Conversion of Ethyne into Methylcarbene and Ethene at a Di-metal Centre: *X*-Ray Structure of $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$

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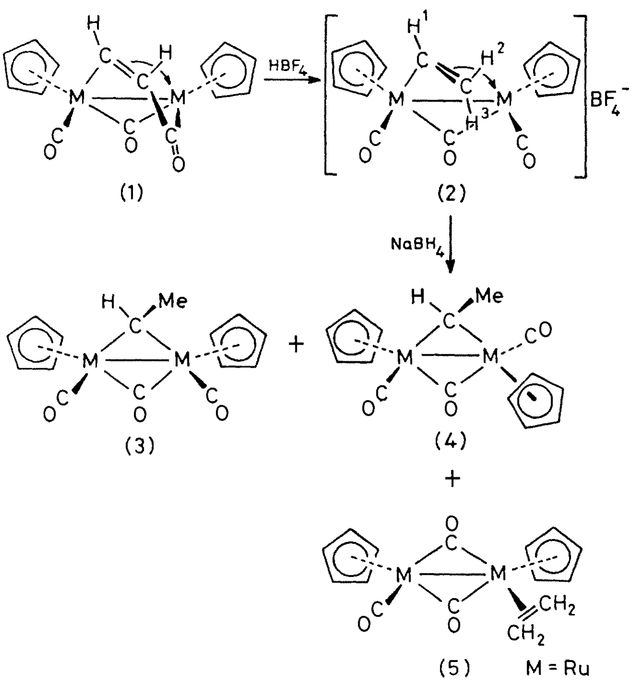
Summary Protonation of the ethyne-derived dimetallocycles $[M_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(O)C_2H_2\}(\eta\text{-}C_5H_5)_2]$ (M = Fe or Ru) provides cationic vinyl complexes $[M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2][BF_4]$ which, with $NaBH_4$, give bridging methylcarbene complexes $[M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ and in the case of ruthenium an additional ethene complex $[Ru_2(CO)(\mu\text{-}CO)_2(C_2H_4)(\eta\text{-}C_5H_5)_2]$; the structure of *cis*-$[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ has been established by *X*-ray diffraction.

Recently we have described the formation from ethyne of di-iron and di-ruthenium metallocycles $[M_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(O)C_2H_2\}(\eta\text{-}C_5H_5)_2]$ (**1**).[1] The complexes exhibit fluxional behaviour which involves a reversible cleavage of the carbonyl–'alkyne' carbon–carbon bond. We now report that upon protonation this bond is broken irreversibly to give cationic μ-vinyl complexes which undergo nucleophilic attack by hydride to produce complexes of methylcarbene and of ethene.

Addition of an equimolar amount of HBF_4 to an acetone solution of (**1a**) or (**1b**) causes an immediate colour change and yields, after crystallisation, red-purple $[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2][BF_4]$, (**2a**) [m.p. 175 °C (decomp.); ν(CO)(CH_2Cl_2) 2 037s, 2 012m, and 1 863m cm^{-1}] or orange $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2)(\eta\text{-}C_5H_5)_2][BF_4]$, (**2b**) [m.p. 225 °C (decomp.); ν(CO)(CH_2Cl_2) 2 036s, 2 010, and 1 869m cm^{-1}] quantitatively. For each of (**2**) the presence of two i.r.-active terminal carbonyl stretching vibrations indicates the relative *cis*-orientation of the pairs of CO and $\eta\text{-}C_5H_5$ ligands which is shown. In addition, ^1H n.m.r. spectra reveal that each exists in solution as two isomers, most likely arising from different orientations of the vinyl bridge with respect to the *cis*-$[M_2(CO)_2(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ unit. The structure of (**3a**), which is derived from (**2a**) and described below, suggests that the major, near exclusive isomer of the cations has the vinyl orientation shown. Moreover, this geometry is predictable in view of the closely related atomic dispositions established for the complexes (**1**) by *X*-ray diffraction.[1] As expected,[2] the cations are fluxional, exhibiting two distinct processes which will be described elsewhere, along with the crystal structure of (**2a**) (under investigation). At −60 °C in $[^2H_6]$acetone the dominant isomer of (**2a**) displays resonances in the ^1H n.m.r. spectrum for two inequivalent cyclopentadienyl ligands [τ 4·25 (s, 5H) and 4·42 (s, 5H)] and for the three protons of the bridging vinyl group [τ − 2·57 (H^1, dd, $J_{1,2}$ 3·5, $J_{1,3}$ 6 Hz), 4·87 (H^2, dd, $J_{2,3}$ 1, $J_{1,2}$ 3·5 Hz), and 7·00 (H^3, dd, $J_{2,3}$ 1, $J_{1,3}$ 6 Hz)]. The α- and β-vinylic carbons appear at 185·8 and 65·3 p.p.m. (downfield of $SiMe_4$), respectively, in the ^{13}C n.m.r. spectrum.



a; M = Fe
b; M = Ru

The cations (**2**) provide an excellent entry into the chemistry of bridging carbene complexes in that treatment with sodium borohydride in acetone gives a mixture of *cis*-(**3**) and *trans*-(**4**) $[M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$† in high (*ca.* 80%) combined yield. The *cis*:*trans* ratios are of the order of 5:1 and 2:1 for iron and ruthenium, respectively. Although separable by chromatography the isomers interconvert both in the solid state and in solution, where equilibrium is approached rapidly. Addition of $[Ph_3C][BF_4]$ to such a mixture results in hydride abstraction from the methyl group of the bridging carbene and regenerates the μ-vinyl cations, (**2**).

The structure of (**3a**) was determined by *X*-ray diffraction. *Crystal data:* $C_{15}H_{14}Fe_2O_3$, M = 353·7, orthorhombic, space group *Pnma*, a = 15·096(9), b = 14·414(8), c = 6·336(4) Å, U = 1379(2) Å^3, Z = 4, $F(000)$ = 720, D_c = 1·70 g cm^{-3}, Mo-K_α radiation (λ = 0·71069 Å), μ(Mo-K_α) = 21·06 cm^{-1}. The structure was solved and refined by conventional heavy-atom Fourier and least-squares methods in the centrosymmetric space group *Pnma*. For 1631 independent reflections [$I > 1{\cdot}5\sigma(I)$] collected at 220 K on a Syntex $R3_m$ diffractometer in the range $3° < 2\theta < 60°$ the current R is 0·048.‡

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† *E.g.* for (**3a**): m.p. 169 °C (decomp.); ν(CO)(hexane) 1 986vs, 1 948m, and 1 797s cm^{-1}; ^1H n.m.r. ($[^2H_8]$toluene) τ − 1·60 (q, J 8 Hz, C*H*Me), 5·83 (s, 2 × C_5H_5), and 6·78 (d, J 8 Hz CH_3); ^{13}C n.m.r. ($[^2H_5]$pyridine) 172·9 (*C*HMe), 87·8 (C_5H_5), and 43·3 (CH_3) p.p.m. For (**4a**): ν(CO) (hexane) 1 948s and 1 797s cm^{-1}; ^1H n.m.r. ($[^2H_8]$toluene) τ − 0·62 (q, J 8 Hz, C*H*Me), 5·63 (s, C_5H_5), 5·72 (s, C_5H_5), and 6·81 (d, J 8 Hz, CH_3); ^{13}C n.m.r. ($[^2H_5]$pyridine) 173·5 (*C*HMe), 89·9 (C_5H_5), 89·4 (C_5H_5), and 44·0 (CH_3) p.p.m.

‡ Atomic co-ordinates are available on request from the director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The molecular structure, which has a crystallographically imposed mirror plane, is shown in the Figure. The iron atoms are at a single bond distance [2·520(1) Å] and are bridged symmetrically by carbonyl and methylcarbene groups, with a dihedral angle of 166° between the FeC(1)Fe′ and FeC(4)Fe′ planes. The FeC(1)Fe′ [78·8(1)] and H(1)-C(1)C(2) [112(2·5)°] angles associated with μ-methylcarbene are close to the corresponding angles determined for a μ-methylene ligand in $[Os_3(\mu\text{-}H)_2(CO)_{10}(\mu\text{-}CH_2)]$ by neutron diffraction [82·1(2) and 106·0(8)°, respectively][3]. Bridging methylcarbene is indicated to be a less effective π-acceptor than bridging CO by consideration of the Fe–C(1) [1·986(3)] and Fe–C(4) [1·902(3) Å] distances. Each iron atom carries a terminal CO and a cyclopentadienyl ligand arranged in a *cis*-geometry, with the methyl group of the carbene *anti* with respect to the pair of C_5H_5 rings. No evidence has been obtained for the formation of isomers of (**3**) in which the methyl group is *syn*.

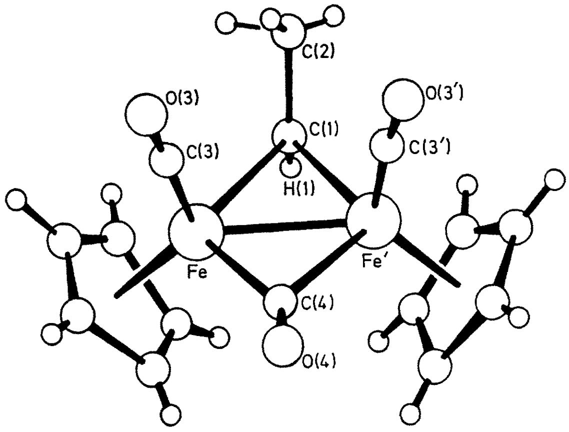

FIGURE. Molecular structure of *cis*-$[Fe_2(CO)_2(\mu\text{-}CO)(\mu CHMe)(\eta\text{-}C_5H_5)_2]$ (**3a**). Bond lengths: Fe–Fe′ 2·520(1), Fe–C(1) 1·986(3), Fe–C(3) 1·747(3), Fe–C(4) 1·902(3), C(1)–C(2) 1·513(6), C(3)–O(3) 1·151(4), C(4)–O(4) 1·183(5) Å. Angles: Fe–C(1)–Fe′ 78·8(1), Fe–C(4)–Fe′ 83·0(1), H(1)–C(1)–C(2) 112(2·5)°.

The implication that (**3**) and (**4**) are formed as a result of initial hydride attack on the β-vinylic carbon of (**2**) was confirmed by treating (**2a**) with sodium borodeuteride, which afforded *cis*- and *trans*-$[Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2D)(\eta\text{-}C_5H_5)_2]$. However, there is evidence that in the reaction of (**2b**) with hydride, attack also occurs at the α-vinylic carbon. A minor, yellow crystalline product of the reaction was identified as the ethene complex $[Ru_2(CO)(\mu\text{-}CO)_2(C_2H_4)(\eta\text{-}C_5H_5)_2]$, (**5**) [m.p. 158—160 °C (decomp.); ν(CO)(cyclohexane) 1 967s and 1 771m cm^{-1}; ^1H n.m.r. ($CDCl_3$) τ 4·84 (s, C_5H_5), 4·99 (s, C_5H_5), and 8·08 (s, C_2H_4)]. The single ^1H n.m.r. shift for ethene broadens on cooling and separates, below *ca.* −50 °C, into two pairs of resonances. Extra cyclopentadienyl signals also develop. We attribute these changes to the slowing of ethene rotation coupled with a 'freezing out' of *cis*- and *trans*-isomers of (**5**). The formation of (**5**) may arise from hydride attack on the minor isomer of (**2b**), which has the α-carbon occupying the more accessible position adjacent to the *cis*-carbonyls rather than, as illustrated for the major isomers, that adjacent to the sterically protective *cis*-cyclopentadienyls.

Taken with previous work,[1] this article describes the conversion of ethyne into methylcarbene and ethene at a di-metal centre. In an attempt to establish the scope of this synthetic route we are investigating the protonation of derivatives of (**1**) and other μ-alkyne complexes, and their subsequent reactivity towards nucleophiles. By appropriate choice of alkyne and nucleophile there is a capacity for producing a range of μ-carbene complexes. To date, analogues of (**3**) and (**4**) containing μ-CHEt and μ-C(Me)Et have been obtained. These μ-carbene complexes exhibit high reactivity towards unsaturated hydrocarbons, which chemistry will be described elsewhere.

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