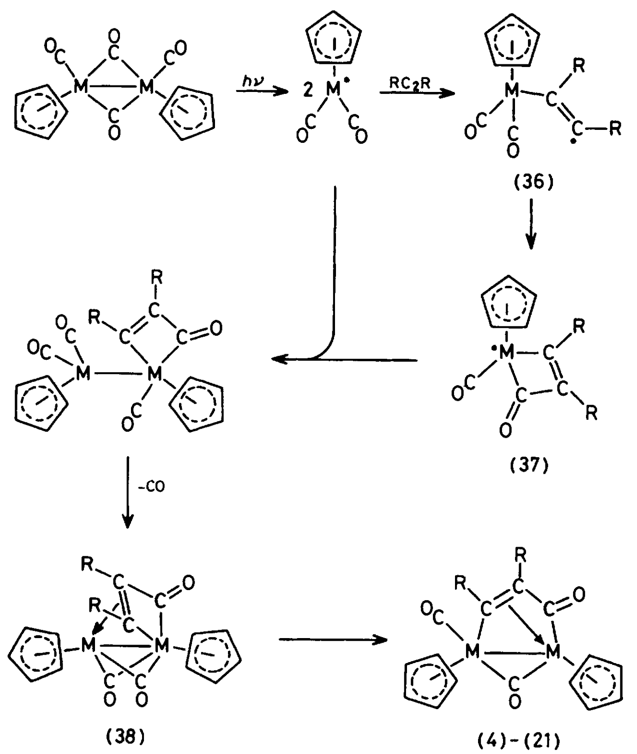
(31) R = CO_2Me
(32) R = CF_3
(33) R = H
(34) R = Me

A minor product of the reaction of diphenylacetylene with $[Ru_2(CO)_4(\eta$-$C_5H_5)_2]$ was identified (Tables 1 and 2) as the unusual complex $[Ru_2(CO)_4(\eta$-$C_5H_5)\{\eta$-$C_5H_4Ru(CO)_2(\eta$-$C_5H_5)\}]$ (35). It displays a very complicated carbonyl i.r. spectrum as a result, presumably, of the presence of both carbonyl-bridged and non-bridged isomers in solution, as is the case with $[Ru_2(CO)_4(\eta$-$C_5H_5)_2]$ itself, but a relatively simple ^1H n.m.r. spectrum



(35)

showing two η-C_5H_5 group signals and the signals typical of a monosubstituted η-C_5H_5R ring. The formation of this compound, which has been shown to arise upon photolysis of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ alone, is strong evidence for the generation of the $Ru(CO)_2(\eta\text{-}C_5H_5)$ radical. Indeed, studies of the photolysis of both $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ have shown that the primary photo-process is dissociation to yield $M(CO)_2(\eta\text{-}C_5H_5)$ radicals.[21] This leads us to suggest that the dimetallacyclopentenone complexes may evolve by the pathway laid out in the Scheme. Four further pieces of evidence may be given in its support: (*a*) the photochemical reaction of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $CF_3C_2CF_3$ affords $[Ru\{C(CF_3)C(CF_3)H\}(CO)_2(\eta\text{-}C_5H_5)]$ [20] as a major product, implicating the radical (36); (*b*) metallacyclobutenones like (37) are known; [3] (*c*) the dimetallacycle present in (38) is known in the ditungsten complex (24) [4] and there is evidence for its existence as a minor isomer (23) of (4), as discussed previously; and (*d*) the greater reactivity of diphenylacetylene with $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$; compared with the other alkynes studied here, can be attributed to the ability of phenyl groups to stabilise (36) through delocalisation.



SCHEME

CONCLUSION

The chemistry of the new dimetallacyclopentenone complexes is dominated by the lability of the bond between the alkyne and CO. This is shown by the fluxionality of the complexes, the alkyne-exchange reaction, and the isomerisation to dimetallacyclobutenes. The ease with which carbon–carbon bonds are made and broken at the dinuclear metal centres is striking, and suggests that dimetallacycles may play a more significant role in the catalysis of organic reactions than previously suspected. Later parts of this series will reveal that the lability of the dimetallacyclopentenones may be exploited to establish a substantial organic chemistry of di-iron and diruthenium centres.

EXPERIMENTAL

I.r. spectra were obtained with a Perkin-Elmer 257 instrument and calibrated using the absorption of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were recorded with either JEOL PS 100 or FX 200 spectrometers, the latter operating in the Fourier-transform mode. Carbon-13 n.m.r. spectra were similarly obtained using a JEOL FX 90 instrument, mass spectra with an AEI MS 902 spectrometer operating with field-desorption ionisation for samples of low volatility.

Reactions were performed in a nitrogen atmosphere, employing solvents dried by distillation over an appropriate drying agent as follows: alkanes (lithium aluminium hydride, calcium hydride, or Na–K alloy); toluene, tetrahydrofuran, and diethyl ether (sodium–benzophenone or Na–K alloy); acetone (anhydrous sodium sulphate). Chromatography was with alumina columns, unless stated otherwise. The u.v. irradiation source was a 250-W mercury lamp, held 20—40 cm from a silica glass reaction flask containing reagents and solvent agitated with a magnetic follower.

The complexes $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [22] and $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [23] were prepared by literature methods. Alkynes were used as supplied by B.D.H. (propyne), Koch-light (but-2-yne, phenylacetylene), and Aldrich (diphenylacetylene, dimethyl acetylenedicarboxylate); acetylene (British Oxygen) was purified by passing the gas in turn through water and sulphuric acid, then over solid potassium hydroxide and solid calcium chloride.

Physical, analytical, and spectroscopic data for new compounds are collected in Tables 1 and 2.

Preparations.—$[Fe_2(CO)_2\{\mu\text{-}C(O)C_2H_2\}(\eta\text{-}C_5H_5)_2]$ (4). Acetylene was gently bubbled through a toluene (200 cm^3) solution of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (2 g, 5.65 mmol) under u.v. irradiation for 5 d. The deep red solution turned brown and a brown powder precipitated. After evaporation of solvent under reduced pressure the residue was dissolved in dichloromethane–hexane and subjected to chromatography. Elution with hexane developed a yellow and a grey band. The former contained a trace of ferrocene and the latter yielded 0.19 g (10%) of green crystalline $[Fe_2(CO)(\mu\text{-}C_4H_4)(\eta\text{-}C_5H_5)_2]$ (30). Further elution with acetone–dichloromethane (1 : 9) gave a dark green band which provided 0.83 g (42%) of green crystalline (4). Final elution with neat methanol gave 60 mg (3%) of an air-sensitive green oil, tentatively identified as $[Fe_2(CO)(\mu\text{-}C_4H_4CO)(\eta\text{-}C_5H_5)_2]$ (33) on the basis of its i.r. [ν(CO) 1 962s and 1 706m cm^{-1}] spectrum.

$[Fe_2(CO)_2\{\mu\text{-}C(O)C_2Me_2\}(\eta\text{-}C_5H_5)_2]$ (5). But-2-yne (2.3 g, 42.6 mmol) was condensed (−196 °C) into a silica Young's tube containing a toluene (100 cm^3) solution of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (1.5 g, 4.24 mmol), which was then irradiated for 10 d. Chromatography as above, eluting with acetone–dichloromethane (1 : 9), separated bright green and olive green bands, but the former converted rapidly into the latter on leaving the column and was not identified. The combined material afforded 0.26 g (16%) of green crystalline (5). Further elution with acetone provided a trace of an air-sensitive green oil with an i.r. spectrum [ν(CO) 1 950s and 1 681s cm^{-1}] suggestive of $[Fe_2(CO)(\mu-C_4Me_4CO)(\eta-C_5H_5)_2]$ (34).

$[Fe_2(CO)_2\{\mu-C(O)C_2Ph_2\}(\eta-C_5H_5)_2]$ (6). A toluene (200 cm^3) solution of diphenylacetylene (6 g, 34 mmol) and $[Fe_2(CO)_4(\eta-C_5H_5)_2]$ (2 g, 5.65 mmol) was irradiated for 28 d. Chromatography, eluting with dichloromethane–hexane (4 : 1), then gave a brown band from which 0.27 g (11%) of brown powdery (6) was obtained.

$[Fe_2(CO)_2\{\mu-C(O)C_2(CO_2Me)_2\}(\eta-C_5H_5)_2]$ (7). A tetrahydrofuran (150 cm^3) solution of dimethyl acetylenedicarboxylate (3 g, 21 mmol) and $[Fe_2(CO)_4(\eta-C_5H_5)_2]$ (2 g, 5.65 mmol) was irradiated for 17 h. Chromatography, eluting with acetone–dichloromethane (1 : 9), developed a brown band which gave 2.26 g (86%) of dark brown crystalline (7). A dark green band was eluted in methanol, producing a few crystals of (31).

$[Fe_2(CO)_2\{\mu-C(O)C_2(H)Me\}(\eta-C_5H_5)_2]$ (8)/(9). Propyne (2.3 g, 57 mmol) was condensed (−196 °C) into a silica Young's tube containing a toluene (100 cm^3) solution of $[Fe_2(CO)_4(\eta-C_5H_5)_2]$, which was then irradiated for 4 d. Chromatography, eluting with acetone–dichloromethane (1 : 9), produced a green band which contained 1.16 g (56%) of the mixture of isomers (8) and (9). Bands containing traces of compounds with i.r. spectra characteristic of species analogous to (30) and (31) were also eluted.

$[Fe_2(CO)_2\{\mu-C(O)C_2(H)Ph\}(\eta-C_5H_5)_2]$ (10). A toluene (200 cm^3) solution of phenylacetylene (3.5 g, 34 mmol) and $[Fe_2(CO)_4(\eta-C_5H_5)_2]$ (2 g, 5.65 mmol) was irradiated for 16 h. Chromatography of the reaction mixture yielded a brown band on eluting with dichloromethane–hexane (4 : 1), from which 1.7 g (71%) of (10) were obtained.

$[Fe_2(CO)_2\{\mu-C(O)C_2(Me)Ph\}(\eta-C_5H_5)_2]$ (11)/(12). A solution of methyl(phenyl)acetylene (2.6 g, 22 mmol) and $[Fe_2(CO)_4(\eta-C_5H_5)_2]$ (2.0 g, 5.65 mmol) in toluene (200 cm^3) was irradiated for 19 d. Chromatography, eluting with acetone–dichloromethane (1 : 6), then afforded 2.1 g (84%) of dark green crystals of a mixture of isomers (11) and (12).

$[Ru_2(CO)_2\{\mu-C(O)C_2Ph_2\}(\eta-C_5H_5)_2]$ (13). A mixture of diphenylacetylene (1.68 g, 9.50 mmol) and $[Ru_2(CO)_4(\eta-C_5H_5)_2]$ (1.4 g, 2.36 mmol) in toluene (150 cm^3) was irradiated for 40 h, accompanied by a colour change from orange to dark red. Chromatography, eluting with dichloromethane–hexane (7 : 3), separated a yellow band which yielded 45 mg (3%) of yellow crystalline (35). This was followed, on elution with dichloromethane–acetone (20 : 1), by an orange band which afforded 0.92 g (49%) of orange crystalline (13).

$[Ru_2(CO)_2\{\mu-C(O)C_2H_2\}(\eta-C_5H_5)_2]$ (14). Acetylene was passed through a boiling toluene (125 cm^3) solution of (13) (0.25 g, 0.42 mmol) for 0.5 h, during which time the initially orange solution turned deep brown. After evaporation of solvent at reduced pressure the residue was washed several times with pentane and then recrystallised from dichloromethane–hexane to give brown needles of (14) in 90% yield (0.17 g).

$[Ru_2(CO)_2\{\mu-C(O)C_2Me_2\}(\eta-C_5H_5)_2]$ (15). But-2-yne (0.7 g, 13.9 mmol) was condensed (−196 °C) into a Carius tube containing (13) (0.5 g, 0.85 mmol) in toluene (50 cm^3) which, after sealing, was heated at 100 °C for 60 h. Chromatography on Florisil, eluting with dichloromethane–hexane (1 : 1), gave a small amount of $[Ru_2(CO)_4(\eta-C_5H_5)_2]$ followed, on eluting with neat dichloromethane, by an orange band yielding 0.31 g (80%) of orange crystalline (15).

$[Ru_2(CO)_2\{\mu-C(O)C_2(H)Me\}(\eta-C_5H_5)_2]$ (16)/(17). Propyne (0.7 g, 17.5 mmol) was condensed (−196 °C) into a Carius tube containing (13) (0.5 g, 0.85 mmol) in toluene (30 cm^3) which, after sealing, was heated at 100 °C for 36 h. After evaporation of solvent at reduced pressure the residue was washed several times with hexane and recrystallised from dichloromethane–hexane to give 0.307 g (80%) of an orange-red crystalline mixture of (16) and (17).

$[Ru_2(CO)_2\{\mu-C(O)C_2(H)Ph\}(\eta-C_5H_5)_2]$ (18)/(19). A mixture of (13) (0.25 g, 0.42 mmol) and phenylacetylene (0.85 g, 8.4 mmol) was heated in boiling toluene (100 cm^3) for 15 min. Chromatography, eluting with dichloromethane, then developed an orange band which produced 0.13 g (59%) of a mixture of (18) and (19) as orange flakes.

$[Ru_2(CO)_2\{\mu-C(O)C_2(Me)Ph\}(\eta-C_5H_5)_2]$ (20)/(21). A mixture of (13) (1 g, 1.68 mmol) and methyl(phenyl)acetylene (3 g, 25.9 mmol) was heated in boiling toluene (250 cm^3) for 10 min. Chromatography, eluting with dichloromethane, gave an orange band from which 0.75 g (84%) of an orange crystalline mixture of (20) and (21) was obtained.

$[Ru_2(CO)_2(\mu-CO)\{\mu-C_2(CO_2Me)_2\}(\eta-C_5H_5)_2]$ (29). A mixture of (13) (0.4 g, 0.67 mmol) and dimethyl acetylenedicarboxylate (0.6 g, 4.2 mmol) was heated in boiling toluene (100 cm^3) for 10 min. Chromatography, eluting with dichloromethane–hexane (9 : 1), afforded a yellow band which gave 0.17 g (46%) of yellow crystalline (29).

$[Fe_2(CO)_2(\mu-CO)\{\mu-C_2(CO_2Me)_2\}(\eta-C_5H_5)_2]$ (28). (*a*) Dark green (7) (0.52 g, 0.98 mmol) melted upon heating at 160 °C *in vacuo* for 10 min in a Young's tube, to produce a brown solid on cooling. Chromatography gave purple and orange bands on eluting with acetone–hexane (1 : 9) and (1 : 4) respectively. These yielded 70 mg (13%) of the *trans* and 0.43 g (83%) of the *cis* isomer of (28) in turn.

(*b*) A toluene (200 cm^3) solution of (7) (0.43 g, 0.81 mmol) was heated at reflux for 25 min, then chromatographed as in (*a*) to provide *trans* and *cis* isomers of (28) in 22% (95 mg) and 69% (0.3 g) yields respectively.

(*c*) A mixture of (4) (0.1 g, 0.28 mmol) and dimethyl acetylenedicarboxylate (0.1 g, 0.7 mmol) in toluene (100 cm^3) was heated at reflux for 30 min, then chromatographed as in (*a*) to yield 21 mg (14%) of the *trans* isomer of (28) and 20 mg (14%) of the *cis*.

The *trans* isomer of (28) was converted completely into the *cis* form on heating in toluene for 1.5 h.

X-*Ray Data Collection and Structure Determination*.—After preliminary photography which identified the space group and allowed calculation of approximate axial lengths, a crystal of $[Ru_2(CO)(\mu-CO)\{\mu-\sigma:\eta^3-C(O)C_2Ph_2\}(\eta-C_5H_5)_2]$ (13) of dimensions (0.25 × 0.2 × 0.1 mm) was transferred to a Syntex $P2_1$ diffractometer and aligned for data collection according to methods described earlier.[24,25] Of the total of 5 555 independent reflections measured in the range $2.9 \leqslant 2\theta \leqslant 60°$, 3 726 were deemed observed according to the criterion $I \geqslant 3.0\sigma(I)$, and only these were used in subsequent solution and refinement of the structure.

Crystal data. $C_{27}H_{20}O_3Ru_2$, $M = 594.6$, Orthorhombic, space group *Pbca*, $a = 14.797(3)$, $b = 17.805(8)$, $c = 16.739(8)$ Å, $U = 4\,410(3)$ Å^3, D_m not measured, $Z = 8$, $D_c = 1.79$ g cm^{-3}, $F(000) = 2\,352$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 9.9 cm^{-1}.

Two reflections ($13\bar{1}$ and $\bar{6}14$) were remeasured every 50 observations and indicated no significant crystal decomposition. The intensities were corrected for the effects of decay, *X*-ray absorption, Lorentz, and polarisation. All computation was carried out on the South Western Universities network using the SHELX-76 system of programs.[26]

The structure was solved by heavy-atom methods and all atoms (including hydrogen) were located. The atoms of the phenyl and cyclopentadienyl rings were incorporated into the model as rigid groups with C–C 1.396 Å and C–H 1.08 Å. All other atoms were refined freely. Non-hydrogen atoms were assigned anisotropic thermal parameters. The isotropic thermal parameters of all 20 hydrogen atoms were tied to a common variable. Refinement was by full-matrix least squares with an optimised weighting scheme of the form $w = 1.2014\ [\sigma^2(F) + 0.0007|F|^2]^{-1}$ where $\sigma(F)$ is the estimated error in $|F_{\text{obs.}}|$ based on counting statistics. Convergence was reached at *R* 0.033 (*R′* 0.035) and the final electron-density synthesis showed no peaks > 0.7 e Å^{-3} and no troughs < -0.6 e Å^{-3}. Atomic scattering factors were those of ref. 27 for hydrogen and ref. 28 for all other atoms. Corrections for the real and imaginary parts of anomalous scattering were applied for all atoms.[29] Table 6 lists the derived atomic co-ordinates. Thermal parameters and a comparison of $|F_o|$ *vs.* $|F_c|$ are deposited as Appendices * A and B respectively.

TABLE 6

Atomic positional (fractional co-ordinates) parameters for (13)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	−0.033 4(1)	0.143 6(1)	0.146 5(1)
Ru(2)	0.041 5(1)	0.196 3(1)	0.008 5(1)
C(1)	0.006 9(3)	0.252 4(2)	0.118 6(2)
C(2)	0.098 1(3)	0.271 7(2)	0.101 4(2)
C(3)	0.155 4(3)	0.210 8(2)	0.072 1(2)
C(4)	0.050 8(3)	0.096 8(2)	0.063 9(2)
C(5)	0.064 6(3)	0.135 7(2)	0.216 1(3)
C(6)	0.131 0(2)	0.350 4(1)	0.089 0(2)
C(7)	0.202 7(2)	0.375 1(1)	0.136 3(2)
C(8)	0.233 3(2)	0.449 0(1)	0.129 7(2)
C(9)	0.192 2(2)	0.498 1(1)	0.075 9(2)
C(10)	0.120 5(2)	0.473 3(1)	0.028 6(2)
C(11)	0.089 9(2)	0.399 5(1)	0.035 2(2)
C(12)	−0.057 4(2)	0.315 5(2)	0.135 3(1)
C(13)	−0.038 6(2)	0.362 1(2)	0.200 3(1)
C(14)	−0.094 4(2)	0.423 3(2)	0.216 8(1)
C(15)	−0.169 0(2)	0.438 0(2)	0.168 3(1)
C(16)	−0.187 8(2)	0.391 5(2)	0.103 4(1)
C(17)	−0.132 0(2)	0.330 2(2)	0.086 9(1)
C(18)	−0.178 8(2)	0.169 3(2)	0.183 1(2)
C(19)	−0.181 0(2)	0.135 6(2)	0.106 3(2)
C(20)	−0.144 9(2)	0.062 0(2)	0.113 2(2)
C(21)	−0.120 4(2)	0.050 2(2)	0.194 2(2)
C(22)	−0.141 4(2)	0.116 6(2)	0.237 5(2)
C(23)	−0.069 8(2)	0.199 3(3)	−0.089 4(2)
C(24)	−0.016 2(2)	0.133 5(3)	−0.096 7(2)
C(25)	0.074 3(2)	0.156 0(3)	−0.111 7(2)
C(26)	0.076 6(2)	0.235 7(3)	−0.113 7(2)
C(27)	−0.012 4(2)	0.262 5(3)	−0.099 9(2)
O(1)	0.232 3(2)	0.190 5(2)	0.078 6(2)
O(2)	0.084 6(2)	0.037 8(2)	0.053 0(2)
O(3)	0.122 7(2)	0.127 7(2)	0.259 8(2)

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