

Preliminary communication

SEQUENTIAL METHYLENE ADDITION TO AN ALKYNE COORDINATED AT A DIRUTHENIUM CENTRE

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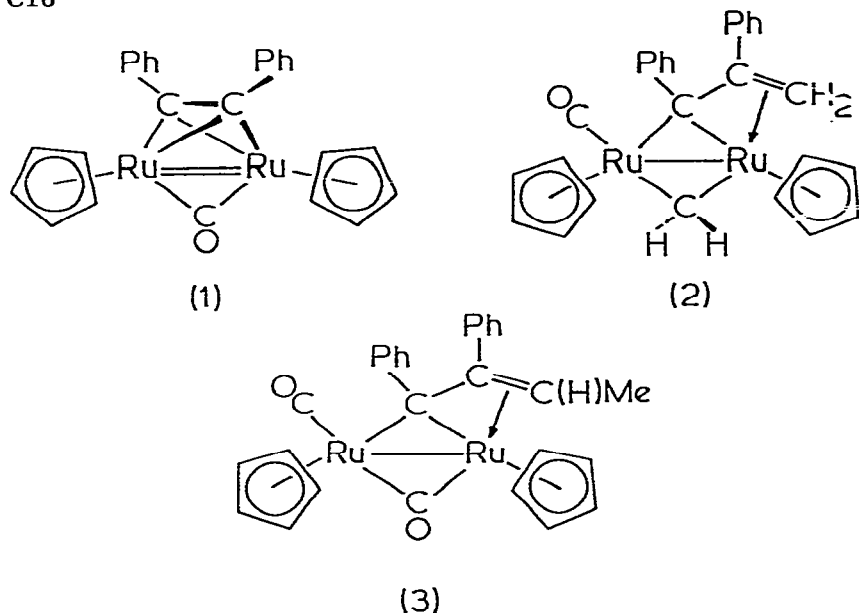
Summary

The metal—metal double-bonded μ -alkyne complex $[\text{Ru}_2(\mu\text{-CO})(\mu\text{-C}_2\text{Ph}_2)(\eta\text{-C}_5\text{H}_5)_2]$ (**1**) reacts with diazomethane at 0°C to yield $[\text{Ru}_2(\text{CO})(\mu\text{-CH}_2)\{\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{CH}_2\}(\eta\text{-C}_5\text{H}_5)_2]$ (**2**) incorporating two methylene units, one bridging the metal atoms and one linked with the alkyne. Upon heating, a second carbon—carbon bond formation occurs to link the methylene groups and give $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{H})\text{Me}\}(\eta\text{-C}_5\text{H}_5)_2]$ (**3**); the structures of **1** and **2** were established by X-Ray diffraction.

Carbon—carbon bond formation at polynuclear metal centres in complexes is of interest because of its possible relation to processes occurring on a metal surface in catalysis. Special attention in this respect is focussed on the mechanism of carbon chain growth in the Fischer—Tropsch Synthesis [1—3]. We report here the sequential addition of two methylene groups to an alkyne coordinated at a diruthenium centre, one step of which has features in common with a recent proposal for carbon chain growth during CO hydrogenation [2,3].

Green-black crystalline $[\text{Ru}_2(\mu\text{-CO})(\mu\text{-C}_2\text{Ph}_2)(\eta\text{-C}_5\text{H}_5)_2]$ (**1**) is formed in ca. 50% yield by UV irradiation of $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-C}(\text{O})\text{C}_2\text{Ph}_2\}(\eta\text{-C}_5\text{H}_5)_2]$ [4] in tetrahydrofuran solution. IR ($\nu(\text{CO})$ (CH_2Cl_2) 1771s cm^{-1}) and ^1H NMR (δ (CDCl_3) 4.89 (s, 10 H, $2\text{C}_5\text{H}_5$) and 7.40 (m, br, 10 H, $2\text{C}_6\text{H}_5$)) spectra indicated the structure illustrated, for which a formal double metal—metal bond is required by the eighteen electron rule. An X-ray diffraction study has established that this is indeed the case.

Crystal data: $\text{C}_{25}\text{H}_{20}\text{ORu}_2$, $M = 538.5$, orthorhombic, space group $Pbca$, $a = 24.585(6)$, $b = 9.279(2)$, $c = 17.621(4)$ Å, $U = 4020(2)$ Å³, $Z = 8$, $F(000) = 2128$, $D_c = 1.78$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 14.9$ cm⁻¹; $R = 0.036$ for 1637 independent reflections (at 298 K in range $4 \leq 2\theta \leq 50^\circ$ with $I \geq 2\sigma(I)$), Nicolet P3m



diffractometer, Mo- K_{α} X-radiation, $\lambda = 0.71069 \text{ \AA}$). The $\eta\text{-C}_5\text{H}_5$ ring attached to Ru(2) is disordered.

The molecular structure of **1** is presented in Fig. 1, showing a diruthenium unit bridged transversely by a diphenylacetylene ligand and also by a carbonyl group, such that the central Ru_2C_3 core has approximate C_{2v} symmetry. The ruthenium–ruthenium distance of $2.505(1) \text{ \AA}$ is substantially shorter than typical Ru–Ru single bonds (cf. Ru–Ru in **2** of $2.713(1) \text{ \AA}$) and accords with formal double bonding.

Ample precedent exists for the reaction of a metal–metal double bond with diazomethane to provide a dimetallacyclopropane complex [5]. However, a tetrahydrofuran solution of **1** reacts readily with diazomethane at 0°C to incorporate not just one but two methylene groups, in forming orange crystalline $[\text{Ru}_2(\text{CO})(\mu\text{-CH}_2)\{\mu\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{CH}_2\}(\eta\text{-C}_5\text{H}_5)_2]$ (**2**) in ca. 75% yield. The IR spectrum ($\nu(\text{CO})$ (CH_2Cl_2) 1934s cm^{-1}) clearly showed that the carbonyl ligand, initially bridging in **1**, had now become terminally bound, while $^1\text{H NMR}$ revealed that the bridging site had become occupied by a methylene group (δ (CDCl_3) 9.00 (s, 1H, CH) and 7.03 ppm (s, 1H, CH)) and that the second methylene had interacted with the μ -alkyl to form a coordinated “vinylcarbene” ligand (δ 6.95 (m, br, 10H, $2\text{C}_6\text{H}_5$), 3.12 (d, J 2Hz, 1H, CH), and -0.30 ppm (d, J 2Hz, 1H, CH)), of a known type [6,7]. Each of these features was established by an X-ray diffraction study.

Crystal data: $\text{C}_{27}\text{H}_{24}\text{ORu}_2 \cdot \frac{1}{4}\text{C}_6\text{H}_{14}$, $M = 588$, monoclinic, space group $I2$, $a = 20.386(9)$, $b = 8.202(3)$, $c = 28.710(11) \text{ \AA}$, $\beta = 90.51(4)^\circ$, $U = 4800(3) \text{ \AA}^3$, $Z = 8$, $F(000) = 2256$, $D_c = 1.62 \text{ g cm}^{-3}$, $\mu(\text{Mo-}K_{\alpha}) = 12.49 \text{ cm}^{-1}$; $R = 0.033$ for 3916 independent reflections (data collection procedure as for **1**). The two crystallographically independent molecules show very similar geometry and there is a molecule of n-hexane disordered around a site of two-fold symmetry.

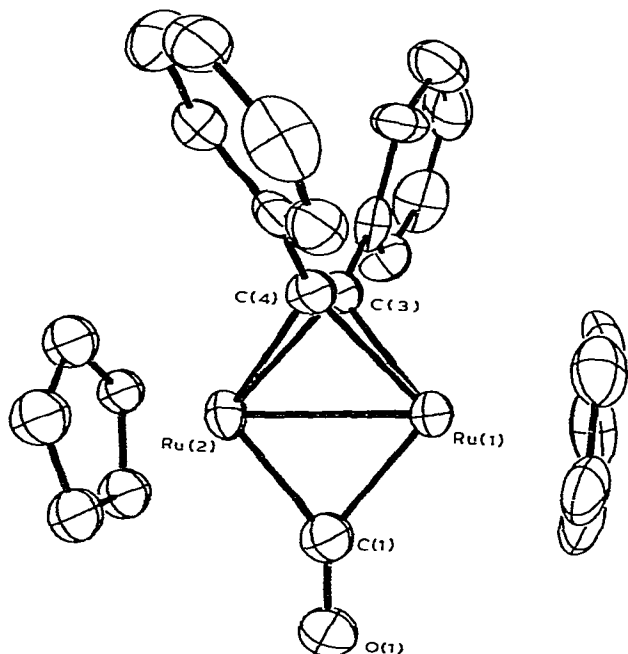


Fig. 1. The molecular structure of $[Ru_2(CO)(\mu-CO)(\mu-C_2Ph)(\eta-C_5H_5)_2] (1)$. Important molecular dimensions are: Ru(1)—Ru(2) 2.505(1), C(3)—C(4) 1.336(12), Ru(1)—C(1) 2.005(9), Ru(2)—C(1) 2.000(9), Ru(1)—C(3) 2.091(9), Ru(1)—C(4) 2.110(9), 2.110(9), Ru(2)—C(3) 2.088(9), Ru(2)—C(4) 2.135(9) Å.

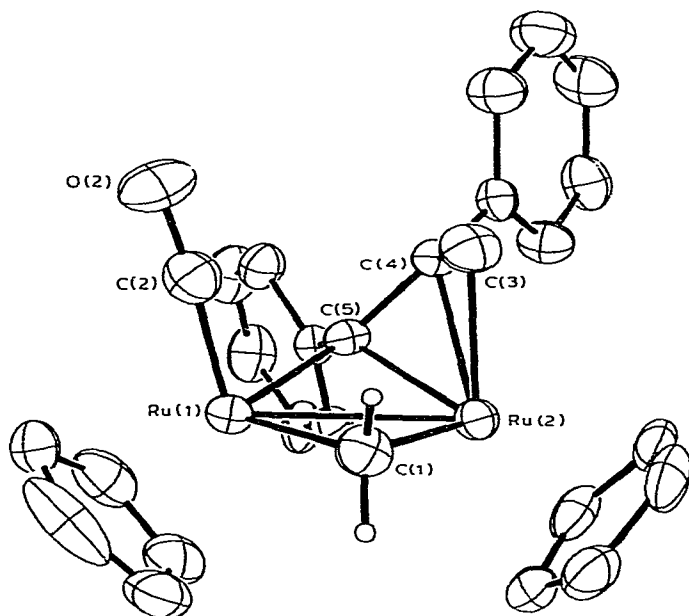


Fig. 2. The molecular structure of one of the crystallographically distinct molecules of $[Ru_2(CO)(\mu-CH_2)(\mu-C(Ph)C(Ph)CH_2)(\eta-C_5H_5)_2] (2)$. Important averaged molecular dimensions are: Ru(1)—Ru(2) 2.713(1), Ru(1)—C(1) 2.072(7), Ru(2)—C(1) 2.069(7), Ru(1)—C(5) 2.081(7), Ru(2)—C(5) 2.089(7), Ru(2)—C(4) 2.152(7), Ru(2)—C(3) 2.142(8), Ru(1)—C(2) 2.199(10), C(3)—C(4) 1.439(11), C(4)—C(5) 1.431(10) Å.

The molecular structure of **2** is illustrated in Fig. 2, showing the presence of one methylene bridging a single Ru—Ru bond, and another linked with diphenylacetylene in a C(Ph)C(Ph)CH₂ ligand. Carbon C(5) is equidistant from each ruthenium, allowing it to be seen as a μ -carbon and the ligand as a whole to be represented as in **2**.

Previous work in our laboratory has shown that two μ -carbons associated with a diruthenium centre can be induced thermally to bond together, creating an olefin [8]. In the case of **2** such a reaction would lead to 2,3-diphenylbuta-1,3-diene. Thermolysis of **2** at 200°C does produce a variety of organic products, but none of these is this diene. Examination of the molecular structure of **2** suggests a possible reason for this apparent failure to link the bridging carbons, in that although the C(1) . . . C(5) separation is only 3.07(2) Å, the methylene carbons C(1) and C(3) are much closer together, at 2.78(2) Å. That carbon—carbon bond formation occurs preferentially to link C(1) and C(3) within this molecule is confirmed by the formation of [Ru₂(CO)(μ -CO)-{ μ -C(Ph)C(Ph)C(H)Me}(η -C₅H₅)₂] (**3**) in ca. 25% yield by heating **2** in xylene at reflux; **3** was obtained previously by 'insertion' of PhC₂Ph into [Ru₂(CO)₂(μ -CO){ μ -C(H)Me}(η -C₅H₅)₂] [6]. Clearly, linking of the two methylene groups and a subsequent hydrogen shift has occurred, while an additional molecule of CO has also been incorporated, most likely scavenged from some decomposition of **2**. Treating **2** with CO (10 atm, 140°C) does afford **3**. Recently it was observed that [Os₃(CO)₉(μ -CH₂)(μ_3 -C₂Ph₂)], whose acetylenic carbons are each 2.86 Å distant from the methylene carbon, also undergoes carbon—carbon bond formation on heating to link the hydrocarbon ligands [9].

This work suggests that the spatial proximity of carbon atoms may be a significant factor in determining the path by which hydrocarbon fragments combine at a dinuclear metal centre. In addition, the last step of the carbon chain growth process in the sequence **1** → **2** → **3** can be seen as a combination of coordinated olefinic and methylene groups. This is strongly reminiscent of a recent proposal for carbon homologation in Fischer—Tropsch Synthesis, which envisages such olefin-methylene linkage occurring on a metal surface [2,3].

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