Combination of Alkynes with μ-Carbenes at a Dimetal Centre, and *X*-Ray Structure of $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(CO_2Me)C(CO_2Me)CHMe\}(\eta\text{-}C_5H_5)_2]$: Implications for Metathesis and Alkyne Polymerisation

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Summary Bridging methylcarbene complexes $[M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ (M = Fe or Ru) react with alkynes RC_2R^1 ($R = R^1 = H$, Me, CO_2Me; R = Me, $R^1 = H$) under u.v. irradiation to produce complexes $[M_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CRCR^1CHMe)(\eta\text{-}C_5H_5)_2]$, shown through an *X*-ray diffraction study of $[Fe_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}C(CO_2Me)C(CO_2Me)CHMe\}(\eta\text{-}C_5H_5)_2]$ to arise from linking of the μ-carbene and alkyne.

THE chemistry of carbene complexes of transition metals has attracted much investigation, not least because of their implication in the metathesis[1,2] of alkenes. Almost all study has been concerned with carbenes co-ordinated at a mononuclear metal centre and has been associated with mechanistic schemes for metathesis based on monometallocycles. By comparison, the reactivity of carbenes co-ordinated at a dinuclear metal centre ('bridging carbenes') is effectively unexplored. Very recently, however, the possibility of metathesis involving bridging carbenes and ditungsten[3,4] metallocycles has been discussed, and it has also been suggested[5] that di-iron metallocycles are intermediates in the production of propene from $[Fe_2(CO)_8(\mu\text{-}CH_2)]$ and ethene. In the course of studies[6–8] on the reactivity of dinuclear metal centres we have developed[8] a convenient synthesis of μ-carbene di-iron and diruthenium complexes, and now report that these are highly reactive towards ethyne and other alkynes, forming stable dimetallocycles through carbon–carbon bond formation.

The μ-methylcarbene complexes $[M_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)(\eta\text{-}C_5H_5)_2]$ (**1**) exist in solution as *cis* (predominantly) and *trans* isomers, the *cis* iron complex having been found to adopt, in the solid state at least, the *anti* methyl group orientation illustrated.[8] Each complex (**1**) reacts with ethyne under u.v. irradiation (toluene solution, silica glass flask, 250 W mercury lamp, 3 and 25 h respectively) to give crystalline olive-green $[Fe_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCHMe)(\eta\text{-}C_5H_5)_2]$ (**2a**) (85%)† or orange $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCHMe)(\eta\text{-}C_5H_5)_2]$ (**2b**) (55%), respectively. No

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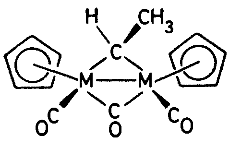
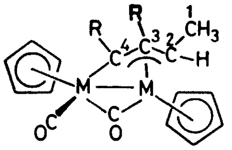
† (**2a**): m.p. 178—182 °C(decomp); ν(CO)(hexane) 1 961s, and 1 793m cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 11·86 (d, *J* 6 Hz, C^4H), 4·71 (s, C_5H_5), 4·61 (dd, *J* 3 and 6 Hz, C^3H), 4·36 (s, C_5H_5), 1·22 (d, *J* 3 Hz, C^1H_3), and −0·48 (m, C^2H); ^{13}C n.m.r. (CD_3COCD_3) 173·4 (C^4), 88·2 (C^3), 86·2 (C_5H_5), 83·5 (C_5H_5), 58·5 (C^2), and 21·4 (C^1) p.p.m.

crystals of (**2a**) or (**2b**) suitable for an *X*-ray diffraction study could be obtained. However, (**1a**) and (**1b**), and analogues containing μ-CHEt or μ-CMe$_2$, also react with other alkynes such as propyne, but-2-yne or dimethyl acetylenedicarboxylate, and [Fe$_2$(CO)(μ-CO){μ-η^1,η^3-C(CO$_2$Me)C(CO$_2$Me)CHMe}(η-C$_5$H$_5$)$_2$] (**2c**),‡ which does form suitable crystals, was selected for a structural investigation.

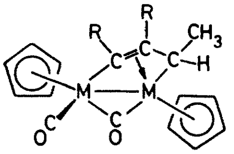


(1)

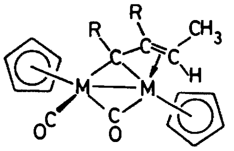


(2)

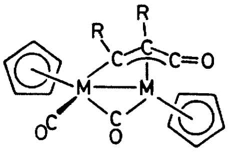
(a) M = Fe, R = H
(b) M = Ru, R = H
(c) M = Fe, R = CO$_2$Me



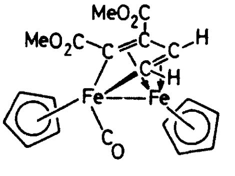
(3)



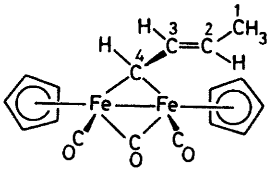
(4)



(5)



(6)



(7)

Crystal data: C$_{20}$H$_{20}$Fe$_2$O$_6$, *M* 467·7, monoclinic, space group $P2_1/n$, a = 8·064(4), b = 15·817(6), c = 30·777(12) Å, β = 94·50(4)°, U = 3913·5 (2·8) Å^3, Z = 8, F(000) = 1 920, Mo-K_α *X*-radiation ($\bar{\lambda}$ = 0·710 69 Å), μ(Mo-K_α) = 15·1 cm^{-1}.

The structure was solved using direct methods. The two molecules of the asymmetric unit were found to be pseudosymmetrically related and subsequent refinement of the model had to be severely damped as a consequence. In addition, two of the cyclopentadienyl ligands were disordered and these were refined as independent rigid groups with isotropic thermal parameters. An obvious disordering of the methoxy carbon atoms could not be successfully incorporated in the model. For 4134 independent reflections [$I \geqslant 3{\cdot}0\,\sigma(I)$] collected at room temperature on a Syntex $P2_1$ diffractometer in the range $2{\cdot}9 < 2\theta < 55{\cdot}0°$, R is currently 0·10.§

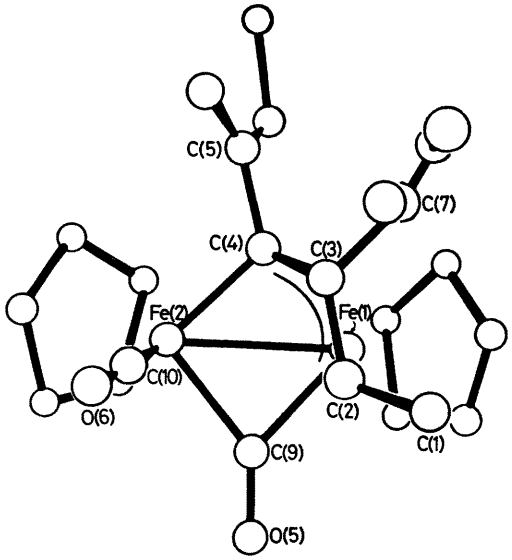


FIGURE. Molecular structure of (**2c**). Averaged bond lengths for two molecules: Fe(1)–Fe(2) 2·540(2), Fe(1)–C(2) 2·111(13), Fe(1)–C(3) 2·042(12), Fe(1)–C(4) 1·969(12), Fe(1)–C(9) 1·891(12), Fe(2)–C(4) 1·968(12), Fe(2)–C(9) 1·970(12), Fe(2)–C(10) 1·754(14), C(1)–C(2) 1·551(20), C(2)–C(3) 1·433(18) C(3)–C(4) 1·457(17), C(9)–O(5) 1·180(15), C(10)–O(6) 1·151(17) Å. Angles: C(1)–C(2)–C(3) 118·5(1·1), C(2)–C(3)–C(4) 119·3(1·1), C(2)–C(3)–C(7)-122·7 (1·2), C(7)–C(3)–C(4) 117·5(1·1), C(3)–C(4)–C(5) 117·9(1·0)°. Only one of the two equally populated orientations of the disordered cyclopentadienyl ligands is shown.

The molecular structure (Figure) is formally derived by the 'insertion' of dimethyl acetylenedicarboxylate into an iron–carbene bond of (**1a**) to give a three-carbon bridging system. This is perhaps best represented in the allylic mode (**2**) in view of the similarity of the carbon–carbon distances within the bridge and the essentially trigonal geometries of the atoms C(2—4). However, the n.m.r. shift (δ − 1·08) of the proton attached to C(2) is of the order expected for C(2) being σ-bonded to Fe(1), *i.e.* as in (**3**), while a case can also be made for the 'vinylcarbene' representation (**4**) in that C(4) is equidistant from the iron atoms, and C(2) and C(3) from Fe(1). The iron atoms are at a single bond distance, bridged nearly symmetrically by a carbonyl, and bear cyclopentadienyl ligands in the *cis* orientation which is favoured by (**1**).

The overall structure is strikingly related to that of the complexes (**5**), derived from the reactions of alkynes with [{M(CO)$_2$(η-C$_5$H$_5$)}$_2$] (M = Fe, Ru).[6] However, whereas the 'alkyne–CO' link in the complexes (**5**) is very labile, shown especially in their fluxional behaviour[6] and thermal

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‡ (**2c**): m.p. 165 °C(decomp.); ν(CO)(hexane) 1 944s and 1 799s cm^{-1}; ^{1}H n.m.r. (C$_6$D$_5$CD$_3$) δ 4·35 (s, C$_5$H$_5$), 4·30 (s, C$_5$H$_5$), 3·77 (s, CO$_2$CH$_3$), 3·40 (s, CO$_2$CH$_3$), 1·12 (d, *J* 7 Hz, C^{1}CH$_3$), and −1·08 (q, *J* 7 Hz, C^{2}H); ^{13}C n.m.r. (CDCl$_3$) 179·7, 175·0, 170·9 (2 × CO$_2$Me and C^4), 87·9 (C$_5$H$_5$ and C^3), 86·0 (C$_5$H$_5$), 56·3 (C^2), 52·2 (CO$_2$CH$_3$), 51·9 (C$_2$CH$_3$), and 20·6 (C^1) 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.

isomerisation,[9] the 'alkyne–carbene' link in (**2**) is not. Each of (**2**) is stereochemically rigid and stable at temperatures up to 100 °C. Slow transformation of (**2c**) does occur, in boiling toluene over several days, to produce [$Fe_2(CO)\{C_2H_2C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2$] (**6**) quantitatively, analogues of which are known. This extraordinary reaction comprises a double β-elimination from the C-Me group of (**2c**), bringing C(1) into co-ordination with Fe(1) and Fe(2).

The representation (**4**), although simplistic, suggested that treatment with CO might release 'olefinic' C(2)–C(3) from complexation, and it does. A high yield of the *cis* vinylcarbene complex (**7**)¶ and its *trans* isomer is produced when an acetone solution of (**2a**) is subjected to 100 atm of CO at 50 °C for *ca.* 17 h. From the size of the coupling between the protons on C^2 and C^3 these are mutually *trans*, as expected from the structure of (**2c**). Heating to 100 °C or u.v. irradiation of (**7**) regenerates (**2a**) rapidly.

This communication describes observations which have implications for both alkene metathesis and alkyne polymerisation. The formation of a dimetallocycle by combination of a μ-carbene with an alkyne encourages speculation over the role of such carbenes in metathesis at dinuclear metal centres. Moreover, the sequence (**1a**) → (**2a**) → (**7**) comprises the transformation of one μ-carbene to another *via* ethyne 'insertion'; successive insertions and rearrangements of this type provide a mechanism for alkyne polymerisation at a dimetal centre. The generation of μ-methylcarbene upon adsorption of ethyne on platinum[10] or nickel[11] surfaces has been discussed.

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¶ (**7**): m.p. 157—161 °C (decomp.); ν(CO)(hexane) 1 987s, 1 950m, and 1 799s cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 11·62 (d, *J* 13 Hz, C^4H), 7·38 (t, *J* 13 Hz, C^3H), 6·52 (m, C^2H), 4·64 (s, 2 × C_5H_5), and 1·76 (d, *J* 7 Hz, C^1H_3); ^{13}C n.m.r. ($CDCl_3$) 165·4 (C^4), 159·0 (C^3), 116·2 (C^2), 87·5 (2 × C_5H_5), and 17·3 (C^1) p.p.m.

[1] R. H. Grubbs, *Progr. Inorg. Chem.*, 1978, **24**, 1.
[2] J. J. Rooney and M. Stewart, *Catalysis*, 1978, **1**, 277.
[3] F. Garnier, P. Krausz, and J. E. Dubois, *J. Organomet. Chem.*, 1979, **170**, 195.
[4] J. Levisalles, H. Rudler, F. Dahan, and Y. Jeannin, *J. Organomet. Chem.*, 1980, **188**, 193.
[5] C. E. Sumner, P. E. Riley, R. E. Davis, and R. Pettit, *J. Am. Chem. Soc.*, 1980, **102**, 1752.
[6] A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Chem. Commun.*, 1980, 409.
[7] S. R. Finnimore, S. A. R. Knox, and G. E. Taylor, *J. Chem. Soc., Chem. Commun.*, 1980, 411.
[8] A. F. Dyke, S. A. R. Knox, P. J. Naish, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1980, 441.
[9] D. L. Davies, A. F. Dyke, A. Endespelder, S. A. R. Knox, P. J. Naish, A. G. Orpen, D. Plaas, and G. E. Taylor, *J. Organomet. Chem.*, in the press.
[10] H. Ibach, H. Hopster, and B. Sexton, *Appl. Surf. Sci.*, 1977, **1**, 1.
[11] J. C. Hemminger, E. L. Muetterties, and G. A. Somorjai, *J. Am. Chem. Soc.*, 1979, **101**, 62.