Organic Chemistry of Dinuclear Metal Centres. Part 3.[1] μ-Carbene Complexes of Iron and Ruthenium from Alkynes *via* μ-Vinyl Cations

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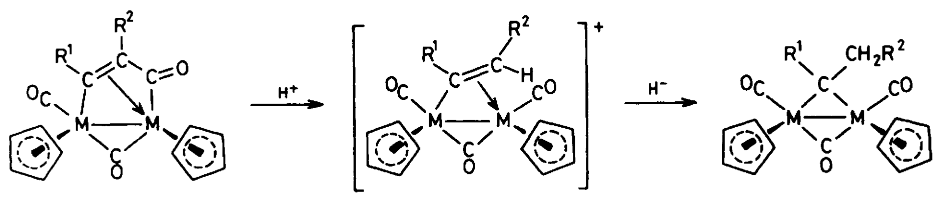
Protonation of the complexes $[M_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2R_2\}(\eta\text{-}C_5H_5)_2]$ [M = Fe or Ru; R_2 = H_2, Ph_2, H(Me), or H(Ph)] with $HBF_4{\cdot}OEt_2$ results in rapid carbon–carbon bond cleavage and formation of the μ-vinyl cations $[M_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(R){=}C(H)R\}(\eta\text{-}C_5H_5)_2]^+$, containing a *cis* arrangement of R groups. Addition of $HBF_4{\cdot}OEt_2$ to $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Me_2\}(\eta\text{-}C_5H_5)_2]$ produces the cation $[Ru_2(CO)(\mu\text{-}CO)(\{\mu\text{-}C(H)(O)C_2Me_2\}(\eta\text{-}C_5H_5)_2]^+$, which isomerises slowly to $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me){=}C(H)Me\}(\eta\text{-}C_5H_5)_2]^+$. The μ-vinyl cations exist in solution as isomers with *cis* and *trans* orientations of terminal ligands, shown by variable-temperature n.m.r. to interconvert; *cis* isomers additionally display a fluxional oscillation of the μ-vinyl ligand. Treatment of the cations with $NaBH_4$ yields μ-carbene complexes $[M_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(R)CH_2R\}(\eta\text{-}C_5H_5)_2]$ in good yield, also as *cis* and *trans* isomers which interconvert in solution. These result from hydride addition to the β-carbon of the μ-vinyl, but addition to the α-carbon is apparent in the low-yield co-formation of the terminal ethylene complex $[Ru_2(CO)(\mu\text{-}CO)_2(C_2H_4)(\eta\text{-}C_5H_5)_2]$ from the cation $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]^+$. Addition of sodium tetrahydroborate to $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(H)(O)C_2Me_2\}(\eta\text{-}C_5H_5)_2]^+$ provides the complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Me)C(Me)CH_2\}(\eta\text{-}C_5H_5)_2]$, completing a conversion of metallacyclic CO to CH_2. Regeneration of the μ-vinyl cation $[M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]^+$ is achieved by treatment of $[M_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)Me\}(\eta\text{-}C_5H_5)_2]$ with $[CPh_3][BF_4]$.

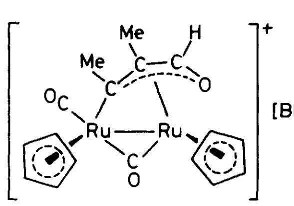
In Part 1 of this Series we reported the syntheses of di-iron and diruthenium complexes $[M_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2R_2\}(\eta\text{-}C_5H_5)_2]$ (1)—(12) through reactions of alkynes with $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$.[2] The chemistry of these dimetallacyclopentenone complexes was marked by the ease with which the alkyne–CO link is broken, and this feature is again apparent in their protonation, which is described herein. The μ-vinyl cations which are formed are attacked by nucleophiles to yield μ-carbene complexes, completing a sequence of reactions by which an alkyne is converted to a carbene co-ordinated at a dinuclear metal centre. Current interest in such complexes[3] is high because they may serve as models for carbenes bound to a metal surface, as in the Fischer–Tropsch synthesis of hydrocarbons.[4,5] Aspects of this work have appeared as preliminary communications.[6,7]



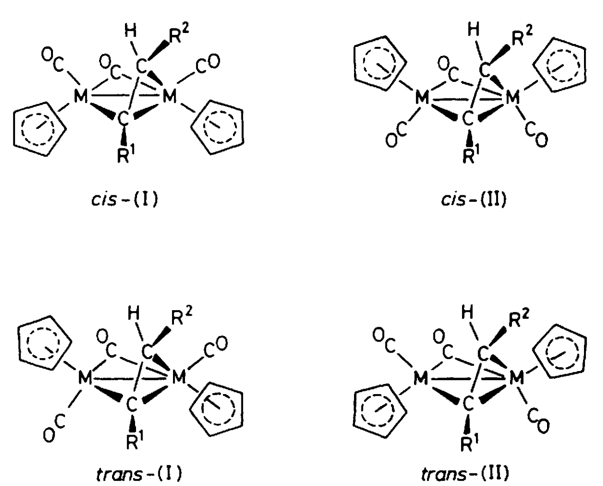
M = Fe; R¹ = R² = H	(1)	(13)	(27)
M = Fe; R¹ = H, R² = Me	(2)	(14)	(28)
M = Fe; R¹ = Me, R² = H	(3)	(15)	(29)
M = Fe; R¹ = R² = Me	(4)	(16)	(30)
M = Fe; R¹ = H, R² = Ph	(5)	(17)	(31)
M = Ru; R¹ = R² = H	(6)	(18)	(32)
M = Ru; R¹ = H, R² = Me	(7)	(19)	(33)
M = Ru; R¹ = Me, R² = H	(8)	(20)	(34)
M = Ru; R¹ = R² = Ph	(9)	(21)	(35)
M = Ru; R¹ = H, R² = Ph	(10)	(22)	(36)
M = Ru; R¹ = Ph, R² = H	(11)	(23)	(37)
M = Ru; R¹ = R² = Me	(12)	(24)	(38)
M = Fe; R¹ = H, R² = D			(39)
M = Fe; R¹ = H, R² = CN			(40)
M = Fe; R¹ = H, R² = $PMe_2Ph^+BF_4^-$			(41)

Results and Discussion

μ-Vinyl Cations.—Synthesis. Addition of $HBF_4{\cdot}OEt_2$ to an acetone or dichloromethane solution of the di-iron and diruthenium complexes $[M_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2R_2\}(\eta\text{-}C_5H_5)_2]$ (1)—(11) results in immediate cleavage of the alkyne–CO link. The 'alkyne' portion of the dimetallacycle is protonated, generating μ-vinyl cations $[M_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CR^1{=}C(H)R^2\}(\eta\text{-}C_5H_5)_2][BF_4]$ (13)—(23) in which R¹ and R² are *cis* to one another, while the metallacyclic ketonic carbonyl is transformed into a terminal ligand. Different behaviour is shown by the diruthenium complex (12), derived from but-2-yne, which yields the appropriate μ-vinyl cation (24) only very slowly and *via* a readily isolated intermediate (25). This anomaly is discussed in detail below. Infrared spectra indicated that the μ-vinyl complexes are formed in clean,



(25)



cis-(I) cis-(II)

trans-(I) trans-(II)

Figure 1. Isomers of μ-vinyl cations

quantitative reactions, and this was confirmed when crystallisation gave the μ-$CH{=}CH_2$ species (13) and (18) in 98 and 95% yields respectively. Purple crystalline (13) and yellow crystalline (18) are air stable both in the solid state and in common polar organic solvents at room temperature. The other di-iron μ-vinyl complexes are isolated in lower yields but display similar stability. Isolation of the other diruthenium complexes as analytically pure substances proved difficult; they were, however, readily characterised by i.r. and n.m.r. spectroscopy (Tables 1 and 2).

The pairs of isomeric complexes (2)/(3), (7)/(8), and (10)/(11) for which $R^1 \neq R^2$ are inseparable; indeed at elevated temperatures they interconvert.[2] At room temperature they exist in ratios of 20 : 1, 7 : 1, and 10 : 1 respectively. Protonation could therefore be expected to produce solutions of the paired cations (14)/(15), (19)/(20), and (22)/(23). In practice (14) was formed as the major component of a mixture with (15) but protonation of the (10)/(11) mixture gave (23) alone. Although neither (19) nor (20) was identified, the nature of the μ-carbene complexes derived from the cation mixture confirms that both are present.

Structure. In order to establish the nature of the μ-vinyl complexes an *X*-ray diffraction study was undertaken on the compound $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2][BF_4]$ (13). The results of this study are described in detail in the following paper.[8] The cation contains an $Fe_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2$ unit with *cis* dispositions of the pairs of terminal CO and η-C_5H_5 ligands relative to the $Fe_2(\mu\text{-}CO)$ plane. Bridging the single metal–metal bond [2.595(2) Å] is a vinyl group σ-bound to one iron and η²-bound to the other, with a carbon–carbon distance of 1.40(2) Å which reflects some occupancy of the π* orbital. The CH carbon of the vinyl is equidistant from each iron atom and lies in the same plane as the $Fe_2(\mu\text{-}CO)$ grouping; it may therefore be thought of as a ' bridging ' carbon. The CH_2 group of the vinyl is oriented *anti* with respect to the pair of η-C_5H_5 ligands so that it lies on the same side of the molecule as the pair of *cis* carbonyls. Although this is certainly favourable sterically, electronic influences may also dictate that the vinyl group is co-ordinated effectively *trans* to η-C_5H_5 rather than to strongly π-accepting CO.

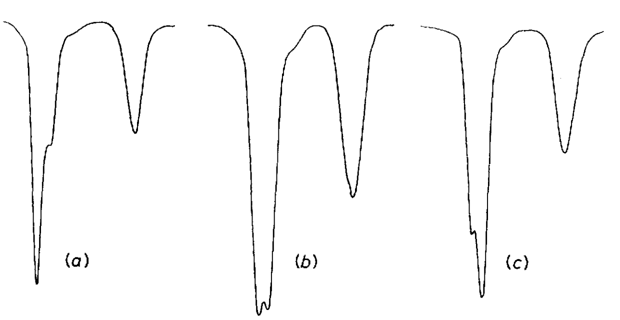


Figure 2. I.r. spectra (CO stretching region) of μ-vinyl cations in CH_2Cl_2: (*a*) (13), (*b*) (14)/(15), (*c*) (16)

There are four possible structural isomers of the μ-vinyl cations, represented in Figure 1. If the vinyl group does indeed seek to be co-ordinated *trans* to η-C_5H_5 rather than CO then *cis*-(I) and *trans*-(I) are favoured. However, steric factors are likely to be important in determining the relative stability of the four isomers. It was recognised earlier[2] that substituents on the bridging carbon of the complexes (1)—(12) are held in a crowded position adjacent to two *cis* cyclopentadienyl ligands; this is reflected, for example, in the formation of (2) and (10) in preference to (3) and (11) when $[M_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and RC_2H (R = Me or Ph) react. The relative stabilities of the four forms of the cations should therefore depend on the degree to which steric interactions between the cyclopentadienyl ligands and the R^1 and $C(H)R^2$ groups carried by the bridging vinyl carbon are minimised. When $R^1 = H$ it is clear that, whatever the nature of R^2, the order of stability on these grounds will be *cis*-(I) > *trans*-(I) > *trans*-(II) > *cis*-(II), and it is the *cis*-(I) structure which is indeed adopted by the $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)(\eta\text{-}C_5H_5)_2]^+$ cation in the solid state. However, when $R^1 = R^2 \neq H$, and especially when $R^1 \neq H$ and $R^2 = H$, the *trans*-(I) form could become of equal or even greater stability than *cis*-(I).

Infrared and n.m.r. evidence presented below will reveal that only one *cis* and one *trans* form of each cation is encountered, and from this point these will be taken to be *cis*-(I) and *trans*-(I) species.

Infrared spectra. I.r. spectra show that both *cis* and *trans* forms of the μ-vinyl cations are present in solution, and that their relative abundance is dependent on the nature of the substituents in the μ-vinyl. This can be seen by reference to Figure 2, which displays i.r. spectra for a series of di-iron μ-vinyl cations. Spectrum (*a*) is due to the μ-$CH{=}CH_2$ complex (13) and is entirely in accord with a *cis*-$Fe_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2$ unit, as found in the solid state. One strong and one weak i.r.-active terminal carbonyl band are predicted for such an arrangement, arising from the symmetric and antisymmetric stretching of this pair of carbonyls. As methyl substitution in the vinyl group increases, through μ-$CH{=}C(H)Me$ in (14) to μ-$C(Me){=}C(H)Me$ in (16), a corresponding increase in intensity of the weak terminal carbonyl band is observed in spectrum (*b*) and again in (*c*), when it has become the more intense. A similar trend exists for the analogous diruthenium μ-vinyl cations. For a *trans*-$Fe_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2$ unit only one i.r.-active terminal carbonyl band is predicted (the antisymmetric stretching), and the growth in intensity of the band in passing from (*a*) to (*c*) can be attributed to an increase in the proportion of a *trans* isomer whose single CO band is accidentally degenerate with the weaker band of the *cis* isomer

Table 1. Physical and other data for new compounds

Compound	Colour	M.p./°C	Analysis [a] (%) C	Analysis [a] (%) H	*M* [a,b]
(13)	Purple	175—176 [c]	41.0 (40.9)	2.9 (2.9)	353 (353) [d]
(14)/(15)	Purple	190 [c]	—	—	367 (367) [d]
(16)	Purple	173—179 [c]	43.3 (43.6)	3.5 (3.6)	381 (381) [d]
(17)	Purple	90 [c]	48.6 (48.8)	3.5 (3.3)	429 (429) [d]
(18)	Yellow	224—225 [c]	33.7 (33.8)	2.5 (2.4)	444 (444) [d]
(21)	Yellow	—	—	—	596 (596) [d]
(24)	Yellow	222—223 [c]	37.2 (36.6)	3.2 (3.1)	472 (472) [d]
(27)	Orange	169 [c]	50.9 (50.9)	3.6 (3.9)	354 (354)
(28)	Orange	176—179 [c]	52.2 (52.2)	4.4 (4.4)	368 (368)
(29)	Dark red	147—150 [c]	52.1 (52.2)	4.5 (4.3)	368 (368)
(30)	Orange	157—161 [c]	53.3 (53.4)	4.7 (4.6)	382 (382)
(31)	Red	148—150	58.6 (58.6)	4.2 (4.2)	430 (430)
(32)	Yellow	168—170	40.4 (40.5)	3.2 (3.2)	445 (445)
(34)	Yellow	180—185	42.0 (41.9)	3.7 (3.5)	459 (459)
(37)	Yellow	228 [c]	48.3 (48.4)	3.4 (3.5)	521 (521)
(38)	Yellow	142—143	43.3 (43.2)	4.0 (3.8)	473 (473)
(39)	Orange	169 [c]	50.9 (50.9)	4.0 (4.2)	355 (355)
(40)	Orange	140—150 [c]	50.0 (50.7)	3.5 (3.4) [e]	379 (379)
(41)	Red	175—176	47.1 (47.7)	4.2 (4.2) [f]	491 (491) [d]

[a] Calculated values in parentheses. [b] Mass spectrometry with electron-impact ionisation unless otherwise stated. [c] Melts with decomposition. [d] Mass spectrometry with field-desorption ionisation; cation only. [e] N 3.1 (3.7)%. [f] P 5.7 (5.4)%.

The bridging carbonyl bands of the *cis* and *trans* isomers are evidently of very similar frequency.

The increased tendency towards a *trans* configuration for the μ-C(Me)=C(H)Me cation (16) was predicted above. The same steric arguments lead to the expectation that the μ-CH=C(H)Me cation (14) will favour the *cis* form even more strongly than the unsubstituted (13), but that the μ-C(Me)=CH_2 cation (15) will favour a *trans* form. The *trans* form observed in the i.r. spectrum of a (14)/(15) mixture is therefore most likely due to (15). This steric effect is nicely illustrated by the i.r. spectra of the di-iron μ-CH=C(H)Ph cation (17) and the diruthenium μ-C(Ph)=CH_2 cation (23). While cation (17) displays the expected spectrum characteristic of the *cis* form, this structure is clearly destabilised when bulky phenyl is attached directly to the bridging vinyl carbon, as in (23), whose spectrum indicates a high proportion of *trans* isomer in solution (Table 2).

N.m.r. spectra and fluxionality. The μ-vinyl cations are fluxional. Characterisation by n.m.r. was therefore based on data obtained at low temperatures (in the range −40 to −90 °C), when interconversion ceased and distinct species were observable (Table 2). Both *cis* and *trans* isomers of the μ-vinyl cations were detected under these conditions. These are indistinguishable by n.m.r. (each has inequivalent CO and C_5H_5 ligands) and the i.r. evidence of their relative abundance is therefore a useful aid in their assignment. The fact that *cis* and not *trans* isomers can be expected to display an oscillatory fluxionality (see below) is also discriminatory.

Consider first the unsubstituted μ-vinyl complexes (13) and (18). At low temperatures their ^1H n.m.r. spectra are very similar, seen in Figure 3. For the diruthenium complex, there are two sets of signals corresponding to the presence of two isomers, assigned as *cis* (major) and *trans* (minor) on the basis of the i.r. spectrum. Although the weak cyclopentadienyl resonances of the *trans* isomers of both (13) and (18) are observable, only for (18) is the concentration of the *trans* isomer sufficient to allow detection of its μ-vinyl protons. The μ-vinyl ^1H resonances (Table 2) of (13) and (18) are of the classic form observed in $[Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)]$,[9] $[Fe_2(CO)_6(\mu\text{-}SMe)(\mu\text{-}CHCH_2)]$,[10] and $[Mo_2(CO)_4(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2]^+$,[11] with coupling constants of 12, 7, and 1—2 Hz which are as expected for *J*(*trans*), *J*(*cis*), and *J*(*geminal*) respectively. The signal of (13) and (18) at *ca.* δ 10—12 p.p.m. is readily assigned to the vinylic CH proton on the basis of the couplings, and those at *ca.* δ 5 and 3 p.p.m. to the methylenic protons *cis* and *trans* to it. The low-field shift of the μ-CH proton is not unexpected. In each of the complexes (1)—(12), when R^1 = H (*i.e.*, when a μ-CH group is present) a similar low-field signal in the range δ 10—13 is observed.[2] This is characteristic of a proton attached to a μ-carbene carbon atom,[3] and the vinyl groups in (13) and (18) do indeed exhibit a ^{13}C n.m.r. shift typical of such a carbon, at 185.8 and 163.6 p.p.m. respectively. A striking comparison is with the μ-carbene complex $[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)Me\}(\eta\text{-}C_5H_5)_2]$ (27), which displays an n.m.r. signal for the μ-C(*H*)Me proton at δ 11.60 and for the μ-*C*(H)Me carbon at 172.9 p.p.m.

Mono-substituted μ-vinyl complexes are readily identified as either of μ-C(H)=C(H)R or μ-C(R)=CH_2 type by the presence or absence of a low field ^1H n.m.r. signal due to μ-C(H). For μ-C(H)=C(H)R the R group is shown to be *cis* to μ-C(H) by a *trans* coupling of *ca.* 12 Hz between the two vinyl protons. The arrangement of substituents in μ-C(R)=C(H)R cations is not established unequivocally by n.m.r., but if the protonation to give these is of the same stereospecificity as above then the R groups will be mutually *cis*.

The variations in the ^1H n.m.r. spectra of the μ-vinyl cations can be understood in terms of the occurrence of two independent dynamic processes in solution, summarised in Figure 4. These are (*a*) a *cis* $\rightleftharpoons$ *trans* isomerisation of the C_5H_5 and CO ligands and (*b*) the well known [12] oscillation (σ–π interconversion) of a μ-vinyl between two metal atoms. In common with mechanisms proposed for *cis* $\rightleftharpoons$ *trans* isomerisation in the iron and ruthenium complexes $[M_2(CO)_2(\mu\text{-}CO)_2(\eta\text{-}C_5H_5)_2]$ [13] and $[M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CR_2)(\eta\text{-}C_5H_5)_2]$ (see Figure 7) it is likely that the interconversion of the μ-vinyl cations occurs *via* bridge-opening, rotation about the unsupported metal–metal bond, and bridge-closure, as illustrated. The fluxional μ-vinyl oscillation (*b*) renders the C_5H_5 ligands of a *cis* isomer equivalent while maintaining the independence of the methylenic protons, but cannot make the C_5H_5 ligands of a *trans* isomer equivalent. The oscillation

Table 2. I.r. and n.m.r. data for μ-vinyl and related cations

Compound	Carbonyl bands (cm^{-1}) [a]	^1H N.m.r. (δ/p.p.m.) [b,c]	^{13}C N.m.r. (δ/p.p.m.) [b]
(13)	2 037s, 2 012m, 1 863m	3.00 (dd, *J* 2 and 12, 1 H), 5.13 (dd, *J* 2 and 7, 1 H), 5.58 (s, 5 H), 5.75 (s, 5 H), 12.57 (dd, *J* 7 and 12, 1 H) [d]	65.3 (CH_2), 89.8 (C_5H_5), 93.0 (C_5H_5), 185.8 (CH)
(14)/(15)	2 031s, 2 015s, 1 864m	*cis*: 3.72 (s, 3 H), 5.67 (s, 5 H), 5.85 (s, 5 H), 11.96 (d, *J* 12, 1 H) [e] *trans*: 5.37 (s, 5 H), 5.57 (s, 5 H) [e,f]	—
(16)	2 026s, 2 009s, 1 862m	*cis*: 1.97 (s, 3 H), 3.81 (s, 3 H), 5.88 (s, 5 H), 6.19 (s, 5 H) [f,g] *trans*: 6.27 (s, 5 H), 6.41 (s, 5 H) [f,g]	*cis*: 21.3 (CH*Me*), 38.8 (C*Me*), 79.3 (*C*HMe), 91.6 (C_5H_5), 92.3 (C_5H_5), 160.3 (*C*Me) [h] *trans*: 21.1 (CH*Me*), 38.6 (C*Me*), 82.2 (*C*HMe), 92.3 (C_5H_5), 94.1 (C_5H_5) [h]
(17)	2 029s, 2 006m, 1 858m	*cis*: 4.72 (d, *J* 13, 1 H), 5.32 (s, 5 H), 5.96 (s, 5 H), 7.44 (m, 3 H), 7.91 (m, 2 H), 12.78 (d, *J* 13, 1 H) [i]	—
(18)	2 035s, 2 010m, 1 869m	*cis*: 3.69, (dd, *J* 1 and 12, 1 H), 5.19 (dd, *J* 1 and 7, 1 H), 6.01 (s, 5 H), 6.14 (s, 5 H), 11.22 (dd, *J* 7 and 12, 1 H) [j] *trans*: 4.05 (dd, *J* 1 and 7, 1 H), 5.09 (dd, *J* 1 and 11, 1 H), 5.87 (s, 5 H), 5.97 (s, 5 H), 10.32 (dd, *J* 7 and 11, 1 H) [j]	*cis*: 59.3 (CH_2), 91.5 (C_5H_5), 94.5 (C_5H_5), 163.6 (CH), 196.3 (CO), 199.9 (CO) *trans*: 92.5 (C_5H_5), 93.6 (C_5H_5) [f]
(19)/(20)	2 037s, 2 019s, 1 871m	—	—
(21)	2 032s, 2 016s, 1 872m	5.74 (s, 5 H), 5.82 (s, 5 H), 7.24 (br, 10 H) [f]	—
(23)	2 038s, 2 017s, 1 874m	*cis*: 3.84 (d, *J* 3, 1 H), 5.30 (d, *J* 3, 1 H), 5.80 (s, 5 H), 5.92 (s, 5 H), 7.4—7.9 (m, 5 H)	—
(24)	2 028s, 2 009s, 1 869m	*cis*: 2.06 (d, *J* 7, 3 H), 3.60 (s, 3 H), 4.18 (q, *J* 7, 1 H), 6.18 (s, 5 H), 6.30 (s, 5 H) [k] *trans*: 2.06 (d, *J* 7, 3 H), 3.52 (s, 3 H), 4.64 (q, *J* 7, 1 H), 6.00 (s, 5 H), 6.06 (s, 5 H) [k]	—
(25)	2 020s, 1 875m	2.22 (s, 3 H), 3.84 (s, 3 H), 5.62 (s, 5 H), 5.78 (s, 5 H), 9.50 (s, 1 H)	17.1 (Me), 37.6 (Me), 89.7 (C_5H_5), 91.8 (C_5H_5), 218.0 (CH) [l]

[a] CH_2Cl_2 solution. [b] [$^2H_6$]Acetone solution. [c] Coupling constants in Hz. [d] At −60 °C. [e] At −50 °C; signals due to Me and μ-CH=C(*H*)Me protons partly obscured by acetone and H_2O resonances respectively. [f] Other signals unobserved. [g] At −30 °C. [h] At −75 °C. [i] At −90 °C. [j] At −50 °C. [k] At −46 °C. [l] [$^2H_3$]Nitromethane solution.

is, in any event, unlikely to occur in a *trans* isomer since a sterically very unfavourable *trans*-(II) configuration would be traversed.

The n.m.r. spectrum of (18) at various temperatures clearly shows [Figure 3(*a*)] that a *cis* $\rightleftharpoons$ *trans* isomerisation occurs on the n.m.r. time scale. On warming above −50 °C the signals due to the isomers coalesce, until at 50 °C only two cyclopentadienyl resonances and one set of three vinyl proton resonances are present. Such an isomerisation must generate two C_5H_5 signals as long as the μ-vinyl is rigidly and asymmetrically bound to the diruthenium centre. It is apparent that the δ 6.14 signal of the *cis* isomer coalesces with the δ 5.87 of the *trans*, and the δ 6.01 signal of the *cis* with the δ 5.97 of the *trans*, the different chemical-shift separations resulting in different coalescence rates. At 50 °C the process is evidently not rapid enough to complete the pair-wise averaging of the C_5H_5 signals, and one of the two seen at this temperature is not fully sharpened. Higher temperatures could not be achieved with the acetone solvent, and (18) reacted with both pyridine and nitromethane substitutes.

The ^1H n.m.r. spectrum of (13) varies with temperature similarly to (18), and at 30 °C the spectrum of (13) strongly resembles that of (18) at 50 °C [Figure 3(*b*)]. A similar *cis* $\rightleftharpoons$ *trans* isomerisation is therefore indicated. However, above 30 °C the C_5H_5 signals of (13) broaden further and at 50 °C are approaching coalescence. We suggest that the onset of μ-vinyl oscillation within the *cis* isomer is responsible. Unfortunately, it was also not possible to obtain spectra above 50 °C for (13) because of solvent restrictions and the limiting high-temperature spectrum was not achieved. The μ-vinyl oscillation of (13) is of higher energy than *cis* $\rightleftharpoons$ *trans* isomerisation; it is likely that a similar oscillation occurs for (18), but of even higher energy so that it is unobserved by n.m.r. below the 50 °C accessible to us.

The clearest evidence of μ-vinyl oscillation is provided by the n.m.r. spectrum of the di-iron μ-C(H)=C(H)Ph cation (17) at various temperatures. Steric arguments predict that this complex should strongly favour a *cis* configuration, confirmed by the i.r. spectrum, and at −90 °C only a single isomer is observed. On warming, the two C_5H_5 signals of the isomer broaden, coalesce at −60 °C, and at 0 °C appear as a sharp singlet, in accord with the fluxional motion (*b*) of Figure 4.

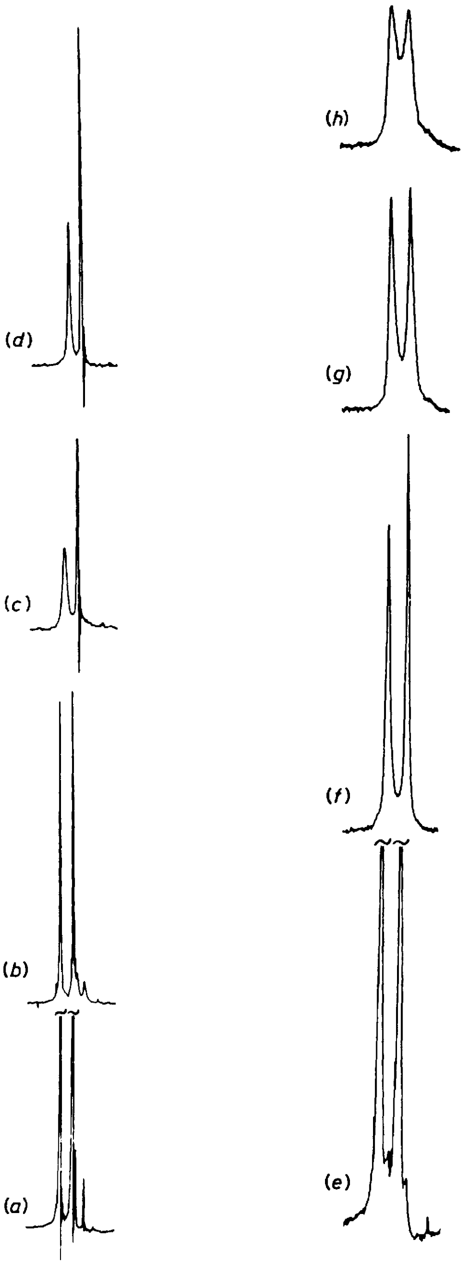


Figure 3. Proton n.m.r. spectra (η-C_5H_5 signals) in [$^2H_6$]acetone of (18) at (*a*) −50, (*b*) 0, (*c*) 30, (*d*) 50 °C and of (13) at (*e*) −60, (*f*) 30, (*g*) 40, and (*h*) 50 °C

Based on a coalescence temperature of 213 K and a chemical-shift separation of 64 Hz for the C_5H_5 signals in the absence of exchange a free energy of activation of 43 kJ mol^{-1} may be calculated for the μ-vinyl oscillation. By comparison with (17), the μ-C(Ph)=CH_2 diruthenium cation (23) exists in solution predominantly as a *trans* isomer which shows no sign of fluxionality up to 70 °C, as expected.

For the di-iron μ-C(Me)=C(H)Me cation (16) two pairs of C_5H_5 signals are seen at −90 °C in the ^{1}H n.m.r. spectrum, in the intensity ratio *ca.* 2.25 : 1. The less intense pair is, by reference to Figure 2(*c*), due to the *cis* isomer and, in confirmation, on warming to 10 °C only this pair broadens and coalesces as a result of μ-vinyl oscillation. On warming further, *cis* $\rightleftharpoons$ *trans* isomerisation occurs and all the cyclopentadienyl signals coalesce to give a sharp singlet above 55 °C. Similar behaviour is observed for the diruthenium analogue

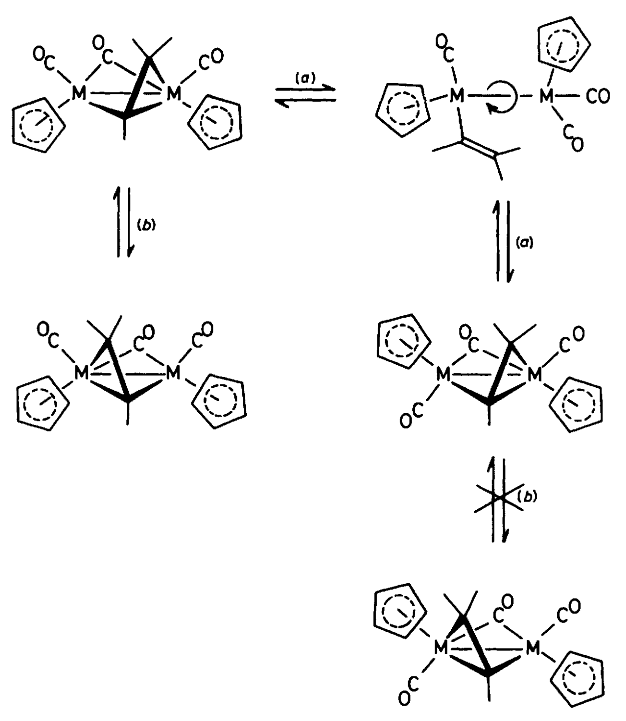


Figure 4. Dynamic processes for μ-vinyl cations

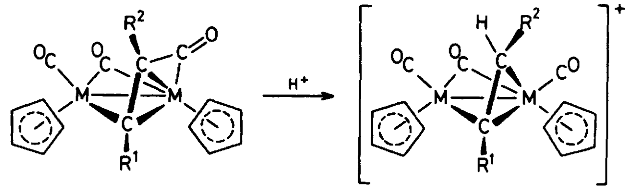


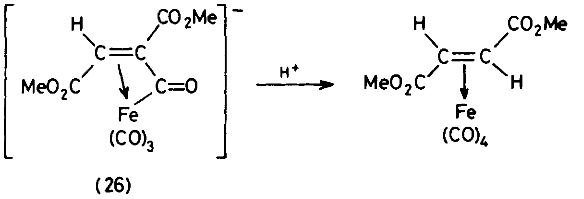
Figure 5. Stereochemistry of protonation

(24), which exists as *cis* and *trans* isomers in *ca.* 1 : 2 ratio at −50 °C. Compared with (13) and (18) methyl substitution as in (16) and (24) resulted in *cis* $\rightleftharpoons$ *trans* isomerisation now being of higher energy than μ-vinyl oscillation.

The n.m.r. spectrum of the mixture of μ-C(H)=C(H)Me and μ-C(Me)=CH_2 cations (14) and (15) reveals at −80 °C the presence of only two species, seen as one strong and one weak pair of C_5H_5 signals in *ca.* 10 : 1 ratio. The i.r. spectrum [Figure 2(*b*)], and a low-field ^{1}H n.m.r. signal at δ 11.96 of the correct intensity, identify the major species as the *cis* form of (14). No other low-field signal is observed, indicating that the minor species is an isomer of (15), containing a μ-C(Me) rather than μ-C(H) group. This methyl signal is seen at δ 3.72, a shift which may be compared with that of δ 3.81 for the corresponding methyl of the cation (16). On warming, the signals of *cis*-(14) coalesce at *ca.* −30 °C and appear as a sharp singlet at 0 °C, whereas those of *trans*-(15) are unchanged at this temperature. Again, the ability of a μ-vinyl oscillation to cause averaging of C_5H_5 environments in a *cis*, but not *trans*, isomer is apparent. Above 0 °C the C_5H_5 signals of *trans*-(15) also broaden and at 50 °C are unobserved, an indication either of a *cis* $\rightleftharpoons$ *trans* isomerisation of (15) or possibly a (14) $\rightleftharpoons$ (15) interconversion. The latter possibility is discussed below for the μ-vinyl cations in general.

Mechanism of protonation. An *X*-ray diffraction study on the dimetallacyclopentenone complex (9) established the structure which in Figure 5 is generalised for (1)—(12). The two substituents R^1 and R^2 are in a *cis* arrangement on a co-ordinated double bond, and the two C_5H_5 ligands are *cis* with respect to the M–M bond. Proton n.m.r. spectra of the μ-vinyl cations (14) and (17) clearly show that it is the $C(R^2)$ carbon which is protonated and that R^1 and R^2 retain their *cis* orientation upon protonation, as shown in Figure 5. Such stereoselectivity would be expected if initial attack was on the dimetal centre, followed by an intramolecular *endo* proton transfer to carbon $C(R^2)$. Creation of diplatinum μ-vinyl cations *via* proton migration from the dimetal centre to carbon has recently been observed.[14]

A related protonation occurs for the mononuclear iron complex (26).[15] Again an acyl to terminal carbonyl transformation is involved and the geometry of the olefinic portion of the ligand is retained.



(26)

Inspection of Figure 5 suggests that the *cis*-(I) isomer of the cations will be the kinetically controlled product of protonating (1)—(12), which have *cis* η-C_5H_5 ligands.

There is strong evidence that, whether preceded by metal protonation or not, the ketonic carbon of the dimetallacyclopentenones is protonated prior to the eventual production of the μ-$C(R^1)$=C(H)R^2 vinyl cations. Addition of $HBF_4{\cdot}OEt_2$ to complex (12) results in the immediate formation of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(H)(O)C_2Me_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ (25), isolated as orange crystals in near quantitative yield. The ^1H n.m.r. spectrum (Table 2) shows, in addition to the signals for inequivalent cyclopentadienyl and methyl groups, one at δ 9.50 (1 H) attributed to a formyl proton. The possibility of *O*-protonation was excluded by the addition to the n.m.r. sample of D_2O, which did not affect the signal at δ 9.50. Protonation at carbon was confirmed by the presence of a ^{13}C n.m.r. signal at 218.0 p.p.m. with the high intensity expected of a carbon bearing a proton exerting a nuclear Overhauser effect; other carbons without a hydrogen substituent were unobserved. The i.r. spectrum displays only single terminal and bridging carbonyl bands, indicating that no C–C cleavage occurs on protonation, and the absence of any ν(C=O) in the range 1 500—1 800 cm^{-1} suggests that the formyl carbonyl group is side-on co-ordinated to ruthenium, as depicted in (25). In this way the cation can satisfy the 18-electron rule without creating a new terminal CO ligand.

The cation (25) slowly isomerises to the μ-vinyl cation (24) in acetone at room temperature, being quantitatively converted after 16 h. It is therefore apparent that the formation of the remaining μ-vinyl cations (13)—(23) may also follow this unusual path, where transfer of a proton from the metallacyclic ketonic carbon to the $C(R^2)$ carbon occurs with simultaneous C–C bond cleavage. The high stability of (25) compared with other analogous intermediates is, however, difficult to account for.

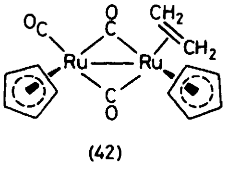
Once the dimetallacycle is cleaved and a μ-vinyl cation created it may yet be possible for a hydrogen shift to occur to provide a more thermodynamically stable μ-vinyl species. It was seen that there is some n.m.r. evidence that the isomeric μ-C(H)=C(H)Me and μ-C(Me)=CH_2 di-iron cations (14) and (15) may interconvert. Moreover, protonation of the 20 : 1 (2) : (3) mixture affords the cations (14) and (15) in *ca.* 10 : 1 ratio, and the amounts of μ-carbene complexes (28) and (29) derived from this cation mixture accord with a (14) : (15) ratio of nearer 2 : 1. Likewise, protonation of the 7 : 1 mixture of the diruthenium dimetallacyclopentenones (7) and (8) provides a mixture of μ-vinyl cations from which the μ-carbene complexes (33) and (34) are obtained in 1 : 3.5 ratio, indicating that the μ-C(Me)=CH_2 cation (20) is the major component and not the expected μ-C(H)=C(H)Me species (19). The exclusive formation of the μ-C(Ph)=CH_2 cation (23) from the 10 : 1 mixture of (10) and (11) is a further example of the lack of correlation between the composition of a mixture of isomeric dimetallacyclopentenones and the composition of the mixture of μ-vinyl cations formed on its protonation. These observations are explained by the presence of an equilibrium between μ-C(H)=C(H)R and μ-C(R)=CH_2 cations in solution. For μ-C(H)=C(H)Me and μ-C(Me)=CH_2 such an interconversion has been shown to occur in dimolybdenum cations.[16] Thus, protonation of the μ-allene complex $[Mo_2(CO)_4(\mu\text{-}CH_2{=}C{=}CH_2)(\eta\text{-}C_5H_5)_2]$ gives $[Mo_2(CO)_4\{\mu\text{-}C(H){=}C(H)Me\}(\eta\text{-}C_5H_5)_2]^+$ and not $[Mo_2(CO)_4\{\mu\text{-}C(Me){=}CH_2\}(\eta\text{-}C_5H_5)_2]^+$, which must be formed initially. Vinyl isomerisation of this type probably involves a temporary hydrogen shift to a bonding site on the dimetal centre.

μ-Carbene Complexes.—Synthesis. Treatment of the cations (13)—(24) with $NaBH_4$ in acetone at room temperature or below effects rapid hydride addition to the β-carbon of the μ-vinyl, generating the appropriate μ-carbene complex (27)—(38). Anomalously, no μ-carbene complex (35) is obtained after adding $NaBH_4$ to the cation (21). This cannot be because a μ-C(Ph)CH_2Ph complex is unstable on steric grounds, since the μ-CPh_2 analogue may be obtained by a different route and is quite stable.[17] Addition of deuteride, cyanide, or dimethylphenylphosphine to (13) occurs also at the β-carbon of the μ-vinyl, to form (39), (40), and (41) respectively.

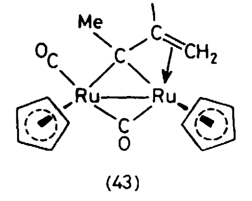
The mixtures of μ-C(H)=C(H)Me and μ-C(Me)=CH_2 cations (14)/(15) and (19)/(20) each give mixtures of μ-C(H)Et and μ-CMe_2 carbene complexes. However, the relative amounts of (28) and (29) (1.8 : 1) and (33) and (34) (1 : 3.5) are unrelated to the compositions of the (14)/(15) (10 : 1) and (19)/(20) [derived from 7 : 1 (7)/(8)] mixtures of μ-vinyl cations. This is accounted for by the ability of μ-C(H)=C(H)R and μ-C(R)=CH_2 cations to interconvert, as discussed earlier. Conversion of μ-CMe_2 to μ-C(H)Et has been observed in dicobalt complexes,[18] but up to 114 °C for (29) and 140 °C for (34) no such rearrangement occurred.

The μ-carbene complexes exist as isomers with both *cis* and *trans* arrangements of the CO and C_5H_5 ligands, a feature discussed in more detail below. For iron, the *trans* isomers are purple and the *cis* isomers orange, while for ruthenium both *cis* and *trans* are yellow. The isomers are often separable by chromatography but *cis* $\rightleftharpoons$ *trans* interconversion occurs rapidly in solution and the μ-carbene complexes were therefore characterised as mixtures of isomers (Tables 1 and 3).

Addition of $NaBH_4$ to the diruthenium μ-CH=CH_2 cation (18) gave not only the μ-C(H)Me complex (32), but a low yield of the terminal ethylene complex $[Ru_2(CO)(\mu\text{-}CO)_2(C_2H_4)(\eta\text{-}C_5H_5)_2]$ (42), providing evidence for a small degree of hydride attack on the α-carbon of the μ-vinyl. This species is obtainable [17] in much higher yield (60—70%) directly from the reaction of ethylene with (9), and its chemistry will be dis-



(42)



(43)

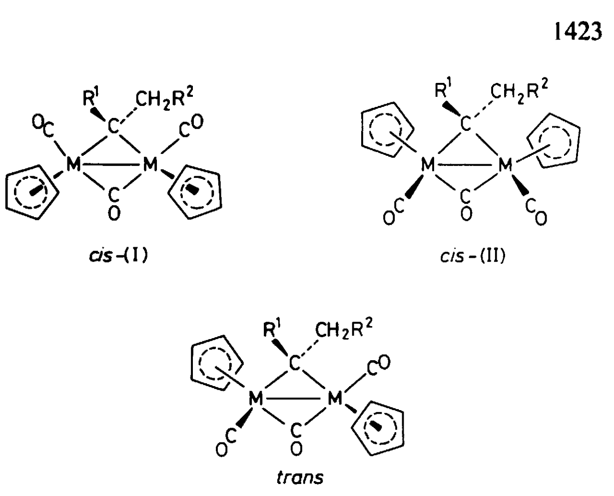
cussed more fully in a forthcoming publication. It is interesting to note that its formation here, by the sequence of H^+ and H^- addition to (6), which is formed from acetylene, concludes an acetylene to ethylene transformation at a diruthenium centre. No other olefin complex was formed in these syntheses, although propene and but-2-ene analogues of (42) are known.[19] The di-iron analogue of (42) exists but is unstable unless held under an atmosphere of ethylene; [19] its non-appearance as a product of treating (13) with $NaBH_4$ is not, therefore, evidence that it is not formed.

When $NaBH_4$ is added to the μ-C(Me)=C(H)Me cation (24) the expected μ-C(Me)Et carbene complex (38) is produced. However, hydride addition to (25), the established precursor of (24), affords not only (38) but also the complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(Me)C(Me)CH_2\}(\eta\text{-}C_5H_5)_2]$ (43). It is evident that hydride reduction of the co-ordinated formyl has occurred to give a methylene group, presumably *via* an alcohol intermediate. Complex (43) has been prepared previously by another route and its structure determined by *X*-ray diffraction.[7] Its formation by successive addition of H^+ and H^- to (12) represents, however, a unique transformation of metallacyclic carbonyl to methylene. One mechanism proposed for hydrocarbon chain growth in the Fischer–Tropsch synthesis involved CO ' insertion ' into a surface metal alkyl, followed by conversion of acyl carbonyl to methylene, and so on.[20] Although this has lost popularity recently in the face of other mechanisms, the conversion of (12) to (43) suggests that a related process involving CO as a member of a dimetallacycle is not inconceivable, at least as one of what are probably several pathways leading to carbon chain growth.

The μ-vinyl to μ-carbene synthesis is reversible in that hydride abstraction from the methyl group of the μ-C(H)Me complexes (27) and (32) is effected by treatment with $[CPh_3][BF_4]$, giving (13) and (18) respectively in good yield. This route to (13) has also been discovered by Pettit and co-workers.[21]

Structure. An *X*-ray diffraction study was undertaken on the μ-C(H)Me complex (27) and is described in detail in the following paper.[8] The complex has been prepared by two other routes, (*a*) hydride addition to the μ-methylcarbyne cation $[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)\}(\eta\text{-}C_5H_5)_2]^+$ (ref. 22) and (*b*) heating $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $Ph_3P{=}C(H)Me$,[22] and its structure independently determined.[23] Structural studies have also been completed on related $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ [22] and $[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)(CO_2Bu^t)\}(\eta\text{-}C_5H_5)_2]$,[24] obtained by treating $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $Ph_3P{=}CH_2$ and $CH(CO_2Bu^t)N_2$ respectively.

The iron atoms of (27) are at a single bond distance [2.520(2) Å] and are bridged symmetrically by a carbonyl and a methylcarbene ligand such that there is a dihedral angle of 166° between the FeC(carbene)Fe and FeC(carbonyl)Fe planes. The FeC(carbene)Fe [78.8(1)] and $HCCH_3$ [112(2.5)°] angles are normal for what is now a wide range of structurally established μ-carbene complexes.[3] The pairs of carbonyl and cyclopentadienyl ligands of (27) are disposed *cis* with respect to the central $Fe_2(\mu\text{-}C)_2$ core, and the methyl group is *anti* to the C_5H_5 ligands.



cis-(I) cis-(II)

trans

Figure 6. Isomers of μ-carbene complexes

There are three possible isomers, two *cis* and one *trans*, for the complexes of μ-carbenes with different carbon substituents. They are shown in Figure 6. When $R^1 = CH_2R^2$ then *cis*-(I) and *cis*-(II) are identical, and only single *cis* and *trans* isomers are possible. For reasons outlined earlier when discussing μ-vinyl cations, the relative stabilities of the isomers of the μ-carbene complexes can be expected to depend strongly on the sizes of the R^1 and CH_2R^2 groups, and the minimisation of their interactions with the sterically demanding C_5H_5 ligands. When $R^1 = H$ the order of stability is then *cis*-(I) > *trans* > *cis*-(II), and it is *cis*-(I) which is indeed adopted by (27) and $[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)(CO_2Bu^t)\}(\eta\text{-}C_5H_5)_2]$ [24] in the solid state, but when the R^1 and CH_2R^2 groups are identical (*e.g.* $\mu\text{-}CMe_2$) or similar [*e.g.* μ-C(Me)Et] in size the balance between isomers is predicted to be more even. On the single occasion when R^1 is larger than CH_2R^2 [in the μ-C(Me)Ph complex (37)] the preferred isomer will be *cis*-(II). There is no firm evidence for the existence of more than one *cis* isomer for any of the μ-carbene complexes, and *cis* is from this point to be understood as implying the form with the larger μ-carbene substituent oriented *anti* with respect to the cyclopentadienyls.

Infrared spectra. The *cis* and *trans* isomers of the μ-carbene complexes display carbonyl i.r. spectra (Table 3) of the same form as the corresponding isomers of the μ-vinyl cations. The normally dominant *cis* component is therefore seen as two terminal and one bridging carbonyl bands, with the *trans* revealing its presence by overlapping and increasing the intensity of the lower-energy terminal band and the bridging band.

N.m.r. spectra and isomerisation. Unlike the μ-vinyl cations, the *cis* and *trans* isomers of the μ-carbene complexes can be distinguished by ^1H and ^{13}C n.m.r. spectra (Table 3). Thus, for a complex of a μ-carbene with different substituents, the *cis* form displays one C_5H_5 resonance and the *trans* form two. Both the *cis* and *trans* forms of a complex of a μ-carbene with identical substituents have a single C_5H_5 resonance, but the existence of two substituent environments for the *cis* and only one for the *trans* now discriminates between the isomers.

Noteworthy features of the n.m.r. spectra are the now characteristic [3] low-field shifts of both the μ-carbon (δ 172—183 for iron, 142—186 p.p.m. for ruthenium) and the μ-C(H) proton (δ 10.6—11.8 for iron, 10.1—11.0 p.p.m. for ruthenium) of a μ-carbene ligand.

The ratios of *cis* : *trans* isomers in solution are readily determined by n.m.r. and fulfil predictions of their relative stabilities based on steric effects. Thus, in $[^2H_8]$toluene at room temperature, the *cis* : *trans* ratios for the di-iron complexes of $\mu\text{-}CMe_2$ (29), μ-C(H)Me (27), μ-C(H)Et (28), and $\mu\text{-}C(H)CH_2Ph$ (31), with progressively different-sized substituents, are *ca.* 0.8 : 1, 4.6 : 1, 9.5 : 1, and >50 : 1 respectively. A similar trend is apparent for the diruthenium complexes of $\mu\text{-}CMe_2$ (34), μ-C(Me)Et (38), μ-C(H)Me (32), and μ-C(Me)Ph (37), whose respective *cis* : *trans* ratios are *ca.* 0.7 : 1, 1.3 : 1, 4 : 1, and >40 : 1 in $[^2H_1]$chloroform at room temperature.

The *cis* : *trans* ratio for the μ-carbene complexes varies with the solvent. For example, the 4.6 : 1 ratio for the μ-C(H)Me complex (27) in $[^2H_8]$toluene becomes *ca.* 13 : 1 in $[^2H_5]$pyridine, and in $[^2H_6]$acetone only the *cis* form is

Table 3. I.r. and n.m.r. data for μ-carbene compounds

Compound	Carbonyl bands (cm^{-1})	^{1}H N.m.r. (δ/p.p.m.)	^{13}C N.m.r. (δ/p.p.m.)
(27)	1 986s, 1 948m, 1 797s [a]	*cis*: 3.22 (d, *J* 8, 3 H), 4.17 (s, 10 H), 11.60 (q, *J* 8, 1 H) [b]	*cis*: 43.3 (Me), 87.8 (C_5H_5), 172.9 (CH), 214.2 (CO), 273.7 (μ-CO) [c]
		trans: 3.19 (d, *J* 8, 3 H), 4.28 (s, 5 H), 4.37 (s, 5 H), 10.62 (q, *J* 8, 1 H) [b]	*trans*: 44.0 (Me), 89.4 (C_5H_5), 173.5 (CH), 88.7 (C_5H_5) [c,d]
(28)	1 987s, 1 950w, 1 797m [a]	*cis*: 1.51 (t, *J* 8, 3 H), 3.25 (quin, *J* 8, 2 H), 4.18 (s, 10 H), 11.38 (t, *J* 8, 1 H) [b]	*cis*: 20.9 ($CH_2\mathit{C}H_3$), 50.4 ($\mathit{C}H_2CH_3$), 87.5 (C_5H_5), 182.9 (CH), 213.6 (CO) [c]
		trans: 4.18 (s, 5 H), 4.28 (s, 5 H) [b,d]	*trans*: 89.1 (C_5H_5), 90.4 (C_5H_5) [c,d]
(29)	1 982s, 1 942s, 1 791m [a]	*cis*: 2.96 (s, 3 H), 3.08 (s, 3 H), 4.15 (s, 10 H) [b]	—
		trans: 3.01 (s, 6 H), 4.26 (s, 10 H) [b]	
(30)	1 981m, 1 942s, 1 788m [a]	1.50 (m, 6 H), 3.00 (m, 4 H), 3.12 and 3.16 (2 s, 6 H), 4.65 (m, 20 H) [e,f]	—
(31)	1 976s, 1 935m, 1 775m	4.36 (d, *J* 9, 2 H), 4.66 (s, 10 H), 7.42 (m, 5 H), 11.76 (t, *J* 9, 1 H) [g]	61.7 ($\mathit{C}H_2Ph$), 87.2 (2 C_5H_5), 125.7 (Ph), 128.4 (Ph), 147.0 (Ph), 178.4 ($\mathit{C}HCH_2Ph$), 212.7 (CO) [d,e]
(32)	1 974s, 1 933m, 1 776m [h]	*cis*: 3.04 (d, *J* 7, 3 H), 5.18 (s, 10 H), 10.94 (q, *J* 7, 1 H) [e]	*cis*: 43.2 (Me), 89.3 (C_5H_5), 142.9 (*C*HMe) [d,e]
		trans: 3.16 (d, *J* 7, 3 H), 5.18 (s, 5 H), 5.24 (s, 5 H), 10.14 (q, *J* 7, 1 H) [e]	*trans*: 91.0 (C_5H_5), 91.9 (C_5H_5) [d,e]
(33)	*i*	*cis*: 1.23 (t, *J* 6, 3 H), 10.53 (t, *J* 8, 1 H) [e,j]	—
(34)	1 972s, 1 932m, 1 777m [h]	*cis*: 2.78 (s, 3 H), 3.16 (s, 3 H), 4.68 (s, 10 H) [b]	*cis*: 54.3 (Me), 56.1 (Me), 90.9 (C_5H_5), 175.7 ($\mathit{C}Me_2$), 200.6 (CO) [d,e]
		trans: 3.02 (s, 6 H), 4.82 (s, 10 H) [e]	*trans*: 55.7 (Me), 92.3 (C_5H_5), 175.1 ($\mathit{C}Me_2$) [d,e]
(37)	1 987s, 1 943w, 1 780m [h]	2.99 (s, 3 H), 5.29 (s, 10 H), 6.9—7.5 (m, 5 H) [e]	59.9 (Me), 91.4 (C_5H_5), 124.3 (Ph), 126.7 (Ph), 129.8 (Ph), 168.3 (Ph), 178.1 (*C*MePh), 198.5 (CO), 245.8 (μ-CO) [e]
(38)	1 973s, 1 934m, 1 775m [h]	*cis*: 1.25 (t, *J* 7, 3 H), 2.97 (s, 3 H), 3.09 (q, *J* 7, 2 H), 5.21 (s, 10 H) [e]	*cis*: 17.4 ($CH_2\mathit{C}H_3$), 51.3 ($C\mathit{C}H_3$), 58.3 ($\mathit{C}H_2CH_3$), 91.0 (C_5H_5), 184.7 (*C*MeEt), 200.4 (CO) [d,e]
		trans: 1.31 (t, *J* 7, 3 H), 3.03 (s, 3 H), 3.10 (m, 2 H), 5.24 (s, 5 H), 5.25 (s, 5 H) [e]	*trans*: 18.3 ($CH_2\mathit{C}H_3$), 50.6 ($C\mathit{C}H_3$), 58.4 ($\mathit{C}H_2CH_3$), 92.3 (2 C_5H_5, br), 185.7 (*C*MeEt), 199.7 (CO), 200.1 (CO) [e]
(39)	1 986s, 1 948m, 1 797s [a]	3.14 (dd, J_{HH} 7, J_{HD} <2, 2 H), 4.70 (s, 10 H), 12.03 (t, J_{HH} 7, J_{HD} <2, 1 H) [e]	—
(40)	1 991s, 1 952m, 1 806m [a]	3.86 (d, *J* 8, 2 H), 4.78 (s, 10 H), 10.89 (t, *J* 8, 1 H) [e]	—
(41)	1 978s, 1 939m, 1 791m	2.62 (d, J_{HP} 14, 6 H), 4.49 (dd, J_{HH} 8, J_{HP} 14, 2 H), 4.80 (s, 10 H), 11.71 (d of t, J_{HH} 8, J_{HP} 14, 1 H) [g]	—

[a] Hexane solution. [b] [$^2H_8$]toluene solution. [c] [$^2H_5$]pyridine solution. [d] Other signals unobserved. [e] [$^2H_1$]chloroform solution. [f] Overlapping signals of two isomers. [g] [$^2H_6$]acetone solution. [h] CH_2Cl_2 solution. [i] Complex inseparable from (34). [j] Other signals obscured by those of (34).

detectable. Likewise, the 0.8 : 1 ratio for the μ-CMe_2 complex (29) in [$^2H_8$]toluene becomes *ca.* 2 : 1 in [$^2H_6$]acetone. More polar solvents clearly favour the *cis* isomer. These observations imply the existence of a *cis* ⇌ *trans* equilibrium, which was confirmed and investigated by variable-temperature n.m.r. spectroscopy. The *cis* : *trans* ratios for the di-iron complexes of μ-C(H)Me (27), μ-C(H)Et (28), and μ-CMe_2 (29) were determined in the range 0—105 °C in a solvent of low polarity, [$^2H_8$]toluene, in which a measurable proportion of *trans* isomer is present. Significant increases in the *trans* isomer population were observed, the *cis* : *trans* ratios decreasing from *ca.* 4.6 : 1 to 2.2 : 1 at 105 °C for (27), from *ca.* 9.5 : 1 to 4.1 : 1 at 105 °C for (28), and from *ca.* 0.9 : 1 to 0.7 : 1 at 75 °C for (29). From plots of log{[*cis*][*trans*]$^{-1}$} *versus* T^{-1} the thermodynamic parameters shown below were obtained.

	Δ*H*/kJ mol^{-1}	Δ*S*/J K^{-1} mol^{-1}	ΔG_{298}/kJ mol^{-1}
(27)	−17.6 ± 0.6	−40.2 ± 2.0	−5.6 ± 1.2
(28)	−9.5 ± 1.0	−13.5 ± 3.0	−5.5 ± 2.0
(29)	−3.1 ± 0.5	−10.5 ± 1.0	0.0 ± 0.8

On warming above 75 °C the ^{1}H n.m.r. signals of the methyl and C_5H_5 groups of the *cis* and *trans* isomers of the μ-CMe_2 complex (29) coalesce, and a single sharp signal is

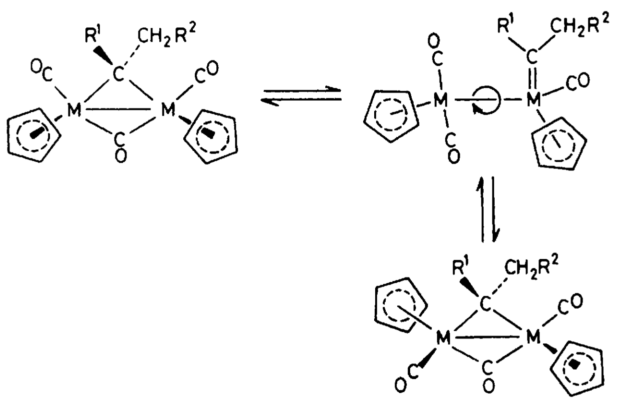


Figure 7. Mechanism of *cis* ⇌ *trans* isomerisation of μ-carbene complexes

seen for each at 114 °C. The free energy of activation for *cis* ⇌ *trans* interconversion is evidently low enough for this complex that at these temperatures the isomerisation occurs on the n.m.r. time scale. Similar behaviour is shown by the μ-CMe_2 complex of ruthenium (34), and has been briefly reported previously.[25] The study of this species and its phosphine-substituted derivatives sheds considerable light on the mechanism of *cis* ⇌ *trans* isomerisation; full details will be given in a future Part of this Series. The proposed mechanism is depicted in Figure 7, generalised for the complexes under discussion here. It envisages a concerted bridge-opening reaction to form a transient terminal carbene complex, which undergoes rotation about the metal–metal bond followed by bridge-closure to generate a new isomer.

Mechanism of formation. The μ-carbene complexes appear to be formed by nucleophilic attack on the β-carbon of a μ-vinyl cation, releasing this carbon from co-ordination while the α-carbon remains bridging. There is firm evidence for some hydride attack on the α-carbon of the μ-vinyl, however, in the formation of the ethylene complex (42) from the μ-CH=CH_2 cation (18). It was therefore possible that attack actually occurred in preference at this carbon, to generate an unstable species containing an $M{-}CH_2{-}CH_2{-}M$ dimetallacyclobutane ring which rearranges by a minor pathway to yield (42) but primarily by a hydrogen shift to give the μ-C(H)Me product (32). This type of rearrangement is found for the di-iron complex $[FeCF_2CF_2Fe(\mu\text{-}SMe)_2(CO)_6]$, which at 35 °C rearranges to the μ-carbene species $[Fe_2\{\mu\text{-}C(F)CF_3\}(\mu\text{-}SMe)_2(CO)_6]$ by a fluoride shift.[26] However, initial attack of hydride at the β-carbon of (18) was established by treating the cation with $NaBD_4$. This afforded only the μ-$C(H)CH_2D$ complex (39), shown clearly by the ^1H n.m.r. spectrum; addition to the α-carbon followed by a ^1H- or D-shift would yield a mixture of μ-$C(H)CH_2D$ and μ-$CDCH_3$ complexes.

Conclusions

The synthesis of μ-carbene complexes from the readily available alkyne-derived species (1)—(12) *via* μ-vinyl cations is a quick and efficient preparative route. In effect, an alkyne RC_2R is transformed through successive addition of H^+ and H^- into μ-$C(R)CH_2R$ at di-iron and diruthenium centres. The generality of the synthesis makes available a wide range of simple μ-carbene species, whose reactivity will be described in future Parts of this Series.

Experimental

Techniques and instrumentation were as described in Part 1[2] of this Series. Tetrafluoroboric acid was employed as the diethyl ether complex. Chromatography was on silica gel or alumina. Physical, analytical, and spectroscopic data for new compounds are collected in Tables 1, 2, and 3 respectively.

Preparation of μ-*Vinyl Complexes.*—All but one of these complexes were obtained by the same method. A few drops of $HBF_4 \cdot OEt_2$ were added to an acetone or dichloromethane solution of the appropriate complex (1)—(12) (*ca.* 0.5 mmol in 100 cm^3) at room temperature, causing an immediate colour change. After confirming by i.r. spectroscopy that starting material was consumed, solvent was removed at reduced pressure and the residue washed several times with diethyl ether. The powder so obtained was recrystallised from dichloromethane (iron complexes) or acetone–diethyl ether (ruthenium complexes), to provide crystalline samples in the following yields: (13) 98, (14)/(15) 42, (16) 76, (17) 71, and (18) 95%. The ruthenium complexes (19)—(23) did not crystallise well and poor analytical data were obtained.

Preparation of $[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)C(H)Me\}(\eta\text{-}C_5H_5)_2][BF_4]$ (24). (*a*) *Protonation of* $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Me_2\}(\eta\text{-}C_5H_5)_2]$ (12). Addition of a few drops of $HBF_4 \cdot OEt_2$ to a dichloromethane (50 cm^3) solution of (12) (70 mg, 0.15 mmol) resulted in a slight darkening of the solution. Evaporation of solvent, washing the residue with diethyl ether, and recrystallisation from dichloromethane, gave 75 mg (90%) of orange crystalline $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(H)(O)C_2Me_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ (25).

(*b*) *Isomerisation of* $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(H)(O)C_2Me_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ (25). An orange solution of (25) (40 mg, 0.07 mmol) in acetone (*ca.* 5 cm^3) became yellow over 17 h at room temperature. Evaporation of solvent and recrystallisation of the residue from acetone–diethyl ether gave 35 mg (88%) of yellow crystalline (24).

Preparation of μ-*Carbene Complexes.*—$[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)Me\}(\eta\text{-}C_5H_5)_2]$ (27). Addition of $NaBH_4$ (0.2 g, 5.26 mmol) to an acetone (100 cm^3) solution of (13) (0.72 g, 1.64 mmol) resulted in an immediate colour change from purple to orange. Evaporation of solvent and chromatography of the residue yielded overlapping purple and orange bands of *trans*-(27) and *cis*-(27) respectively, on eluting with dichloromethane–hexane (2 : 3). On removal from the column the purple fraction rapidly isomerised to the orange. The combined fractions were recrystallised from dichloromethane–hexane, giving 0.47 g (81%) of dark orange crystalline (27).

In the same manner (13) and $NaBD_4$ gave a 69% yield of (39).

$[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)Et\}(\eta\text{-}C_5H_5)_2]$ (28) *and* $[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CMe_2\}(\eta\text{-}C_5H_5)_2]$ (29). As above, $NaBH_4$ (30 mg, 0.79 mmol) and (14)/(15) (120 mg, 0.26 mmol) were mixed in acetone (100 cm^3), and chromatography subsequently gave overlapping purple and orange bands. These were removed from the column as one fraction, which afforded an orange powder on evaporating the solvent. N.m.r. spectroscopy showed this to contain a mixture of *cis* and *trans* isomers of (28) and (29) in *ca.* 1.8 : 1 ratio. The total yield was 80 mg (83%). Crystallisation from dichloromethane–hexane gave first red needles of (28) and then dark red crystals of (29) as the pure compounds.

$[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)Et\}(\eta\text{-}C_5H_5)_2]$ (30). After briefly stirring $NaBH_4$ (25 mg, 0.66 mmol) and (16) (157 mg, 0.33 mmol) in acetone (100 cm^3), chromatography as above gave purple and orange bands which were combined to yield 91 mg (71%) of the *trans* and *cis* isomers of (30) after crystallisation from dichloromethane–hexane.

$[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)CH_2Ph\}(\eta\text{-}C_5H_5)_2]$ (31). Addition of $NaBH_4$ (0.12 g, 3.16 mmol) to an acetone (100 cm^3) solution of (17) (0.52 g, 1.0 mmol) effected an immediate colour change to red. Chromatography, eluting with dichloromethane–hexane (1 : 1), gave purple and red bands of *trans*- and *cis*-(31) respectively, which were combined to afford 0.28 g (65%) of (31) after recrystallisation.

$[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)Me\}(\eta\text{-}C_5H_5)_2]$ (32). Addition of $NaBH_4$ (0.2 g, 5.26 mmol) to an acetone (125 cm^3) solution of (18) (0.68 g, 1.28 mmol) resulted in darkening in colour after 10 min. Chromatography, eluting with dichloromethane–hexane (2 : 3), developed three yellow bands. The first contained *trans*-(32) which, after leaving the column, converted rapidly to *cis*-(32), the compound in the second band. The combined yield of *cis*- and *trans*-(32) was 0.3 g (53%) after crystallisation from dichloromethane–hexane. The third band was eluted with dichloromethane–hexane (1 : 1) and provided 15 mg (3%) of yellow crystalline (42),[17] identified by i.r. and n.m.r. spectra.

$[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)Et\}(\eta\text{-}C_5H_5)_2]$ (33) *and* $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ (34). Addition of $NaBH_4$ (0.2 g, 5.26 mmol) to an acetone (150 cm^3) solution of the cations (19) and (20), obtained by protonation of the (7)/(8) (0.61 g, 1.33 mmol) mixture, resulting in rapid reaction. Chromatography, eluting with dichloromethane–hexane (1 : 1), gave a single yellow band from which 0.28 g (46%) of a 3.5 : 1 mixture of yellow crystalline (34) and (33) was obtained as *cis* and *trans* isomers. Crystallisation from dichloromethane–hexane provided a pure sample of (34), but it was not possible to isolate (33) pure even after repeated chromatography and crystallisation.

$[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)Ph\}(\eta\text{-}C_5H_5)_2]$ (37). Addition of $NaBH_4$ (0.2 g, 5.26 mmol) to an acetone (150 cm^3) solution of the cation (23), obtained from the (10)/(11) mixture (0.74 g, 1.43 mmol), produced an immediate lightening. Chromatography gave one yellow band with dichloromethane–hexane (1 : 1), containing 0.32 g (42%) of yellow crystalline (37).

$[Ru_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(Me)Et\}(\eta\text{-}C_5H_5)_2]$ (38). An excess of $NaBH_4$ (0.1 g, 2.63 mmol) was added to an acetone (100 cm^3) solution of (24) (0.13 g, 0.23 mmol) at —78 °C and the mixture stirred for 0.5 h. Chromatography gave one yellow-green band, eluted with dichloromethane–hexane (2 : 3), from which 55 mg (50%) of yellow crystalline (38) was obtained after recrystallisation.

Reaction of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(H)(O)C_2Me_2\}(\eta\text{-}C_5H_5)_2][BF_4]$ (25) *with* $NaBH_4$. The $NaBH_4$ (0.1 g, 2.63 mmol) was added to an acetone (50 cm^3) solution of (25) (0.25 g, 0.45 mmol) at −78 °C and the mixture stirred for 2 h. Chromatography yielded two bands: one yellow-green, eluted with dichloromethane–hexane (1 : 1), containing 31 mg (15%) of (38), and one yellow, eluted with dichloromethane–hexane (3 : 1), from which 75 mg (37%) of yellow crystalline (43)[7] was obtained. This was identified by its i.r., ^1H n.m.r., and mass spectra.

$[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)CH_2CN\}(\eta\text{-}C_5H_5)_2]$ (40). The salt KCN (20 mg, 0.31 mmol) was added to an acetone (100 cm^3) solution of (13) (100 mg, 0.22 mmol) and the mixture stirred for 15 min. Chromatography, eluting with dichloromethane, gave a single orange band from which 55 mg (64%) of orange crystalline (40) was obtained after recrystallisation from dichloromethane–hexane.

$[Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)CH_2PMe_2Ph\}(\eta\text{-}C_5H_5)_2][BF_4]$ (41). The compound PMe_2Ph (40 mg, 0.29 mmol) was added to an acetone (50 cm^3) solution of (13) (94 mg, 0.21 mmol). After evaporation, chromatography of the residue, eluting with dichloromethane, developed one red band. This gave (0.1 g, 86%) red crystals of (41) from dichloromethane.

Reaction of $[M_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(H)Me\}(\eta\text{-}C_5H_5)_2]$ [M = Fe (27) *or* Ru (32)] *with* $[CPh_3][BF_4]$. Complex (27) or (32) was treated with an equimolar amount of $[CPh_3][BF_4]$ in the minimum of dichloromethane at 0 °C for *ca.* 0.5 h. Addition of hexane then precipitated (13) and (18), respectively, in near quantitative yield.

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