Stereochemical Control of Alkyne Oligomerisation at a Diruthenium Centre: *X*-Ray Structures of $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}C_4H_4CMe_2)(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(\mu\text{-}CO)\{\mu\text{-}C_4(CO_2Me)_4CH_2\}(\eta\text{-}C_5H_5)_2]$

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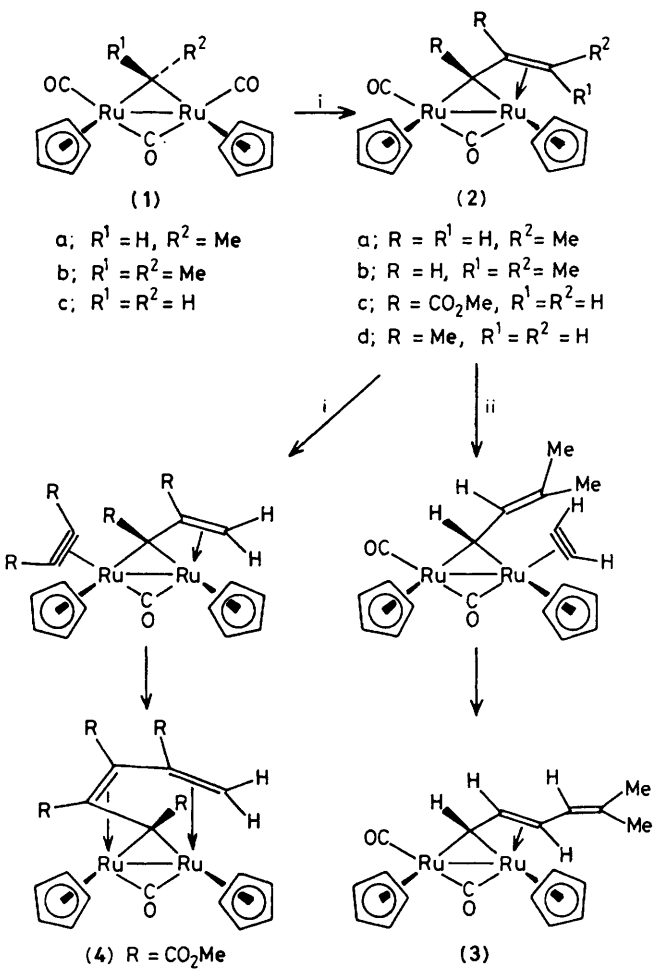
The μ-carbene complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe_2)(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2]$ undergo double insertion with ethyne and dimethyl acetylenedicarboxylate, respectively, to yield the title compounds; these complexes have been shown by *X*-ray diffraction to contain five-carbon chains of differing stereochemistry, attributed to the different steric demands of the carbene substituents.

We[1,2] and others[3,4] have proposed a mechanism by which alkyne oligomerisation and polymerisation could be effected, initiated by a μ-carbene complex of a transition metal. Here we show that diruthenium μ-carbene complexes do cause linking of alkynes and that the stereochemistry of the growing carbon chain is controlled by the nature of the carbene substituents.

As reported earlier,[1] the μ-C(H)Me complex (**1a**) reacts under u.v. radiation with ethyne to give complex (**2a**). The 'insertion' of alkyne is stereospecific; both n.m.r. and *X*-ray diffraction studies established that the co-ordinated olefinic unit of the new C_3 ligand has a *trans* di-substituted configuration, *i.e.* the Me group occupies the R^2 site. We now report that treatment of the μ-CMe_2 complex (**1b**) with ethyne under



Scheme 1. *Reagents:* i, u.v., −CO, RC_2R; ii, u.v., HC_2H.

the same conditions results in the insertion of not just one but two molecules of alkyne, forming yellow crystalline (**3**)† exclusively (Scheme 1). This double insertion is also stereospecific, *X*-ray diffraction‡ revealing that the co-ordinated olefinic unit of the C_5 chain [newly formed C(4)–C(5)] is similarly *trans*. In other words, (**3**) may be seen as a complex of type (**2**) with the extended carbon chain occupying the R^2 site. This is clearly seen in Figure 1, which displays the molecular structure.

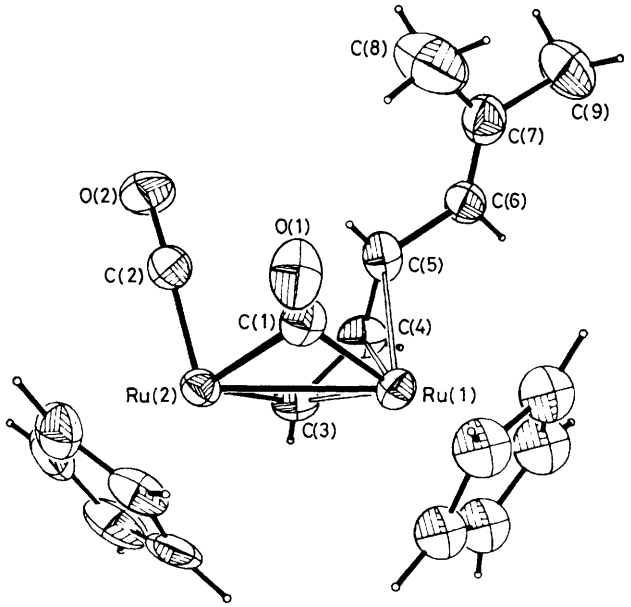


Figure 1. Molecular structure of (**3**). Pertinent molecular dimensions: Ru(1)–Ru(2) 2.716(1), Ru(1)–C(1) 2.008(9), Ru(2)–C(1) 2.109(9), Ru(1)–C(3) 2.118(9), Ru(1)–C(4) 2.141(8), Ru(1)–C(5) 2.239(10), Ru(2)–C(3) 2.022(10), C(3)–C(4) 1.432(14), C(4)–C(5) 1.417(13), C(5)–C(6) 1.479(13), C(6)–C(7) 1.299(14) Å.

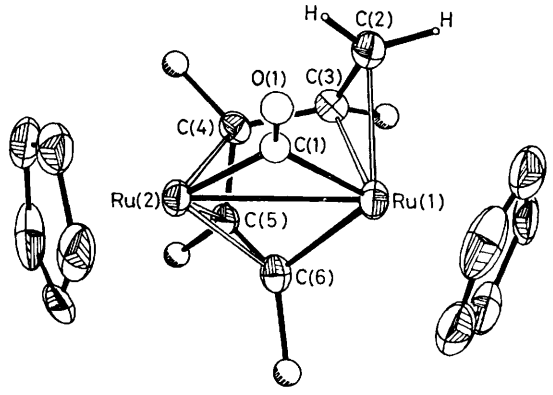


Figure 2. Molecular structure of (**4**); only the ketonic carbons of the CO_2Me groups are shown for clarity. Pertinent molecular dimensions: Ru(1)–Ru(2) 2.763(1), Ru(1)–C(1) 2.025(8), Ru(2)–C(1) 2.026(8), Ru(2)–C(6) 2.113(7), Ru(2)–C(5) 2.137(8), Ru(2)–C(4) 2.197(8), Ru(1)–C(6) 2.093(7), Ru(1)–C(3) 2.168(7), Ru(1)–C(2) 2.203(7), C(6)–C(5) 1.421(9), C(5)–C(4) 1.427(10), C(4)–C(3) 1.513(10), C(3)–C(2) 1.391(11) Å.

In contrast, u.v. irradiation of the μ-CH_2 complex (**1c**) in the presence of dimethyl acetylenedicarboxylate provides orange crystalline (**4**),† identified by *X*-ray diffraction‡ (see Figure 2) as a double insertion product with the point of alkyne linking marked by an olefinic bond of *cis* configuration. The carbon chain now extends through the R^1 site of a molecule of type (**2**). Unlike (**3**) this orients the terminal olefinic unit of the carbon chain so that it may co-ordinate to ruthenium, as is observed. Heating or u.v. irradiation of (**3**) does not induce the formation of an analogue of (**4**), indicating that the geometry of the five-carbon chain is fixed.

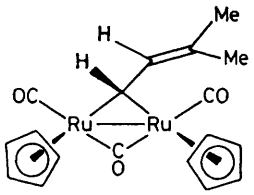
In view of the establishment[1] of the (**1a**) → (**2a**) transformation, the intermediacy of (**2b**) and (**2c**) in the formation of (**3**) and (**4**), respectively, can be assumed with confidence. An explanation of the different modes of alkyne oligomerisation can then be found in the presence or absence of steric crowding

† New compounds were identified by microanalysis and i.r., n.m.r. (^1H and ^{13}C), and mass spectra.

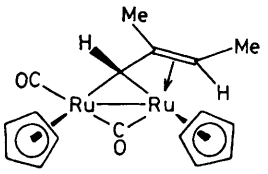
‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Crystal data for (**3**): $C_{19}H_{20}O_2Ru_2$, M = 482.4, orthorhombic, space group $Pna2_1$, a = 14.937(5), b = 11.909(4), c = 9.975(2) Å, U = 1 774.4(9) Å^3, Z = 4, $F(000)$ = 952, D_c = 1.81 g cm^{-3}, μ(Mo-K_α) = 16.8 cm^{-1}; R 0.045 (R' 0.03) for 1822 independent reflections [293 K, $I \geqslant 2\sigma(I)$ in the range $2.9 \leqslant 2\theta \leqslant 60°$, Nicolet $P2_1m$ diffractometer, Mo-K_α X-radiation, $\bar{\lambda}$ = 0.71 069 Å]. The η-C_5H_5 ring attached to Ru(1) is disordered.

Crystal data for (**4**): $C_{24}H_{24}O_8Ru_2$, M = 664.7, monoclinic, space group $P2_1/n$, a = 16.861(7), b = 8.785(5), c = 16.495(6) Å, β = 106.42(3)°, U = 2 344(2) Å^3, Z = 4, $F(000)$ = 1 312, D_c = 1.88 g cm^{-3}, μ(Mo-K_α) = 13.1 cm^{-1}; R' 0.050 (R' 0.039) for 2 795 independent reflections [293 K, $I \geqslant 2\sigma(I)$ in the range $2.9 \leqslant 2\theta \leqslant 55°$; otherwise as for (**3**)].



(5)



(6)

in (2) arising from the μ-carbene substituents. For μ-CH_2 no such crowding is expected, and an *X*-ray diffraction study completed on complex (**2d**) shows this to be so.[5] However, if the terminal CH_2 hydrogens of (**2d**) are 'replaced' by carbon atoms (with C–C 1.51 Å), intramolecular contacts of less than 2.3 Å arise between the carbon in the R^1 site and each of the two carbonyl ligands. The selective formation of complex (**2a**) from a μ-C(H)Me precursor is therefore understandable, but when the precursor is the μ-CMe_2 complex a methyl group *must* occupy the crowded R^1 site in (**2b**). The co-ordination of the olefinic portion of the C_3 ligand is then sterically most unfavourable. We suggest that it is this inducement to dissociate which allows further ethyne co-ordination, followed by a carbon–carbon bond formation which is constrained to generate complex (**3**), in which the crowded site is avoided by the extended carbon chain. Conversely, intermediate (**2c**) will experience no steric inducement to dissociate the olefinic unit and oligomerisation may then proceed *via* CO dissociation, as laid out in Scheme 1. This path requires that the carbon–carbon bond formation produce a *cis* configuration at the point of linking since a *trans* chain, as in (**3**), can not 'wrap around' the Ru_2 centre.

Strong support for steric crowding as the controlling influence over carbon chain growth comes from attempts to synthesise the intermediate (**2b**) by an alternative route. Heating $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2Ph_2\}(\eta\text{-}C_5H_5)_2]$[6] with 3,3-dimethylcyclopropene results in the expected[7] ring-opening of the olefin, to give $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCMe_2)(\eta\text{-}C_5H_5)_2]$ (**5**).† The analogue of (**5**) with a terminal C(H)Me group readily ejects CO to form (**2a**),[1] but (**5**) itself strongly resists co-ordination of its more highly substituted olefinic substituent. In boiling toluene it is stable, and although u.v. irradiation over several days does produce some (**2b**), it is accompanied by its isomer (**6**). Evidently the reluctance of the CMe_2 group to co-ordinate is sufficient even to promote the substantial rearrangement which provides a C(H)Me terminus. Treatment of (**5**) with ethyne generates (**3**) rapidly.

These observations indicate that polyalkynes obtained from a μ-carbene dimetal system could have their stereoregularity controlled through manipulation of steric constraints.

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