Oligomerisation of Alkynes at a Diruthenium Centre

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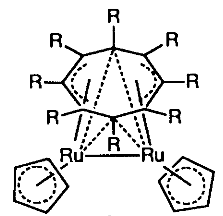
The Ru=Ru double-bonded μ-alkyne complexes $[Ru_2(\mu\text{-}CO)(\mu\text{-}RC_2R)(\eta\text{-}C_5H_5)_2]$ (R = Ph or CF_3) react in heptane or xylene at reflux with alkynes R'C≡CR' (R' = CO_2Me or CF_3) to link up to four molecules of alkyne; the structures of the complexes $[Ru_2(CO)\{\mu\text{-}C_4(CF_3)_4\}(\eta\text{-}C_5H_5)_2]$ (two isomers) and $[Ru_2\{\mu\text{-}C_8(CF_3)_2(CO_2Me)_6\}(\eta\text{-}C_5H_5)_2]$, which contains a C_6 ring with a C_2 'tail', have been established by X-ray diffraction.

The oligomerisation of hydrocarbons at metal centres is an area of substantial importance. We have shown previously that four molecules of alkyne can be linked stepwise at a triple-bonded dimolybdenum centre to produce molecules $[Mo_2(\mu\text{-}C_8R_8)(\eta\text{-}C_5H_5)_2]$ containing an unbranched C_8 chain and have suggested that such a process could model the Reppe nickel-catalysed cyclotetramerisation of ethyne.[1,2] We were unable to induce ring closure at the dimolybdenum centre to generate cyclooctatetraenes, but Wilke and co-workers[3] achieved this at the corresponding dichromium centre. In this communication we describe a study of alkyne linking at the bis(cyclopentadienyl)diruthenium centre, undertaken because the electronic requirements of this centre are compatible with the linking of four alkynes to give co-ordinated cyclooctatetraenes, as in $[Ru_2(\mu\text{-}C_8R_8)(\eta\text{-}C_5H_5)_2]$ **1**, analogous to $[Ru_2(CO)_5(\mu\text{-}C_8H_8)]$.[4] A complex of formulation **1** is known for R = H, but has the unusual sandwich structure **2**;[5] on two-electron oxidation **2** undergoes C–C bond cleavage in order to compensate the dimetal centre electronically, opening the C_8 ring and affording $[Ru_2(\mu\text{-}C_8H_8)(\eta\text{-}C_5H_5)_2]^{2+}$ **3**,[6] analogous to the dimolybdenum complexes $[Mo_2(\mu\text{-}C_8R_8)(\eta\text{-}C_5H_5)_2]$. We report that the diruthenium centre *can* support the stepwise linking of four alkyne molecules and that ring closure does occur. However, the product $[Ru_2(\mu\text{-}C_8R_8)(\eta\text{-}C_5H_5)_2]$ contains not a cyclooctatetraene but an unprecedented C_8 ligand composed of a C_6 ring with a C_2 'tail'.

Like the dimolybdenum centre, the diruthenium centre binds a single molecule of alkyne in a lateral bridging mode in the complexes $[Ru_2(\mu\text{-}CO)(\mu\text{-}RC_2R)(\eta\text{-}C_5H_5)_2]$ (R = Ph **4a**[7] or CF_3 **4b**[8]). Although unsaturated, possessing an Ru=Ru double bond, these complexes react only slowly (1–4 d) with alkynes $R'C_2R'$ (R' = CO_2Me or CF_3) in heptane or xylene at reflux to give metallacyclopentadiene complexes $[Ru_2(CO)(\mu\text{-}C_4R_2R'_2)(\eta\text{-}C_5H_5)_2]$ **5**† in 50–90% yield (Scheme 1). These exist as separable isomers, shown by X-ray diffraction studies‡ on both forms of $[Ru_2(CO)\{\mu\text{-}C_4(CF_3)_4\}(\eta\text{-}C_5H_5)_2]$ **5c** to derive from *cis* and *trans* arrangements of the cyclopentadienyl ligands. The structure of the *trans* form is shown in Fig. 1; the *cis* form has the positions of the CO and C_5H_5 ligands on Ru(2) effectively exchanged.



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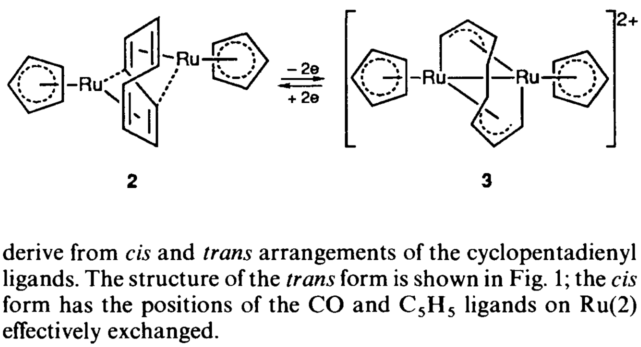

2 **3**

For **5a**–**5c** alkyne linking proceeds no further, but heating **5d** in xylene for 5 d with an excess of dimethyl acetylenedicarboxylate (dmad) gave a four-alkyne complex $[Ru_2\{\mu\text{-}C_8(CF_3)_2(CO_2Me)_6\}(\eta\text{-}C_5H_5)_2]$ **7**† in 40% yield as two separable isomers. No sign of the expected intermediate three-alkyne complex $[Ru_2\{\mu\text{-}C_6(CF_3)_2(CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ of type **6** was obtained, but such species do exist; when **5b** and dmad were subjected to UV irradiation unsymmetrical $[Ru_2\{\mu\text{-}C_6Ph_2\text{-}$

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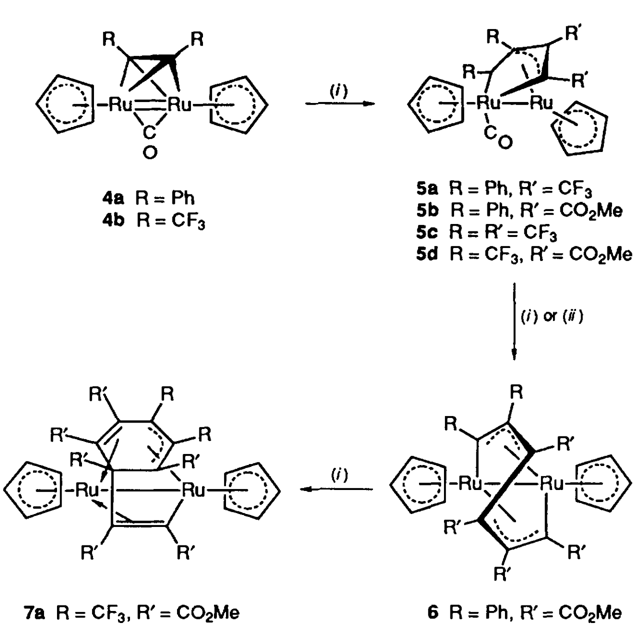
† Compound **5c** was prepared by heating **4b** (0.10 mmol) with hexafluorobut-2-yne (0.47 mmol) in xylene in a sealed tube at 140 °C for 22 h. Chromatography on alumina gave purple-red *trans* and yellow *cis* isomers in 75 and 15% yields respectively. The new complexes were characterised by elemental analyses and IR and NMR (^1H, $^{13}C\text{-}\{^1H\}$ and $^{19}F\text{-}\{^1H\}$) spectroscopy. Selected data: *trans*-**5c**, purple-red crystals, ν(CO) (in hexane) at 1951s cm^{-1}; NMR (in $CDCl_3$): ^1H, δ 5.22 (s, C_5H_5), 5.11 (s, C_5H_5); $^{13}C\text{-}\{^1H\}$, δ 196.2 (s, CO), 146.5 (q, *J* 44, CCF_3), 127.8 (q, *J* 271, CF_3), 123.2 (q, *J* 271, CF_3), 87.4 (s, C_5H_5) and 86.8 (s, C_5H_5); $^{19}F\text{-}\{^1H\}$, δ − 52.8 (q, br, *J* 13, CF_3) and −47.3 (q, br, *J* 13 Hz, CF_3). **6**, orange crystals, ν(CO) (in CH_2Cl_2) at 1735s cm^{-1}; NMR (in $CDCl_3$): ^1H, δ 7.20 (m, br, 2 Ph), 5.27 (s, C_5H_5), 4.94 (s, C_5H_5), 3.76 (s, Me), 3.65 (s, Me), 3.21 (s, Me) and 3.17 (s, Me). **7**, orange crystals, ν(CO) (in CH_2Cl_2) at 1730s cm^{-1}; NMR ($CDCl_3$): ^1H, δ 5.17 (s, C_5H_5), 5.13 (s, C_5H_5), 4.01 (s, Me), 3.82 (s, Me), 3.66 (s, Me), 3.61 (s, Me), 3.56 (s, Me) and 3.52 (s, Me); $^{13}C\text{-}\{^1H\}$, δ 126.6 (q, *J* 277, CF_3), 125.4 (q, *J* 279, CF_3), 92.9 (s, C_5H_5), 89.4 (s, C_5H_5), 72.7 (q, *J* 42, CCF_3) and 34.6 (q, *J* 34, CCF_3); $^{19}F\text{-}\{^1H\}$, δ − 56.5 (q, br, CF_3) and −45.7 (q, *J* 12 Hz, CF_3).

‡ Crystal data. For *trans*-**5c**: $C_{19}H_{10}F_{12}ORu_2$, $M = 684.4$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.012(1)$, $b = 26.941(4)$, $c = 9.143(2)$ Å, $\beta = 113.35(1)°$, $U = 2038.2(5)$ Å^3, $Z = 4$, $D_c = 2.23$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $\mu = 15.7$ cm^{-1}, $F(000) = 1312$, $T = 295$ K, crystal dimensions *ca.* 0.65 × 0.53 × 0.20 mm. Data were collected on a Nicolet P3m diffractometer for a unique quadrant of reciprocal space with $4 < 2\theta < 50°$. The structure was solved by heavy-atom methods and refined by least squares to *R* 0.041 *R'* 0.049, *S* 2.51 and *g* 0.0004 $\{R = \Sigma|\Delta|/\Sigma|F_o|$, $R' = [\Sigma w^{\frac{1}{2}}|\Delta|/\Sigma w^{\frac{1}{2}}|F_o|]$, $S = [\Sigma w\Delta^2/N_{obs} - N_{var})]^{\frac{1}{2}}$; $\Delta = F_o - F_c\}$ for 3313 unique, absorption corrected, observed $[I > 2\sigma(I)]$ intensity data calculations carried out using SHELXTL-PLUS. For **7**: $C_{32}H_{28}F_6O_{12}Ru_2$, $M = 920.7$, monoclinic, space group $P2_1/n$ (no. 14), $a = 21.441(2)$, $b = 14.783(3)$, $c = 21.460(3)$ Å, $\beta = 103.02(1)°$, $U = 6627(2)$ Å^3, $Z = 8$, $D_c = 1.85$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $\mu = 9.9$ cm^{-1}, $F(000) = 3664$, $T = 295$ K, crystal dimensions *ca.* 0.25 × 0.31 × 0.34 mm. Data were collected on an Enraf-Nonius CAD-4 diffractometer for a unique quadrant of reciprocal space with $2 < 2\theta < 50°$. The structure was solved by heavy-atom methods and refined by least squares to *R* 0.029, *R'* 0.029, *S* 1.68 and g 0.0 for 9032 unique, absorption corrected, observed $[I > 2\sigma(I)]$ intensity data. There are two independent but similar molecules per asymmetric unit in the structure. One methyl group C(4F) was disordered. Atomic coordinates, thermal parameters and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 Reagents and conditions: (i) R'C≡CR', xylene or heptane at reflux; (ii) R'C≡CR', UV

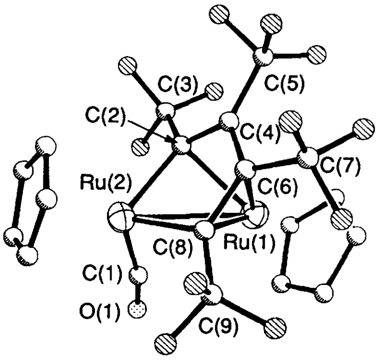


Fig. 1 Molecular geometry of **5c**; all cyclopentadienyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.761(1), Ru(2)–C(1) 1.852(6), Ru(1)–C(2) 2.102(5), Ru(1)–C(4) 2.175(5), Ru(1)–C(6) 2.153(5), Ru(1)–C(8) 2.104(5), Ru(2)–C(2) 2.043(5), Ru(2)–C(8) 2.060(5); Ru(1)–Ru(2)–C(1) 73.1(2)

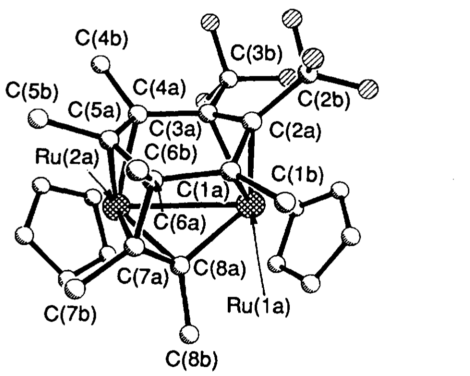


Fig. 2 Molecular structure of first independent molecule of **7**. All cyclopentadienyl hydrogens have been omitted and only the contact carbons of the CO_2Me groups have been shown for clarity. Selected bond lengths (Å), with those for the second independent molecule in parentheses: Ru(1a)–Ru(2a) 2.846(1) [2.819(1)], Ru(1a)–C(1a) 2.140(3) [2.133(4)], Ru(1a)–C(2a) 2.092(3) [2.109(3)], Ru(1a)–C(3a) 2.204(4) [2.201(4)], Ru(1a)–C(8a) 2.070(4) [2.083(4)], Ru(2a)–C(4a) 2.165(3) [2.185(3)], Ru(2a)–C(5a) 2.205(3) [2.198(3)], Ru(2a)–C(7a) 2.188(5) [2.204(5)], Ru(2a)–C(8a) 2.086(5) [2.080(5)]

$(CO_2Me)_4\}(\eta\text{-}C_5H_5)_2]$ **6**† was formed in 35% yield. It therefore appears likely that under thermal conditions a species of type **6** is formed very slowly, but converts rapidly to **7** by reaction with a fourth molecule of alkyne. The structure of one isomer of **7** was determined by an X-ray diffraction study,‡ the results of which are shown in Fig. 2.

In both **5c** and **7** the single-bonded diruthenium unit is bridged by the product of alkyne oligomerisation. For **5c** the ruthenacyclopentadiene unit is puckered (fold angle 23.1°) and is η^4-co-ordinated to the ruthenium not bearing a carbonyl. In **7** the ligand derived from alkyne tetramerisation binds η^3 to Ru(1a) and η^2 to Ru(2a) through the six-membered ring and as a μ-vinyl [σ to Ru(1a) and η^2 to Ru(2a)] through the exocyclic 'tail' alkyne fragment C(7a)–C(8a). The original μ-alkyne fragment [C(2a),C(3a)] forms part of the η^3 section of the six-membered ring.

Comparing the structures of **6** and **7** suggests that the latter arises by *formal* 1,4 addition of the fourth alkyne across the terminal CR carbon and a CR' carbon of an unsymmetrical C_6 chain like that found in **6**. It is possible, however, that the reaction of **6** with the fourth alkyne results first in the formation of an unbranched $C_8R_2R'_6$ ligand similar to that in **3** and that 1,6 ring closure then occurs to give the observed product **7**. Why this path should be favoured at a diruthenium centre rather than 1,8 ring closure to give a cyclooctatetraene is not clear. The formation of two isomers of **7** could reflect the fact that two 1,6 ring closure processes are possible or that addition of the fourth alkyne can in principle occur at either end of the C_6 chain in a complex of type **6**. An X-ray diffraction study on the second isomer of **7** might have clarified this situation but this species could unfortunately not be crystallised.

In conclusion, the linking of three alkynes at a diruthenium centre appears to follow a path similar to that established for the dimolybdenum centre, *i.e.* from a laterally bridged μ-alkyne complex to a metallacyclopentadiene complex and then a C_6 'fly-over' species, as shown in Scheme 1. A fourth alkyne can also be linked, perhaps initially to give a C_8 'fly-over' as with the Mo_2 system, but the electronic requirements of the Ru_2 centre are such that C–C bond formation occurs, to give a ligand based on a C_6 ring with an exocyclic C_2 unit.

Acknowledgements

We are grateful to the SERC for the award of research studentships (to A. F. D., S. E. G. and S. M. N.) and for support, and Johnson Matthey plc for a loan of ruthenium trichloride.

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Received 19*th November* 1992; *Communication* 2/06168F