Organic Chemistry of Dinuclear Metal Centres. Part 8.[1] Organo-Iron–Ruthenium Chemistry. *X*-Ray Structure of *trans*-[FeRu$(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$]†

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The iron–ruthenium complex [FeRu$(CO)_4(\eta\text{-}C_5H_5)_2$] is obtained in 60% yield from the reaction of Na[Fe$(CO)_2(\eta\text{-}C_5H_5)$] with [RuI$(CO)_2(\eta\text{-}C_5H_5)$]. In the solid state a *trans*-[FeRu$(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] structure has been established by *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$ (no. 14), with $Z = 2$ in a unit cell for which $a = 7.064(2)$, $b = 12.518(3)$, $c = 8.011(2)$ Å, and $\beta = 106.23(2)°$. The structure was solved by heavy-atom methods and refined to R 0.0275 (R' 0.0313) for 1 532 independent intensities. The molecule is disordered about a centre of inversion at the mid-point of the metal–metal bond, each metal site being occupied by half an iron and half a ruthenium atom, with an iron–ruthenium bond length of 2.626(1) Å. In solution the *cis*-[FeRu$(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] isomer is dominant, and shown by ^{13}C n.m.r. to be undergoing *cis* $\rightleftharpoons$ *trans* isomerisation with bridge $\rightleftharpoons$ terminal carbonyl exchange at room temperature, but to be static at −80 °C. The complex is an excellent precursor of organo-iron–ruthenium chemistry. Treatment with alkynes $R^1C_2R^2$ ($R^1 = R^2$ = H, Me, Ph, or CO_2Me; R^1 = Me or Ph, R^2 = H) under u.v. irradiation gives complexes [FeRu(CO)$(\mu\text{-}CO)\{\mu\text{-}C(O)CR^1CR^2\}(\eta\text{-}C_5H_5)_2$] in 20—65% yield as a result of alkyne–CO linkage. This link in the complexes derived from ethyne, propyne, and but-2-yne is broken upon protonation, generating μ-vinyl cations [FeRu$(CO)_2(\mu\text{-}CO)(\mu\text{-}CR^1{=}CHR^2)(\eta\text{-}C_5H_5)_2]^+$ ($R^1 = R^2$ = H or Me; R^1 = H, R^2 = Me). These are attacked by hydride at the β carbon of the μ-vinyl to give μ-alkylidene complexes [FeRu$(CO)_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\eta\text{-}C_5H_5)_2$] ($R^1$ = H, R^2 = Me or Et; R^1 = Me, R^2 = Et). Reaction of [FeRu(CO)$(\mu\text{-}CO)\{\mu\text{-}C(O)CPhCPh\}(\eta\text{-}C_5H_5)_2$] with $Ph_3P{=}CHR$ or $CH(CO_2Et)N_2$ in boiling toluene also gives μ-alkylidene complexes [FeRu$(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR)(\eta\text{-}C_5H_5)_2$] (R = H, Me, or CO_2Et) in good yield, through ready displacement of diphenylacetylene. The $\mu\text{-}CH_2$ complex is best obtained (75%) by treating [FeRu$(CO)_4(\eta\text{-}C_5H_5)_2$] with $LiBHEt_3$ then water, and in a related manner sequential addition of methyl-lithium, $HBF_4{\cdot}OEt_2$, and $NaBH_4$ affords [FeRu$(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2$]. Under u.v. irradiation alkynes react with μ-alkylidene complexes [FeRu$(CO)_2(\mu\text{-}CO)(\mu\text{-}CHR^1)(\eta\text{-}C_5H_5)_2$] to give products of alkyne–alkylidene linking [FeRu(CO)$(\mu\text{-}CO)(\mu\text{-}CR^3CR^2CHR^1)(\eta\text{-}C_5H_5)_2$] ($R^1$ = H or Me, $R^2 = R^3$ = H, Me, Ph, or CO_2Me; R^1 = H or Me, R^2 = Me or Ph, R^3 = H). These exist as non-interconverting isomers in which the new C_3 ligand is either bound σ to iron and σ, η^2 to ruthenium or *vice versa*. The scope of organo-iron–ruthenium chemistry closely resembles that of the di-iron system but it is apparent that in reactivity terms there is an order: FeRu > Fe_2 > Ru_2.

The complexes [$M_2(CO)_4(\eta\text{-}C_5H_5)_2$] (M = Fe or Ru) provide an excellent entry into the organic chemistry of di-iron and diruthenium centres (see, for example, refs. 2—9). Our own approach has been recently reviewed,[10] and some aspects have been described in detail in earlier Parts of this Series. In comparison with homodinuclear systems relatively little is known of the organic chemistry of heterodinuclear centres, but there is considerable interest in the latter.[11,12] Alloy catalysts have been found which have different selectivities and greater activities than homometallic catalysts, and it is clearly important to determine what influence heteronuclear character has on the structure and reactivity of co-ordinated hydrocarbons. We have therefore prepared [FeRu$(CO)_4(\eta\text{-}C_5H_5)_2$] in order to carry out a study of the organic chemistry of the iron–ruthenium centre in comparison with di-iron and diruthenium centres. A preliminary report of this work has appeared;[13] while it was in progress the synthesis of [FeRu$(CO)_4(\eta\text{-}C_5H_5)_2$] was reported independently.[14]

Results and Discussion

Synthesis, Structure, and Fluxionality of [FeRu$(CO)_4(\eta\text{-}C_5H_5)_2$].—Red-black crystalline [FeRu$(CO)_4(\eta\text{-}C_5H_5)_2$] (**1**) is formed when [RuI$(CO)_2(\eta\text{-}C_5H_5)$] is treated with Na[Fe$(CO)_2(\eta\text{-}C_5H_5)$] or when [FeI$(CO)_2(\eta\text{-}C_5H_5)$] is treated with Na[Ru$(CO)_2(\eta\text{-}C_5H_5)$]. The best route employs the more nucleophilic [Fe$(CO)_2(\eta\text{-}C_5H_5)]^-$ anion, a yield of *ca.* 60% being obtained as opposed to less than 30% when [Ru$(CO)_2(\eta\text{-}C_5H_5)]^-$ is involved. The complex is stable as a solid in air but solutions in organic solvents decompose over several hours unless held under an atmosphere of nitrogen. In boiling toluene disproportionation to yield [$Fe_2(CO)_4(\eta\text{-}C_5H_5)_2$] and [$Ru_2(CO)_4(\eta\text{-}C_5H_5)_2$] occurs only very slowly.

The crystal and molecular structure of [FeRu$(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2$] (**1a**) was determined by *X*-ray diffraction methods. The molecular geometry and atomic numbering scheme are shown in the Figure and the results are summarised

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† *trans*-Di-μ-carbonyl-1,2-dicarbonyl-1,2-bis(η-cyclopentadienyl)iron-ruthenium.

Supplementary data available (No. SUP 56267, 6 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Bond lengths (Å) and selected bond angles (°) for $[FeRu(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (**1a**)*

M–C(1)	1.974(4)	M–C(2)	1.788(4)
M–C(11)	2.167(5)	M–C(12)	2.159(4)
M–C(13)	2.210(5)	M–C(14)	2.217(5)
M–C(15)	2.209(4)	M–M′	2.626(1)
M–C(1′)	1.972(4)	O(1)–C(1)	1.179(5)
O(2)–C(2)	1.148(5)	C(1)–M′	1.972(4)
C(11)–C(12)	1.378(8)	C(11)–C(15)	1.385(8)
C(12)–C(13)	1.382(8)	C(13)–C(14)	1.357(8)
C(14)–C(15)	1.389(8)		
C(1)–M–C(2)	93.4(2)	C(1)–M–C(11)	150.1(2)
C(2)–M–C(11)	102.5(2)	C(1)–M–C(12)	116.4(2)
C(2)–M–C(12)	97.1(2)	C(11)–M–C(12)	37.1(2)
C(1)–M–C(13)	88.5(2)	C(2)–M–C(13)	124.6(2)
C(11)–M–C(13)	61.6(2)	C(12)–M–C(13)	36.9(2)
C(1)–M–C(14)	95.6(2)	C(2)–M–C(14)	157.8(2)
C(11)–M–C(14)	61.3(2)	C(12)–M–C(14)	60.7(2)
C(13)–M–C(14)	35.7(2)	C(1)–M–C(15)	130.1(2)
C(2)–M–C(15)	136.1(2)	C(11)–M–C(15)	36.9(2)
C(12)–M–C(15)	61.3(2)	C(13)–M–C(15)	60.7(2)
C(14)–M–C(15)	36.6(2)	C(1)–M–M′	48.3(1)
C(2)–M–M′	95.1(1)	C(11)–M–M′	151.3(2)
C(12)–M–M′	161.1(2)	C(13)–M–M′	124.6(1)
C(14)–M–M′	106.0(1)	C(15)–M–M′	117.3(2)
C(1)–M–C(1′)	96.6(2)	C(2)–M–C(1′)	93.4(2)
C(11)–M–C(1′)	107.5(2)	C(12)–M–C(1′)	144.6(2)
C(13)–M–C(1′)	141.4(2)	C(14)–M–C(1′)	105.7(2)
C(15)–M–C(1′)	88.1(2)	M–C(1)–O(1)	138.4(3)
M–C(1)–M′	83.4(2)	O(1)–C(1)–M′	138.1(3)
M–C(2)–O(2)	178.7(4)	M–C(11)–C(12)	71.1(3)
M–C(11)–C(15)	73.2(3)	C(12)–C(11)–C(15)	107.5(5)
M–C(12)–C(11)	71.7(3)	M–C(12)–C(13)	73.6(3)
C(11)–C(12)–C(13)	108.5(5)	M–C(13)–C(12)	69.6(3)
M–C(13)–C(14)	72.4(3)	C(12)–C(13)–C(14)	107.8(5)
M–C(14)–C(13)	71.9(3)	M–C(14)–C(15)	71.4(3)
C(13)–C(14)–C(15)	108.8(5)	M–C(15)–C(11)	69.9(3)
M–C(15)–C(14)	72.0(3)	C(11)–C(15)–C(14)	107.4(5)

* M = 50% Fe + 50% Ru. Primed atoms are related to the unprimed ones by −*x*, −*y*, −*z*.

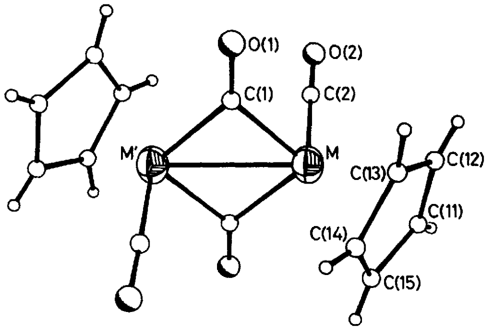


Figure. Molecular structure of $[FeRu(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (**1a**)

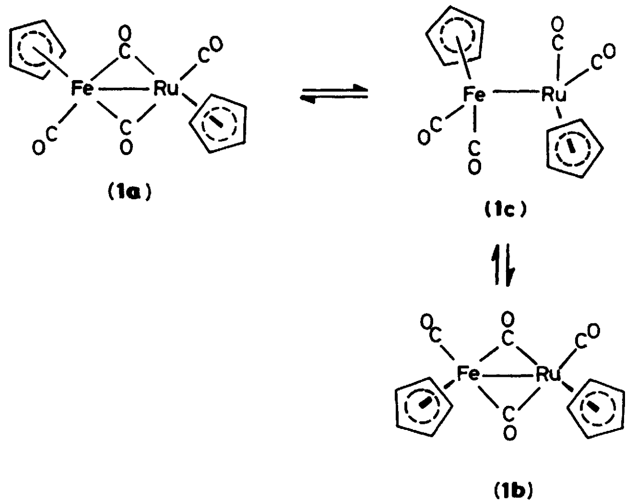
Table 2. Atomic positional parameters (fractional co-ordinates) (× 10^4) with estimated standard deviations in parentheses for $[FeRu(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (**1a**)*

Atom	*x*	*y*	*z*
M	875(1)	634(1)	1 291(1)
O(1)	−1 853(4)	−980(3)	2 024(4)
O(2)	−2 190(5)	2 289(3)	490(5)
C(1)	−1 025(5)	−545(3)	1 126(5)
C(2)	−1 006(6)	1 635(3)	788(5)
C(11)	3 427(7)	1 522(4)	2 769(7)
C(12)	2 363(6)	1 188(5)	3 876(5)
C(13)	2 410(7)	85(5)	3 947(6)
C(14)	3 463(7)	−263(4)	2 874(7)
C(15)	4 130(6)	617(5)	2 145(7)
H(11)	3 572(69)	2 129(38)	2 499(61)
H(12)	1 786(84)	1 486(58)	4 381(74)
H(13)	1 837(60)	−411(32)	4 807(57)
H(14)	3 624(88)	−886(56)	2 732(87)
H(15)	4 820(94)	619(33)	1 456(77)

* M = 50% Fe + 50% Ru.

in Tables 1 and 2. The molecule comprises two metal atoms bridged symmetrically by two carbonyls, with each metal atom also carrying a terminal carbonyl and η^5-cyclopentadienyl group in an overall *trans* configuration (**1a**). The molecule is disordered about a centre of inversion at the mid-point of the metal–metal bond, each metal site being occupied by half an iron atom and half a ruthenium atom. The iron–ruthenium bond length of 2.626(1) Å is approximately midway between the Fe–Fe [2.534(2) Å] and Ru–Ru [2.735(2) Å] distances in *trans*-$[M_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ (M = Fe[15] or Ru[16]). Other molecular dimensions are averaged due to the disorder and are found to lie between the corresponding distances in the di-iron and diruthenium complexes. For example, the metal to carbonyl C distances for the bridging and terminal carbonyls are 1.973(4) and 1.788(4) Å, respectively, in (**1a**) compared with 1.914(5) and 1.748(6) Å in *trans*-$[Fe_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ and 1.99(1) and 1.86(1) Å in *trans*-$[Ru_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$.

The i.r. spectrum of (**1**) in dichloromethane at 25 °C indicates that the *trans* form is not the only species present in solution. Although for (**1a**) only one i.r.-active terminal carbonyl absorption is expected there are two observed, at 1 998s and 1 957m cm^{-1}, in addition to a bridging carbonyl band at 1 773s cm^{-1}. The ^{13}C n.m.r. spectrum, recorded between −80 and 25 °C in CD_2Cl_2, reveals that (**1a**) is actually a minor species in solution, at least in this solvent, and that the *cis* carbonyl-bridged isomer (**1b**) is dominant. At −80 °C the CO region of the ^{13}C n.m.r. spectrum comprises an intense set of sharp signals at δ 199.5, 211.5, and 261.5 p.p.m., and a weak, broad signal at δ 233.2. The ^{13}C n.m.r. spectra of a wide range of di-iron and diruthenium compounds have been reported in previous Parts of this Series, and carbonyls terminally bound to iron or ruthenium have shifts close to δ 215 or 200 respectively. The signals at δ 211.5 and 199.5 for a solution of (**1**) can therefore confidently be assigned to Fe(CO) and Ru(CO) respectively, while that at δ 261.5 is typical of a bridging carbonyl. These three signals therefore correspond to the presence of an isomer of (**1**) which is static, *i.e.* no CO exchange is occurring at −80 °C. However, the weak, broad signal at an intermediate shift of δ 233.2 indicates that there is also present a second isomer, in low concentration, which even at −80 °C is undergoing CO site exchange fast enough to cause environmental averaging on the n.m.r. time-scale. In accord with this conclusion the weak signal sharpens on warming to −60 °C. The others broaden, revealing the onset of CO exchange within the major isomer, but at −30 °C all four signals coalesce into a very broad resonance which on further warming to 25 °C becomes a sharp singlet at δ 231.6. Clearly now CO exchange has become coupled with the interconversion of the isomers so that time-averaged equivalence of all the carbonyls is achieved. Strikingly similar ^{13}C n.m.r. spectra were observed for $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ between −85 and 55 °C by Gansow *et al.*[17] and the solution behaviour of the two complexes is evidently very related. The energetics of the di-iron system have been thoroughly discussed by Bullitt *et al.*[18] and in accord with their analysis, which will not be repeated here, we assign the major species present in the solution of (**1**) as the *cis* carbonyl-


(1a) (1c) (1b)

bridged isomer (**1b**) and the minor species as the *trans* form (**1a**). Both carbonyl exchange and the associated *cis* $\rightleftharpoons$ *trans* isomerisation are effected *via* the unbridged isomer (**1c**), present in an undetectable concentration. The energy barrier to isomerisation in (**1**) appears to be similar to that in $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$, and higher than that in $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$, which displays a single CO resonance at δ 224.0, albeit broad, even at −80 °C in CH_2Cl_2–CD_2Cl_2.[19]

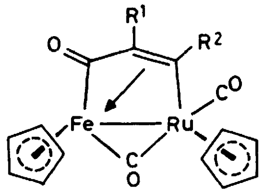
Organo-Iron–Ruthenium Chemistry.—Complex (**1**) is the precursor of a substantial organo-iron–ruthenium chemistry which broadly parallels that of the di-iron and diruthenium systems. No di-iron or diruthenium products are observed in its reactions under either thermal or photochemical conditions and the Fe–Ru bond is clearly sufficiently robust that reactions do not follow a metal–metal bond cleavage pathway. The iron–ruthenium products are mildly air-sensitive in solution and are generally formed in good yield. In the light of data previously obtained for di-iron and diruthenium analogues spectroscopic characterisation of new iron–ruthenium compounds was straightforward; the new data are unremarkable and are collected in Tables 3 and 4.

While $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ reacts with alkynes RC_2R to yield dimetallacyclopentenone complexes of the form $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)CRCR\}(\eta\text{-}C_5H_5)_2]$, $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ gives a similar product only with diphenylacetylene.[20] Complex (**1**) behaves like $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$, reacting under u.v. irradiation with a variety of alkynes $R^1C_2R^2$ ($R^1 = R^2 =$ H, Me, Ph, or CO_2Me; $R^1 =$ Me or Ph, $R^2 =$ H) over 1—16 h to produce the complexes $[FeRu(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)CR^1CR^2\}(\mu\text{-}C_5H_5)_2]$ (**2**)—(**7**) in 20—65% yield. The ^{13}C n.m.r. spectra of the complexes reveal that in each case the ketonic group of the metallacycle is adjacent to the iron atom, as illustrated, the chemical shift of the ketonic carbonyl closely resembling that found in the di-iron system while the terminal carbonyl is seen near δ 200 p.p.m., as expected for binding to ruthenium.[20] Both the di-iron and diruthenium complexes of this type undergo a unique fluxional process in which CO molecules move synchronously in and out of the metallacycle so that the two metal atoms exchange their environments. No such process was observed for (**2**)—(**7**) below *ca.* 80 °C, when decomposition occurred; evidently the structure illustrated is strongly favoured relative to that in which a $\overline{\text{FeRuC(O)CR}^1\text{CR}^2}$ ring is present.

Table 3. Analytical and other data for new compounds

Compound	Colour	Analysis (%)[a] C	Analysis (%)[a] H	$M^{a,b}$
(**1**)	Red-black	42.3 (42.1)	2.3 (2.5)	400 (400)
(**2**)	Brown-green	45.5 (45.3)	3.1 (3.0)	398 (398)
(**3**)	Brown-green	48.4 (48.0)	4.1 (3.8)	*c* (426)
(**4**)	Dark green	58.9 (59.0)	3.6 (3.6)	*c* (550)
(**5**)	Dark green	42.9 (42.9)	3.2 (3.1)[d]	514 (514)
(**6**)	Grey-green	47.0 (46.7)	3.6 (3.4)	412 (412)
(**7**)	Grey-brown	53.1 (53.3)	3.6 (3.4)	*c* (474)
(**8**)	Red	44.2 (44.4)	3.1 (3.2)	514 (514)
(**10**)	Orange-red	43.8 (43.6)	3.1 (3.0)	386 (386)
(**11**)	Red	45.1 (45.1)	3.4 (3.5)	400 (400)
(**12**)	Orange-red	46.8 (46.5)	4.0 (3.9)	414 (414)
(**13**)	Orange	47.5 (47.8)	3.9 (4.2)	*c* (428)
(**14**)	Red	44.6 (44.6)	3.5 (3.5)	458 (458)
(**15**)	Dark red	37.1 (37.2)	3.0 (2.7)	*e* (486)
(**16**)	Red	38.4 (38.5)	3.2 (3.1)	*e* (500)
(**17**)	Orange	40.0 (39.8)	3.5 (3.3)	*e* (514)
(**21**)	Red-brown	46.8 (47.0)	3.6 (3.7)	384 (384)
(**22**)	Dark red	48.2 (48.4)	4.3 (4.0)	398 (398)
(**23**)	Brown	49.6 (49.6)	4.5 (4.4)	412 (412)
(**24**)	Dark red	55.0 (54.9)	4.2 (3.9)	460 (460)
(**25**)	Red-black	60.1 (60.6)	4.2 (4.1)	536 (536)
(**26**)	Dark red	45.0 (45.7)	3.8 (3.6)	500 (500)
(**27**)	Red-purple	48.0 (48.4)	4.1 (4.0)	398 (398)
(**28**)	Red-brown	49.4 (49.6)	4.2 (4.4)	412 (412)
(**29**)	Red-brown	50.4 (50.8)	4.4 (4.7)	426 (426)
(**30**)	Dark red	60.7 (61.2)	4.4 (4.4)	550 (550)
(**31**)	Red-black	47.4 (46.8)	3.9 (3.9)	514 (514)

[a] Calculated values in parentheses. [b] Mass spectrometry, based on ^{102}Ru. [c] No molecular ion observed. [d] Calculated values include $\frac{1}{3}$ CH_2Cl_2 of solvation, observed by n.m.r. [e] Involatile compound.



(**2**) $R^1 = R^2 =$ H
(**3**) $R^1 = R^2 =$ Me
(**4**) $R^1 = R^2 =$ Ph
(**5**) $R^1 = R^2 = CO_2Me$
(**6**) $R^1 =$ Me, $R^2 =$ H
(**7**) $R^1 =$ Ph, $R^2 =$ H

An interesting feature of the alkyne–$[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ reactions is that heteronuclear (**1**) reacts much faster than the homonuclear species. For example, the complexes are consumed by diphenylacetylene in the order: FeRu (16 h) > Ru_2 (2 d) > Fe_2 (28 d). Reactions with other alkynes are restricted to (**1**) and $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ but the same phenomenon is apparent; with ethyne the order is FeRu (1 h) > Fe_2 (5 d); with propyne, FeRu (2 h) > Fe_2 (4 d); with but-2-yne, FeRu (4 h) > Fe_2 (10 d); and with phenylacetylene, FeRu (4 h) > Fe_2 (16 h). This enhanced reactivity will be seen later to arise in other reactions.

In Part 1 [20] of this Series we proposed that the reaction of the dimers $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M = Fe or Ru) with alkynes proceeded *via* initial formation of mononuclear $M(CO)_2(\eta\text{-}C_5H_5)$ radicals. In view of the exclusive formation of heterodinuclear products from the reaction of (**1**) with alkynes this is now very unlikely and a mechanism in which the metal–metal bond is retained throughout is indicated. Since our original suggestion strong evidence had been obtained for the

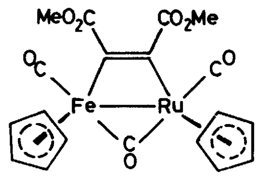
Table 4. I.r. and n.m.r. data for new compounds

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.)[b]
(1)	1 998s, 1 957m, 1 773s	4.68 (s, 5 H, FeC_5H_5), 5.18 (s, 5 H, RuC_5H_5)	88.4 (C_5H_5), 90.6 (C_5H_5), 199.5 (RuCO), 211.5 (FeCO), 233.2 (w, br), 261.5 (μ-CO)[c,d]
(2)	1 977s, 1 812 (sh), 1 796m, 1 757m (C=O)	2.58 (d, *J* 7, 1 H, R^1), 4.60 (s, 5 H, C_5H_5), 5.31 (s, 5 H, C_5H_5), 11.50 (d, *J* 7, 1 H, R^2)	14.0 (CH), 85.7 (C_5H_5), 90.2 (C_5H_5), 168.2 (CH), 199.3 (RuCO), 235.6 (C=O), 248.8 (μ-CO)
(3)	1 971s, 1 798s, 1 753m (C=O)	1.47 (s, 3 H, Me, R^1), 3.55 (s, 3 H, Me, R^2), 4.45 (s, 5 H, C_5H_5), 5.30 (s, 5 H, C_5H_5)	15.0 (Me), 29.1 (Me), 36.8 (*C*Me), 87.4 (C_5H_5), 91.1 (C_5H_5), 188.7 (*C*Me), 200.0 (RuCO), 233.9 (C=O), 250.9 (μ-CO)
(4)	1 979s, 1 802s, 1 755m (C=O)	4.81 (s, 5 H, C_5H_5), 5.16 (s, 5 H, C_5H_5), 7.09 (m, 10 H, 2 Ph)	30.5 (*C*Ph), 87.5 (C_5H_5), 92.7 (C_5H_5), 125.8—134.7 (2 Ph), 186.6 (*C*Ph), 199.7 (RuCO), 238.3 (C=O), 249.5 (μ-CO)
(5)	1 995s, 1 823s, 1 773w (C=O), 1 712m (CO_2Me)	3.68 (s, 3 H, Me), 4.01 (s, 3 H, Me), 4.75 (s, 5 H, C_5H_5), 5.34 (s, 5 H, C_5H_5)	19.4 (*C*CO_2Me), 51.9 (CO_2*Me*), 52.6 (CO_2*Me*), 88.8 (C_5H_5), 91.9 (C_5H_5), 171.4 (*C*O_2Me), 173.1 (*C*O_2Me), 177.4 (*C*CO_2Me), 197.7 (RuCO), 223.4 (C=O), 243.7 (μ-CO)
(6)	1 975s, 1 799s, 1 761m (C=O)	1.55 (s, 3 H, Me), 4.51 (s, 5 H, C_5H_5), 5.30 (s, 5 H, C_5H_5), 11.10 (s, 1 H, R^2)	19.9 (Me), 29.2 (*C*Me), 85.9 (C_5H_5), 90.1 (C_5H_5), 167.2 (CH), 199.3 (RuCO), 236.4 (C=O), 249.7 (μ-CO)
(7)	1 979s, 1 802s, 1 752m (C=O)	4.49 (s, 5 H, C_5H_5), 5.52 (s, 5 H, C_5H_5), 7.40 (m, 5 H, Ph), 12.14 (s, 1 H, R^2)	31.5 (*C*Ph), 86.8 (C_5H_5), 90.5 (C_5H_5), 127—138 (Ph), 185.7 (CH), 199.0 (RuCO), 235.1 (C=O) 249.0 (μ-CO)
(8)	2 012s, 1 977m, 1 807m, 1 707m (CO_2Me)	3.82 (s, 3 H, Me), 3.86 (s, 3 H, Me), 4.89 (s, 5 H, C_5H_5), 5.36 (s, 5 H, C_5H_5)	51.7 (CO_2*Me*), 51.8 (CO_2*Me*), 88.1 (C_5H_5), 91.0 (C_5H_5), 139.2 (2 *C*CO_2Me), 165.5 (*C*O_2Me), 166.1 (*C*O_2Me), 196.7 (RuCO), 209.4 (FeCO), 253.4 (μ-CO)
(10)	1 983s, 1 943mw, 1 780m	(**10a**): 4.73 (s, 5 H, C_5H_5), 5.26 (s, 5 H, C_5H_5), 7.95 (s, 1 H, μ-CH), 9.75 (s, 1 H, μ-CH)	(**10a**): 86.5 (C_5H_5), 89.8 (C_5H_5), 124.5 (CH_2), 200.4 (RuCO), 213.9 (FeCO), 261.3 (μ-CO)
		(**10b**): 4.80 (s, 5 H, C_5H_5), 5.31 (s, 5 H, C_5H_5), 9.02 (s, 1 H, μ-CH), 9.04 (s, 1 H, μ-CH)	(**10b**): 88.2 (C_5H_5), 91.6 (C_5H_5), 126.4 (CH_2)[e]
(11)	1 975s, 1 939w, 1 775m	(**11a**): 3.09 (d, *J* 7, 3 H, Me), 4.66 (s, 5 H, C_5H_5), 5.19 (s, 5 H, C_5H_5), 11.52 (q, *J* 7, 1 H, μ-CH)	(**11a**): 43.3 (Me), 87.0 (C_5H_5), 90.2 (C_5H_5), 158.4 (*C*HMe), 200.8 (RuCO), 213.8 (FeCO), 261.5 (μ-CO)
		(**11b**): 3.24 (d, *J* 7, 3 H, Me), 4.77 (s, 5 H, C_5H_5), 5.28 (s, 5 H, C_5H_5), 12.02 (q, *J* 7, 1 H, μ-CH)	(**11b**): 44.5 (Me), 88.4 (C_5H_5), 90.9 (C_5H_5)[e]
(12)	1 973s, 1 935m, 1 773m	(**12a**): 1.35 (m, 3 H, Me), 3.08 (m, 2 H, CH_2), 4.68 (s, 5 H, C_5H_5), 5.21 (s, 5 H, C_5H_5), 11.24 (t, *J* 7, 1 H, μ-CH)	(**12a**): 20.7 (Me), 49.4 (CH_2), 86.5 (C_5H_5), 89.7 (C_5H_5) 167.3 (*C*HEt), 199.8 (RuCO), 213.0 (FeCO), 262.2 (μ-CO)
		(**12b**): 1.35 (m, 3 H, Me), 3.08 (m, 2 H, CH_2), 4.70 (s, 5 H, C_5H_5), 5.21 (s, 5 H, C_5H_5), 11.82 (t, *J* 7, 1 H, μ-CH)	(**12b**): 21.2 (Me), 49.9 (CH_2), 87.0 (C_5H_5), 89.7 (C_5H_5), 169.1 (*C*HEt), 200.6 (RuCO), 212.6 (FeCO)[e]
(13)	1 971s, 1 933m, 1 771m	1.25—1.52 (m, 3 H, CH_2*C*H_3), 2.80—3.20 (m, 5 H, *Me*C*C*H_2), 4.66, 4.69, 5.19, 5.20 (4 C_5H_5)	
(14)	1 997s, 1 964m, 1 792m, 1 730w (CO_2Et), 1 680w (CO_2Et)	(**14a**): 1.24 (t, *J* 7, 3 H, Me), 4.14 (q, *J* 7, 2 H, CH_2), 4.76 (s, 5 H, C_5H_5), 5.28 (s, 5 H, C_5H_5), 9.73 (s, 1 H, μ-CH)	(**14a**): 14.2 (Me), 60.3 (CH_2), 86.6 (C_5H_5), 89.8 (C_5H_5), 127.2 (*C*O_2Et), 183.6 (*C*HCO_2Et), 197.9 (RuCO), 211.0 (FeCO), 255.8 (μ-CO)
		(**14b**): 4.80 (s, 5 H, C_5H_5), 5.25 (s, 5 H, C_5H_5), 8.80 (s, 1 H, μ-CH)[e]	(**14b**): 88.2 (C_5H_5), 92.5 (C_5H_5)[e]
(15)	2 037s, 2 014w, 1 863m	(**15a**): 3.42 (d, *J* 12, 1 H, C*H*R^2), 5.06 (d, *J* 7, 1 H, R^2), 5.70 (s, 5 H, C_5H_5), 5.94 (s, 5 H, C_5H_5), 11.66 (dd, *J* 7, 12, 1 H, R^1)[f]	(**15a**): 59.8 (CH_2), 92.4 (2 C_5H_5), 175.6 (CH), 199.1 (RuCO), 209.0 (FeCO), 233.8 (μ-CO)
		(**15b**): 5.53 (s, 5 H, C_5H_5), 6.15 (s, 5 H, C_5H_5), 12.20 (dd, *J* 7, 12, 1 H, R^1)[e,f]	(**15b**): 55.5 (CH_2), 88.3 (C_5H_5), 95.0 (C_5H_5), 170.7 (CH), 194.0 (RuCO), 214.0 (FeCO)[e,g]
(16)	2 031s, 2 006w, 1 858m	(**16a**): 2.09 (d, *J* 5, 3 H, Me), 4.40 (m, 1 H, C*H*R^2), 5.63 (s, 5 H, C_5H_5), 5.95 (s, 5 H, C_5H_5), 11.37 (d, *J* 12, 1 H, R^1)[f]	
		(**16b**): 5.35, 5.76 (both s, 5 H, C_5H_5)[e,f]	
(17)	2 029m, 2 010s, 1 860m	(**17a**): 5.61, 5.93 (both s, 5 H, C_5H_5)[e,f]	
		(**17b**): 2.03 (d, *J* 5, 3 H, CH*Me*), 3.48 (s, 3 H, Me, R^1), 4.40 (q, *J* 5, 1 H, C*H*Me), 5.33, 5.74 (both s, 5 H, C_5H_5)[f]	
(18)	1 958m, 1 752s	1.75 (s, 4 H, C_2H_4), 4.85 (s, 5 H, C_5H_5), 4.95 (s, 5 H, C_5H_5)	
(21)	1 946s, 1 773m	(**21a**): −0.44 (dd, *J* 2 and 7, 1 H, C*H*R^1), 2.44 (dd, *J* 2 and 4, 1 H, R^1), 4.54 (m, 1 H, R^2), 4.75 (s, 5 H, C_5H_5), 4.98 (s, 5 H, C_5H_5), 10.82 (d, *J* 6, 1 H, R^3)	(**21a**): 37.0 (CH_2), 79.0 (*C*R^2), 84.1 (C_5H_5), 85.8 (C_5H_5), 163.2 (*C*R^3), 215.5 (FeCO), 254.6 (μ-CO)
(22)	1 943s, 1 769m	(**22a**): −0.47 (dd, *J* 3 and 9, 1 H, C*H*R^1), 2.39 (dd, *J* 3 and 7, 1 H, R^1), 3.51 (s, 3 H, Me), 4.20 (m, 1 H, R^2), 4.75 (s, 5 H, C_5H_5), 4.92 (s, 5 H, C_5H_5)	(**22a**): 41.9 (Me), 42.6 (CH_2), 79.9 (*C*R^2), 84.9 (C_5H_5), 86.6 (C_5H_5), 184.5 (*C*R^3), 215.9 (FeCO), 256.5 (μ-CO)

Table 4 (*continued*)

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.)[b]
		(**22b**): −0.83 (dd, *J* 3 and 9, 1 H, C*H*R^1), 2.10 (dd, *J* 3 and 7, 1 H, R^1), 3.70 (s, 3 H, Me), 4.20 (m, 1 H, R^2), 4.32 (s, 5 H, C_5H_5), 5.24 (s, 5 H, C_5H_5)	(**22b**): 37.9 (Me), 44.1 (CH_2), 82.2 (C_5H_5), 89.5 (C_5H_5), 188.5 (*C*R^3), 202.9 (RuCO), 258.3 (μ-CO)[h]
(**23**)	1 941s, 1 766m	(**23a**): −0.73 (d, *J* 3, 1 H, C*H*R^1), 1.91 (s, 3 H, Me, R^2), 2.49 (d, *J* 3, 1 H, R^1), 3.55 (s, 3 H, Me, R^3), 4.74 (s, 5 H, C_5H_5), 4.87 (s, 5 H, C_5H_5)	(**23a**): 23.7 (Me), 37.4 (CH_2), 43.9 (Me), 85.8 (C_5H_5), 87.1 (C_5H_5), 179.8 (*C*R^3), 216.9 (FeCO), 258.8 (μ-CO)[h]
		(**23b**): −1.11 (d, *J* 3, 1 H, C*H*R^1), 1.91 (s, 3 H, Me, R^2), 2.08 (d, *J* 3, 1 H, R^1), 3.68 (s, 3 H, Me, R^3), 4.28 (s, 5 H, C_5H_5), 5.22 (s, 5 H, C_5H_5)	(**23b**): 21.9 (Me), 38.5 (CH_2), 49.0 (Me), 82.8 (C_5H_5), 90.0 (C_5H_5), 183.4 (*C*R^3), 203.8 (RuCO), 260.0 (μ-CO)[h]
(**24**)	1 948s, 1 775m	(**24a**): −0.26 (dd, *J* 3 and 9, 1 H, C*H*R^1), 2.53 (dd, *J* 3 and 7, 1 H, R^1), 4.26 (dd, *J* 7 and 9, 1 H, R^2), 4.44 (s, 5 H, C_5H_5), 5.10 (s, 5 H, C_5H_5), 7.2—7.8 (m, 5 H, Ph)	
		(**24b**): −0.62 (dd, *J* 3, and 9, 1 H, C*H*R^1), 2.29 (dd, *J* 3 and 7, 1 H, R^1), 4.41 (dd, *J* 7 and 9, 1 H, R^2), 4.47 (s, 5 H, C_5H_5), 5.01 (s, 5 H, C_5H_5), 7.2—7.8 (m, 5 H, Ph)	
(**25**)	1 952s, 1 771m	(**25a**): −0.30 (d, *J* 3, 1 H, C*H*R^1), 2.81 (d, *J* 3, 1 H, R^1), 4.40 (s, 5 H, C_5H_5), 5.14 (s, 5 H, C_5H_5), 7.0—7.6 (m, 10 H, 2 Ph)	(**25a**): 40.7 (CH_2), 86.5 (C_5H_5), 88.5 (C_5H_5), 97.9 (*C*R^2), 124—156 (2 Ph), 181.6 (*C*R^3), 216.0 (FeCO), 258.0 (μ-CO)
		(**25b**): −0.78 (d, *J* 3, 1 H, C*H*R^1), 2.61 (d, *J* 3, 1 H, R^1), 4.54 (s, 5 H, C_5H_5), 4.93 (s, 5 H, C_5H_5), 7.0—7.6 (m, 10 H, 2 Ph)	(**25b**): 45.9 (CH_2), 83.4 (C_5H_5), 91.6 (C_5H_5), 95.0 (*C*R^2), 124—156 (2 Ph), 182.6 (*C*R^3), 203.2 (RuCO), 258.6 (μ-CO)
(**26**)	1 962s, 1 794m, 1 715m (CO_2Me)	(**26a**): −0.67 (d, *J* 3, 1 H, C*H*R^1), 3.11 (d, *J* 3, 1 H, R^1), 3.69 (s, 3 H, Me), 4.00 (s, 3 H, Me), 4.73 (s, 5 H, C_5H_5), 5.05 (s, 5 H, C_5H_5)	(**26a**): 38.4 (CH_2), 52.1 (Me), 52.4 (Me), 87.4 (C_5H_5), 87.5 (C_5H_5), 169.8 (*C*$_2$Me), 170.9 (*C*O$_2$Me), 179.3 (*C*R^3), 214.1 (FeCO), 250.4 (μ-CO)[e]
		(**26b**): −1.03 (d, *J* 3, 1 H, C*H*R^1), 2.87 (d, *J* 3, 1 H, R^1), 3.74 (s, 3 H, Me), 4.03 (s, 3 H, Me), 4.53 (s, 5 H, C_5H_5), 5.18 (s, 5 H, C_5H_5)	(**26b**): 44.0 (CH_2), 84.4 (C_5H_5), 90.6 (C_5H_5), 171.7 (*C*O$_2$Me), 172.9 (*C*O$_2$Me), 179.7 (*C*R^3), 201.2 (RuCO), 251.3 (μ-CO)[e]
(**27**)	1 943s, 1 771m	(**27a**): 0.14 (m, 1 H, C*H*R^1), 1.40 (d, *J* 7, 3 H, CH*Me*), 4.43 (dd, *J* 5 and 8, 1 H, R^2), 4.71 (s, 5 H, C_5H_5), 4.91 (s, 5 H, C_5H_5), 10.63 (d, *J* 6, 1 H, R^3)	(**27a**): 22.4 (Me), 55.8 (*C*R^1), 83.9 (*C*R^2), 84.6 (C_5H_5), 85.6 (C_5H_5), 160.0 (*C*R^3), 216.1 (FeCO), 255.3 (μ-CO)
(**28**)	1 939s, 1 765m	(**28a**): 0.27 (m, 1 H, C*H*R^1), 1.39 (d, *J* 6, 3 H, CH*Me*), 3.47 (s, 3 H, Me, R^3), 4.72 (s, 5 H, C_5H_5), 4.85 (s, 5 H, C_5H_5)[i]	(**28a**): 22.6 (CH*Me*), 41.6 (Me), 56.6 (*C*R^1), 85.3 (*C*R^2), 85.7 (C_5H_5), 86.3 (C_5H_5), 181.4 (*C*R^3), 216.6 (FeCO), 256.9 (μ-CO)
		(**28b**): −0.15 (m, 1 H, C*H*R^1), 1.31 (d, *J* 6, 3 H, CH*Me*), 3.68 (s, 3 H, Me, R^3), 4.25 (s, 5 H, C_5H_5), 5.21 (s, 5 H, C_5H_5)[i]	(**28b**): 21.4 (CH*Me*), 42.3 (Me), 62.2 (*C*R^1), 82.7 (C_5H_5), 85.1 (*C*R^2), 89.2 (C_5H_5), 184.7 (*C*R^3), 203.8 (RuCO), 259.2 (μ-CO)
(**29**)	1 935s, 1 763m	(**29a**): −0.24 (q, *J* 7, 1 H, C*H*R^1), 1.45 (d, *J* 7, 3 H, CH*Me*), 1.90 (s, 3 H, Me, R^2), 3.70 (s, 3 H, Me, R^3), 4.71 (s, 5 H, C_5H_5), 4.77 (s, 5 H, C_5H_5)	(**29a**): 17.4 (Me), 21.0 (CH*Me*), 37.8 (Me), 58.9 (*C*R^1), 86.7 (C_5H_5), 87.0 (C_5H_5), 94.0 (*C*R^2), 178.1 (*C*R^3), 217.7 (FeCO), 259.2 (μ-CO)[e]
		(**29b**): −0.88 (q, *J* 7, 1 H, C*H*R^1), 1.32 (d, *J* 7, 3 H, CH*Me*), 1.95 (s, 3 H, Me, R^2), 3.55 (s, 3 H, Me, R^3), 4.17 (s, 5 H, C_5H_5), 5.21 (s, 5 H, C_5H_5)	(**29b**): 16.0 (Me), 19.5 (CH*Me*), 38.8 (Me), 63.8 (*C*R^1), 83.6 (C_5H_5), 89.9 (C_5H_5), 93.1 (*C*R^2), 182.0 (*C*R^3), 204.8 (RuCO), 260.7 (μ-CO)[e]
(**30**)	1 950s, 1 765m	(**30a**): −0.68 (q, *J* 7, 1 H, C*H*R^1), 1.13 (d, *J* 7, 3 H, CH*Me*), 4.40 (s, 5 H, C_5H_5), 4.65 (s, 5 H, C_5H_5), 7.06 (m, 10 H, 2 Ph)	(**30a**): 22.3 (Me), 57.3 (*C*R^1), 84.6 (C_5H_5), 88.8 (C_5H_5), 123—157 (2 Ph), 189.1 (*C*R^3), 215.7 (FeCO), 261.9 (μ-CO)[h]
		(**30b**): −0.41 (q, *J* 7, 1 H, C*H*R^1), 1.26 (d, *J* 7, 3 H, CH*Me*), 4.58 (s, 5 H, C_5H_5), 4.90 (s, 5 H, C_5H_5), 7.06 (m, 10 H, 2 Ph)	(**30b**): 21.4 (Me), 60.4 (*C*R^1), 83.7 (C_5H_5), 91.2 (C_5H_5), 99.0 (*C*R^2), 123—157 (2 Ph), 181.9 (*C*R^3), 203.9 (RuCO), 259.6 (μ-CO)
(**31**)	1 958s, 1 788m, 1 717m (CO_2Me)	(**31a**): −1.08 (q, *J* 7, 1 H, C*H*R^1), 1.28 (d, *J* 7, 3 H, CH*Me*), 3.76 (s, 3 H, CO_2Me), 3.90 (s, 3 H, CO_2Me), 4.59 (s, 5 H, C_5H_5), 5.04 (s, 5 H, C_5H_5)	(**31a**): 87.0 (C_5H_5), 87.9 (C_5H_5)[d]
	1 958s, 1 788m, 1 717m (CO_2Me)	(**31b**): −0.75 (q, *J* 7, 1 H, C*H*R^1), 1.43 (d, *J* 7, 3 H, CH*Me*), 3.80 (s, 3 H, CO_2Me), 3.93 (s, 3 H, CO_2Me), 4.53 (s, 5 H, C_5H_5), 5.17 (s, 5 H, C_5H_5)	(**31b**): 20.4 (CH*Me*), 51.9 (CO$_2$*Me*), 52.2 (CO$_2$*Me*), 59.7 (*C*R^1), 85.0 (C_5H_5), 90.2 (C_5H_5), 167.3 (*C*O$_2$Me), 171.0 (*C*O$_2$Me), 179.4 (*C*R^3), 202.1 (RuCO), 253.0 (μ-CO)[h]

[a] In CH_2Cl_2. [b] In $CDCl_3$ unless otherwise stated. [c] Fluxional molecule, see text. [d] In CD_2Cl_2. [e] Minor isomer, other signals unobserved. [f] In $(CD_3)_2CO$. [g] In CD_3NO_2. [h] *C*R^2 carbon resonance obscured by C_5H_5 or solvent signals. [i] R^2 proton obscured by C_5H_5 signals.



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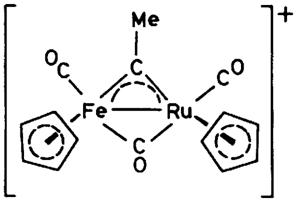


(9)

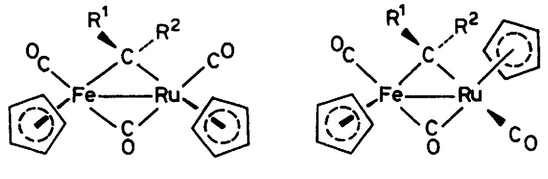
formation of relatively long-lived $[Fe_2(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_2]$, in addition to $Fe(CO)_2(\eta\text{-}C_5H_5)$, upon photolysis of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$.[21] This species reacts thermally with CO to regenerate $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$, suggesting that the reactions of $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (M_2 = Fe_2, Ru_2, or FeRu) with alkynes involve the trapping of photochemically-produced $[M_2(\mu\text{-}CO)_3(\eta\text{-}C_5H_5)_2]$.

The reactions of propyne and phenylacetylene with **(1)** are specific in giving products containing an $\overline{FeRuC(H)C(R)CO}$ ring, *i.e.* the methyl or phenyl substituent occupies the R^1 site in **(6)** and **(7)**. A similar situation arose with homodinuclear $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in that although isomers containing $\overline{M_2C(H)C(R)CO}$ and $\overline{M_2C(R)C(H)CO}$ rings have been isolated the former is favoured; *e.g.* for M = Fe, R = Ph it is the only product and for M = Ru, R = Ph, it dominates by 10:1 over the latter.[20] The R^2 site in a dimetallacyclopentenone complex is crowded, lying between a pair of *cis* cyclopentadienyls, and these observations for the di-iron and diruthenium systems were understandable in purely steric terms. For iron–ruthenium the same influences must be at work to generate the $\overline{FeRuC(H)C(R)CO}$ ring irrespective of the electronic properties of R.

The di-iron and diruthenium analogues of **(2)**—**(7)** make good precursors of organodimetal chemistry because of the ease with which the carbonyl–alkyne link is broken.[10] Indications that **(2)**—**(7)** would behave likewise were obtained when **(5)** isomerised to the dimetallacyclobutene complex *cis*-$[FeRu(CO)_2(\mu\text{-}CO)\{\mu\text{-}C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ **(8)** on heating in toluene, and when **(4)** reacted with but-2-yne to give **(3)** under the same conditions. This lability was exploited in the synthesis of a range of μ-alkylidene iron–ruthenium complexes.

Three routes to μ-alkylidene complexes have been explored: (*i*) treatment of **(1)** with an organolithium reagent; (*ii*) displacement of diphenylacetylene from **(4)** by heating with a diazoalkane or phosphorus ylide; and (*iii*) protonation of **(2)**, **(3)**, and **(6)**, to yield μ-vinyl cations which are subjected to attack by hydride. These will be discussed in turn.

Like $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$[2,8,9] and $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$,[22] complex **(1)** undergoes nucleophilic attack upon treatment with methyl-lithium, subsequent addition of $HBF_4\cdot OEt_2$ providing a deep red solution of what is assumed to be the μ-ethylidyne cation $[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2]^+$ **(9)** [ν(CO) at 2 049s, 2 015m, and 1 856m cm^{-1} in CH_2Cl_2 solution]. No attempt was made to isolate this species but its presence was confirmed by the addition of $NaBH_4$, when the μ-ethylidene complex $[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ **(11)** was formed in good yield. On the basis of its carbonyl i.r. spectrum **(9)** exists as a *cis* isomer in solution, like the Fe_2 and Ru_2 analogues. The situation for **(11)** and other μ-alkylidene complexes is more complicated and is discussed later.



(a) **(b)**

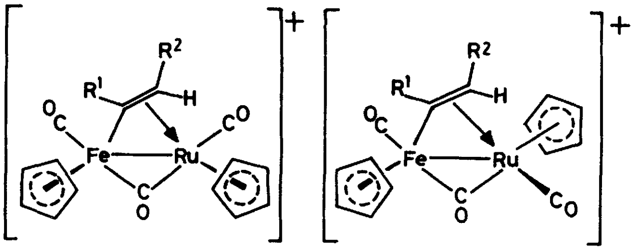
(10a, b) $R^1 = R^2 = H$
(11a, b) $R^1 = H, R^2 = Me$
(12a, b) $R^1 = H, R^2 = Et$
(13a, b) $R^1 = Me, R^2 = Et$
(14a, b) $R^1 = H, R^2 = CO_2Et$

Bercaw and Berry[23] have discovered that the μ-methylene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$, prepared by us[1] *via* the reaction of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)CPhCPh\}(\eta\text{-}C_5H_5)_2]$ with $Ph_3P{=}CH_2$, is better obtained by treating $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $LiBHEt_3$ and then quenching with water. This process is equally successful in generating $[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ **(10)** from **(1)**. Addition of 2.2 equivalents of $LiBHEt_3$ to **(1)** in toluene results, over 3 h, in the formation of an apparently anionic species [ν(CO) at 1 941s and 1 780m cm^{-1}] which on addition of water is converted to **(10)** in high yield. The course of this transformation almost certainly follows that established for the production of $[Os_3(CO)_{11}(\mu\text{-}CH_2)]$ from $[Os_3(CO)_{12}]$ and $LiBHEt_3$, *i.e.* a sequence $CO \longrightarrow CHO^- \longrightarrow CH_2OH^- \longrightarrow CH_2$ (ref. 24).

The lability of the diphenylacetylene in **(4)**, seen earlier in its displacement by but-2-yne, can also be employed in the synthesis of the μ-alkylidene complexes **(10)** and **(11)**. Briefly heating **(4)** with the appropriate ylide $Ph_3P{=}CHR$ (R = H or Me) in toluene gives **(10)** and **(11)** in good yield, but the route is more tedious than those involving organolithium reagents. Heating **(4)** with the thermally robust diazoalkane $CH(CO_2Et)N_2$ affords $[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCO_2Et)(\eta\text{-}C_5H_5)_2]$ **(14)** similarly.

Addition of $HBF_4\cdot OEt_2$ to a suspension of **(2)**, **(3)**, or **(6)** in diethyl ether yields the μ-vinyl cations $[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CR^1{=}CHR^2)(\eta\text{-}C_5H_5)_2]^+$ **(15)**—**(17)** rapidly, in a carbon–carbon bond cleavage reaction which mirrors di-iron and diruthenium chemistry.[25] For the analogous homodinuclear cations four isomers were possible; two were observed (one *cis* and one *trans*) and these exhibited both dynamic *cis* $\rightleftharpoons$ *trans* interconversion and μ-vinyl oscillation on the n.m.r. time-scale.[25] The situation is potentially even more complicated for heterodinuclear **(15)**—**(17)** in that now eight isomers are possible. However, again only two were observed for each complex. On the basis of the i.r. spectra (Table 4) these are a *cis*-**(a)** and a *trans*-**(b)** isomer, with the *cis* form (one strong and one weak terminal carbonyl band) dominating for **(15)** and **(16)**, and the *trans* form (one strong terminal carbonyl band) dominating for **(17)**. This is exactly the situation which arises for the analogous di-iron and diruthenium μ-vinyl cations, and is readily understood in steric terms.[25]

The proton n.m.r. spectra of the μ-vinyl cations (Table 4) reveal the following *cis*:*trans* ratios in $[^2H_6]$acetone at room temperature: **(15a)**:**(15b)**, *ca.* 5:1; **(16a)**:**(16b)**, *ca.* 10:1; **(17a)**:**(17b)**, *ca.* 1:10. Confirmation of the assignment is provided by the cyclopentadienyl ring signals, which are near

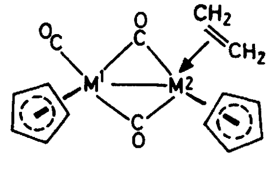


(a) (b)

(15a,b) $R^1 = R^2 = H$

(16a,b) $R^1 = H, R^2 = Me$

(17a,b) $R^1 = R^2 = Me$



(18) $M^1 = Fe, M^2 = Ru$

(19) $M^1 = M^2 = Fe$

(20) $M^1 = M^2 = Ru$

identical for the three *cis* isomers. The ^1H n.m.r. spectra provide no unequivocal information on whether the μ-vinyl group in the cations is π-bound to iron or to ruthenium. The ^{13}C n.m.r. spectrum of (**15**), however, clearly suggests that the π bonding is to ruthenium, as illustrated. The vinylic CH_2 group of (**15**) must be associated either only with ruthenium or only with iron, and the ^{13}C shift should therefore be close to that found in the diruthenium (δ 59.3) or di-iron (δ 65.3 p.p.m.) analogue. The actual value of δ 59.8 p.p.m. strongly indicates that the formulation (**15a**) is correct, and we assume that the same orientation is adopted by (**16**) and (**17**).

The ^1H n.m.r. spectrum of (**16**) reveals the presence of a μ-CH=CHMe group in having a low-field proton signal characteristic of hydrogen on a μ-carbon. Moreover, the coupling between this proton and the other vinylic proton is large (12 Hz), placing the latter *trans* rather than *cis*, for which a coupling of *ca.* 7 Hz is usual. The consequent relative *cis* orientation of the R^1 and R^2 substituents is apparently also adopted in (**17**), since the ^1H n.m.r. shift of the vinylic proton in this cation is identical to that of the *trans* methylene proton in (**16**).

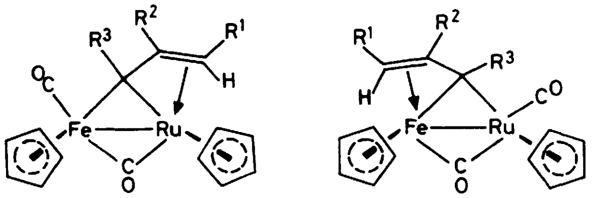
Treatment of the cations (**15**)—(**17**) with sodium tetrahydroborate gives the μ-alkylidene complexes (**11**)—(**13**) in good yield, resulting from hydride attack on the β carbon of the μ-vinyl group. An interesting departure from di-iron and diruthenium chemistry arises in the exclusive formation of the μ-CHEt complex (**12**) from (**16**). With the homodinuclear systems both μ-CHEt and μ-CMe_2 complexes were obtained [in 1.8:1 (Fe_2) and 1:3.5 (Ru_2) ratios respectively], betraying the presence of an equilibrium between μ-CH=CHMe and μ-CMe=CH_2 cations.[25] The specificity for μ-CHEt formation from the Fe–Ru cation shows that μ-CH=CHMe is strongly favoured relative to μ-CMe=CH_2 in this system, but it is not obvious why.

A second product from the reaction of the μ-CH=CH_2 cation (**15**) with $NaBH_4$ was the ethylene complex [FeRu(CO)(μ-CO)$_2$(C_2H_4)(η-C_5H_5)$_2$] (**18**), formed in variable yield (up to 30% on occasion). Both the di-iron (**19**)[26] and diruthenium (**20**)[25] analogues are known; the former is only stable under an atmosphere of ethylene but the latter requires no such protection and is air- and solution-stable. Yellow crystalline (**18**) is much more stable than (**19**), but not quite as stable as (**20**). In the absence of ethylene a ^1H n.m.r. spectrum may be recorded without difficulty, but slow decomposition of the solid prevented the collection of satisfactory analytical data. This is behaviour more compatible with ethylene being co-ordinated to ruthenium than iron in (**8**). The ^1H n.m.r. shift of the rotating ethylene also points in this direction; for (**18**) the shift is δ 1.75 compared with δ 1.33 and 1.92 for (**19**) and (**20**) respectively. Interestingly, complex (**18**), with ethylene bound to ruthenium, is the product expected of hydride attack upon the α carbon of a μ-CH=CH_2 group π-bound to ruthenium, providing additional support for the formulation of (**15**).

We turn now to the structure of μ-alkylidene iron–ruthenium complexes. For the μ-CH_2 complex (**10**) one *cis* and one *trans* isomer are possible and both are observed, in *ca.* 5:1 ratio in $CDCl_3$ at room temperature. For each of (**11**)—(**14**) a mixture of two isomers is also seen, but four are possible. Steric interactions between alkylidene substituents and η-C_5H_5 rings were seen[25] to strongly influence the relative stability of μ-alkylidene di-iron and diruthenium complexes, and on this basis the two most stable isomers will be the *cis*-(**a**) and *trans*-(**b**) forms illustrated. The former is predicted to be the most favourable and i.r. and n.m.r. spectra of (**11**)—(**14**) do indeed show that a *cis* isomer is dominant in solution. For (**11**), (**12**), and (**14**), which contain a μ-CHR alkylidene ligand, the *cis*-(**a**):*trans*-(**b**) ratio is in the range 4—6:1 in $CDCl_3$ at room temperature, but for (**13**), which contains μ-C(Me)Et, a more equal distribution (*ca.* 2:1) is evident and expected.

The isomers of (**10**)—(**14**) could not be separated by crystallisation and only for (**11**) was separation achieved by chromatography. This gave a sample of (**11b**) which isomerised in CH_2Cl_2 solution within 0.5 h to yield an equilibrium mixture of (**11a**) and (**11b**). It is likely that *cis* $\rightleftharpoons$ *trans* isomerisation occurs similarly for the other μ-alkylidene complexes at room temperature. For diruthenium μ-alkylidene complexes it was established[27] that *cis* $\rightleftharpoons$ *trans* isomerisation proceeds *via* a bridge $\rightleftharpoons$ terminal alkylidene ligand migration and the same can be expected for the iron–ruthenium system.

The diruthenium analogues of (**10**) and (**11**) react with a variety of alkynes to produce complexes in which one,[28] two,[29] three,[30] or four[30] molecules of alkyne are linked with the alkylidene in a hydrocarbon chain bound to the dimetal centre. For the di-iron system, however, linking of only one molecule of alkyne with a μ-alkylidene was observed.[28] In order to determine whether the iron–ruthenium centre would support oligomerisation we examined the reactions of (**10**) and (**11**) with alkynes. In the event, products containing only one molecule of alkyne were obtained, even after prolonged reaction with a large excess of alkyne. The crystalline complexes [FeRu(CO)(μ-CO)(μ-$CR^3CR^2CHR^1$)(η-C_5H_5)$_2$] (**21**)—(**31**) were isolated in 10—50% yields as mixtures of isomers (**a**) and (**b**) for all alkynes except ethyne, from which only isomer (**a**) was obtained. The isomers were not separable by chromatography but the (**a**):(**b**) ratio varied slightly upon recrystallisation, reflecting a small difference in solubility. No evidence for (**a**) $\rightleftharpoons$ (**b**) interconversion was obtained; the (**a**):(**b**) ratio for a particular batch of crystals did not vary from one solvent to another, nor on warming. The (**a**):(**b**) ratio is strongly dependent on the nature of the alkyne, but less influenced by the nature of the alkylidene ligand. Thus, for isomers derived from the μ-CH_2 complex (**10**) the ratios (determined by ^1H n.m.r. spectroscopy) are as follows: (**21a**), 100%; (**22a**):(**22b**), 3:2; (**23a**):(**23b**), 3:1; (**24a**):(**24b**), 3:2; (**25a**):(**25b**), 1:3; and (**26a**):(**26b**), 3:1. For isomers derived from the μ-CHMe complex (**11**) the corresponding data are:



(a) (b)

(21a) $R^1 = R^2 = R^3 = H$
(22a,b) $R^1 = R^2 = H, R^3 = Me$
(23a,b) $R^1 = H, R^2 = R^3 = Me$
(24a,b) $R^1 = R^2 = H, R^3 = Ph$
(25a,b) $R^1 = H, R^2 = R^3 = Ph$
(26a,b) $R^1 = H, R^2 = R^3 = CO_2Me$
(27a) $R^1 = Me, R^2 = R^3 = H$
(28a,b) $R^1 = R^3 = Me, R^2 = H$
(29a,b) $R^1 = R^2 = R^3 = Me$
(30a,b) $R^1 = Me, R^2 = R^3 = Ph$
(31a,b) $R^1 = Me, R^2 = R^3 = CO_2Me$

(27a), 100%; **(28a)**:**(28b)**, 3:1; **(29a)**:**(29b)**, 1:4; **(30a)**:**(30b)**, 1:6; and **(31a)**:**(31b)**, 1:10. We have been unable to decipher this pattern of dependency, but since the ratios could partially reflect such variables as the relative stability of the isomers towards u.v. radiation this failure is not perhaps surprising.

From the monosubstituted alkynes RC_2H (R = Me or Ph) complexes **(22)**, **(24)**, and **(28)** are obtained in which the substituent occupies the R^3 position, *i.e.* the alkylidene links specifically with the unsubstituted carbon of the alkyne. This is also the case for the linking of alkylidene ligands with alkynes RC_2H (R = Me or Ph) at di-iron and diruthenium centres.[31] Since methyl and phenyl have opposite inductive effects this specificity is likely to be the result of steric control, the alkylidene linking with the least crowded end of the alkyne.

A steric effect is also evident in the observation that the alkylidene methyl group in **(27)**—**(31)** fills the R^1 position; this is revealed in the large coupling constant between the alkylidene proton and a proton in the R^2 position, consistent with their mutual *trans* orientation. An *X*-ray diffraction study on $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}CMeCMeCH_2)(\eta\text{-}C_5H_5)_2]$,[32] the diruthenium analogue of **(23)**, provides an explanation for this specificity in that the site corresponding to R^1 was recognised[29] as the less crowded of the two which the alkylidene substituents can occupy.

In addition to a product **(21)**—**(31)** the reactions of **(10)** and **(11)** with alkynes RC_2R (R = H or Me) and RC_2H (R = Me or Ph) also afford a dimetallacyclopentenone complex **(2)**, **(3)**, **(6)**, or **(7)**, in 25—45% yield. At first sight this suggests that **(10)** and **(11)** dissociate either a molecule of CO or the alkylidene on photolysis, with species $[FeRu(CO)_2(CHR)(\eta\text{-}C_5H_5)_2]$ and $[FeRu(CO)_3(\eta\text{-}C_5H_5)_2]$ then co-ordinating an alkyne, followed by alkyne–CHR or alkyne–CO linking respectively. However, if this is so a dimetallacyclopentenone product should also have been isolated from reactions of diphenylacetylene and dimethyl acetylenedicarboxylate, but no trace of these known complexes was seen. It must therefore be concluded that the first step in the process is an associative one, presumably the reaction of alkyne with photochemically activated **(10)** or **(11)**, followed by the competitive loss of either CO or CHR, and that for alkynes with powerful electron-withdrawing substituents alkyne–alkylidene linking is strongly favoured, resulting in the loss of CO exclusively. Whether CO is lost from ruthenium or iron will determine whether isomer **(a)** or **(b)** is formed.

When attempts were made to induce alkyne oligomerisation by heating **(10)** and **(11)** with an excess of alkyne under u.v. irradiation over several days only low yields of **(21)**—**(31)** were obtained. This suggests that the creation of a vacant site for an incoming alkyne, by loss of CO or de-co-ordination of the double bond in **(21)**—**(31)**, results instead in decomposition.

We saw earlier that **(1)** reacts faster with alkynes than its di-iron or diruthenium analogues. The same is true for **(10)** and **(11)**. For example, the corresponding μ-CHMe complexes of iron–ruthenium, di-iron, and diruthenium are consumed by ethyne in the order: FeRu (1 h) > Fe_2 (2 h)[31] > Ru_2 (16 h).[31]

Conclusions

Both in the range of the products formed and in the speed of reactions the iron–ruthenium system closely resembles the di-iron system. Few restrictions are therefore placed on the organic chemistry of the dimetal centre by its heteronuclear character. Both carbon–carbon bond-formation and -cleavage processes are observed. Interestingly, in reactions with alkynes the reactivity of the FeRu centre does not fall between that of the Fe_2 and Ru_2 centres but is greater than that of the Fe_2 centre. This enhanced reactivity suggests that further study of the organic chemistry of heteronuclear dimetal centres will be worthwhile.

Experimental

Techniques and instrumentation were generally as described in Part 1[20] of this Series. I.r. spectra were recorded with a Nicolet 5-MS Fourier-transform spectrometer. Methyl-lithium (Ventron); $LiBHEt_3$, $NaBH_4$, and $HBF_4{\cdot}OEt_2$ (Aldrich); propyne (B.D.H.); but-2-yne (Koch-light); phenylacetylene, diphenylacetylene, dimethyl acetylenedicarboxylate, and ethyl diazoacetate (Aldrich) were used as supplied. Acetylene (B.O.C.) was purified by passage through water and sulphuric acid, then over potassium hydroxide and calcium chloride. The ylides $Ph_3P{=}CHR$ (R = H or Me) were prepared by the literature method.[33] Data for new compounds are collected in Tables 3 and 4.

Preparations.—$[FeRu(CO)_4(\eta\text{-}C_5H_5)_2]$ **(1)**. A tetrahydrofuran (thf) solution (250 cm^3) of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$, prepared from $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (2.76 g, 7.8 mmol), was added dropwise to a thf solution (25 cm^3) of $[RuI(CO)_2(\eta\text{-}C_5H_5)]$ (5 g, 14.2 mmol), and the mixture stirred for 6 h. Solvent was then removed under reduced pressure and the residue applied as a dichloromethane (10 cm^3) slurry to an alumina column (45 × 4 cm). Elution with dichloromethane–hexane (1:1) developed a single deep red band from which 4.57 g of crude **(1)** was obtained as a red-black powder. Several recrystallisations from dichloromethane–hexane removed $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and yielded pure red-black crystals of **(1)** (3.42 g, 60%).

$[FeRu(CO)(\mu\text{-}CO)(\mu\text{-}COCHCH)(\eta\text{-}C_5H_5)_2]$ **(2)**. While slowly purging with ethyne, a toluene (250 cm^3) solution of **(1)** (1 g, 2.5 mmol) in a silica flask was subjected to u.v. irradiation. After 1 h **(1)** was consumed. The solution was then evaporated under reduced pressure and the residue chromatographed as for **(1)** above. Elution with dichloromethane–acetone (20:1) gave an olive-coloured band which provided 0.2 g (20%) of **(2)** as a green-brown powder after recrystallisation from dichloromethane–hexane.

$[FeRu(CO)(\mu\text{-}CO)(\mu\text{-}COCR^1CR^2)(\eta\text{-}C_5H_5)_2]$ **(3)**—**(7)**. Analogues of **(2)** were prepared in a similar manner, employing 1 g (2.5 mmol) of **(1)** in toluene (250 cm^3) and a five-fold excess of alkyne. Reactions with relatively involatile alkynes (diphenylacetylene, phenylacetylene, dimethyl acetylenedicarboxylate) were continuously purged with nitrogen, while volatile alkynes (propyne, but-2-yne) were condensed into the reaction mixture and irradiation carried out on a closed system. Reaction times (h) and yields (%) respectively were as follows: **(3)**, 4, 32; **(4)**, 16, 65; **(5)**, 16, 60; **(6)** 2, 30; **(7)**, 4, 30.

$[FeRu(CO)_2(\mu\text{-}CO)\{\mu\text{-}C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ **(8)**. A toluene (100 cm^3) solution of **(5)** (0.45 g, 0.88 mmol) was heated at 100 °C for 16 h in a sealed, evacuated Carius tube. Chromatography, eluting with dichloromethane–hexane (3:2), gave a red band which yielded 0.17 g (38%) of red crystalline **(8)** upon recrystallisation from dichloromethane–pentane.

$[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]BF_4$ **(15)**. To a suspension of **(2)** (0.2 g, 0.5 mmol) in diethyl ether (20 cm^3) was added a large excess of $HBF_4\cdot OEt_2$ (*ca.* 1 cm^3). Over 15 min the brown-green suspension was replaced by a dark red one. The solvent and unreacted acid were decanted off and the residual red powder washed several times with diethyl ether before recrystallisation from dichloromethane–hexane (10:1) gave 0.21 g (85%) of **(15)** as dark red crystals.

$[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CR^1{=}CHR^2)(\eta\text{-}C_5H_5)_2]BF_4$ **(16)**, **(17)**. The μ-CH=CHMe **(16)** and μ-CMe=CHMe **(17)** analogues of **(15)** were prepared in the same way, in yields of *ca.* 90%.

$[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ **(10)**. (*a*) To a toluene (100 cm^3) solution of **(1)** (0.5 g, 1.25 mmol) was added 2.75 cm^3 of a 1 mol dm^{-3} solution of $LiBHEt_3$ in diethyl ether. After stirring at room temperature for 3 h water (0.5 cm^3) was added and after a further 0.5 h the mixture was evaporated and chromatographed. Elution with dichloromethane–hexane (1:1) separated an orange band which gave 0.36 g (75%) of deep orange crystalline **(10)** from dichloromethane–hexane.

(*b*) A mixture of **(4)** (3 g, 5.5 mmol) and $Ph_3P{=}CH_2$ (7.5 g, 27.1 mmol) in toluene (250 cm^3) was heated at reflux for 0.5 h, the colour changing from green to red. Chromatography separated PPh_3 on elution with hexane and an orange band due to **(10)** with dichloromethane–hexane (1:1). After recrystallisation from the same solvent mixture 1.2 g (57%) of pure **(10)** was obtained as orange needles.

$[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ **(11)**. (*a*) Methyllithium in diethyl ether (2 mol equiv.) was added to a thf (50 cm^3) solution of **(1)** (0.25 g, 0.63 mmol) and the mixture stirred for 0.5 h. An excess of $HBF_4\cdot OEt_2$ (*ca.* 0.2 cm^3) was added, giving a deep red solution of $[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta\text{-}C_5H_5)_2]^+$ **(9)** [ν(CO) at 2 049s, 2 015m, and 1 856w cm^{-1}] over 0.5 h. An excess of $NaBH_4$ (0.5 g, 13.2 mmol) was now added and after stirring for 0.25 h the solution was evaporated and the residue extracted with several portions of dichloromethane. The combined extracts were washed through a short alumina column with dichloromethane and then chromatographed. Elution with dichloromethane–hexane (1:1) developed two red bands, the first yielding **(11b)** and the second **(11a)**. The former rapidly converted to the latter, the combined yield of red crystalline **(11)** being 0.1 g (39%) after recrystallisation.

(*b*) Heating together **(4)** and $Ph_3P{=}CHMe$ in toluene, as described above for **(10)**, provides **(11)** in 60% yield after chromatography as in (*a*).

(*c*) An excess of $NaBH_4$ (0.15 g, 3.95 mmol) and **(15)** (0.2 g, 0.41 mmol) were mixed in acetone (30 cm^3) at −78 °C, then allowed to warm to room temperature over 0.5 h. Solvent was evaporated and the residue extracted with dichloromethane. The extracts were chromatographed as in (*a*) to provide 0.1 g (61%) of **(11)**, but an additional yellow band gave rise to orange powdery $[FeRu(CO)(\mu\text{-}CO)_2(C_2H_4)(\eta\text{-}C_5H_5)_2]$ **(18)** in a yield varying between 0 and 30% from several reactions performed under apparently identical conditions.

$[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\eta\text{-}C_5H_5)_2]$ **(12)**, **(13)**. These, μ-CHEt **(12)** and μ-C(Me)Et **(13)**, complexes were prepared in a manner similar to that described in (*c*) above, in yields of 82 and 32% respectively.

$[FeRu(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCO_2Et)(\eta\text{-}C_5H_5)_2]$ **(14)**. A toluene (100 cm^3) solution of **(4)** (1.0 g, 1.82 mmol) and ethyl diazoacetate (1.04 g, 12.3 mmol) was heated at reflux for 0.5 h, giving a deep red colour. Chromatography, eluting with dichloromethane–hexane (1:1), yielded traces of **(1)**, while dichloromethane–hexane (10:1) removed a red band from which red needles of **(14)** (0.25 g, 30%) were obtained after recrystallisation from the same solvent mixture. Finally, elution with dichloromethane–acetone (20:1) separated a green band which afforded 50 mg of unreacted **(4)**.

$[FeRu(CO)(\mu\text{-}CO)(\mu\text{-}CHCHCH_2)(\eta\text{-}C_5H_5)_2]$ **(21)**. While slowly purging with ethyne, a toluene (250 cm^3) solution of **(10)** (0.25 g, 0.65 mmol) in a silica flask was subjected to u.v. irradiation. After 0.5 h all of **(10)** was consumed. The solution was evaporated under reduced pressure and the residue chromatographed. Elution with dichloromethane–hexane (1:1) developed a red-brown band which yielded 0.09 g (37%) of crystalline **(21)** from dichloromethane–pentane. Further elution with dichloromethane–acetone (20:1) gave a brown-green band from which 0.09 g (35%) of **(2)** was obtained.

$[FeRu(CO)(\mu\text{-}CO)(\mu\text{-}CR^3CR^2CHR^1)(\eta\text{-}C_5H_5)_2]$ **(22)**—**(31)**. Analogues of **(21)** were prepared in a similar manner, employing 0.2—0.5 g of complexes **(10)** and **(11)**, and a ten-fold excess of alkyne. Experimental variations for the different alkynes were as outlined above for **(3)**—**(7)**. Reaction times (h) and yields (%) respectively were as follows: **(22)**, 2, 13; **(23)**, 6, 27; **(24)**, 16, 50; **(25)**, 16, 31; **(26)**, 16, 41; **(27)**, 1, 32; **(28)**, 3, 10; **(29)**, 8, 31; **(30)**, 48, 29; **(31)**, 16, 39.

The corresponding yields (%) of the dimetallacyclopentenone co-products were: **(6)**, 26; **(3)**, 41; **(7)**, 11; none; none; **(2)**, 40; **(6)**, 35; **(3)**, 35; none; none.

X-Ray Data Collection and Structure Determination.—Crystals of $[FeRu(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ **(1a)** grow as hexagonal prisms. A crystal of dimensions [distance to faces (*hkl*) from centre] 0.125 (100, $\bar{1}00$) × 0.25 (010, $0\bar{1}0$) × 0.3 ($01\bar{1}$, $0\bar{1}1$) × 0.3 (011, $0\bar{1}\bar{1}$) mm was sealed under nitrogen in a Lindemann capillary tube and used for the collection of 1 950 independent diffracted intensities in the range $4 \leqslant 2\theta \leqslant 60°$ (*hkl* range 0, 0, −10 to 11, 18, 10) at 298 K on a Nicolet *P*3 diffractometer. Two check reflections were remeasured every 50 reflections and showed no evidence of crystal decay during data collection. Reflections with $I > 2\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation based on counting statistics only, were considered as observed, a total of 1 532 reflections being used in structure solution and refinement.

Crystal data. $C_{14}H_{10}FeO_4Ru$, $M = 399$, monoclinic, $a = 7.064(2)$, $b = 12.518(3)$, $c = 8.011(2)$ Å, $\beta = 106.23(2)°$, $U = 680.2(3)$ Å^3, $D_m = 1.92$ g cm^{-3} (aqueous flotation), $Z = 2$, $D_c = 1.95$ g cm^{-3}, $F(000) = 392$, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation, $\lambda = 0.710\,69$ Å, and $\mu(\text{Mo-}K_\alpha) = 21.6$ cm^{-1}.

The structure was solved using heavy-atom methods and blocked-cascade least squares. The metal atoms were located in a sharpened Patterson synthesis and subsequent electron-density difference syntheses revealed the positions of all other atoms, including hydrogens. All non-hydrogen atoms were allowed to refine with anisotropic thermal parameters, and the hydrogen atoms were refined freely with isotropic thermal parameters. Due to the disorder of the molecule about a centre of inversion at the mid-point of the metal–metal bond, the iron and ruthenium atoms were each refined with a site occupancy of 0.5, and with positional and thermal parameters which were constrained to be identical. A weighting scheme with $w = [\sigma^2(F) + 0.0002(F)^2]^{-1}$ where $\sigma(F)$ is the estimated standard deviation based on counting statistics only, gave a satisfactory analysis of variance. Refinement converged at R 0.0275 (R' 0.0313), and the final electron-density difference synthesis showed no peaks > 0.38 or < -0.40 e Å^{-3}, the largest peaks lying in close proximity to the metal atoms. Scattering factors were taken from ref. 34 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.[35]

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