

## Carbon–Carbon Bond Formation through Olefin–Methylcarbyne Linkage at a Diruthenium Centre: X-Ray Crystal Structure of $[\text{Ru}_2(\text{CO})-(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{Me})\text{C}(\text{Me})\text{CH}_2\}(\eta\text{-C}_5\text{H}_5)_2]$

By ANDREW F. DYKE, JACQUES E. GUERCHAIS, SELBY A. R. KNOX,\* JEAN ROUÉ,  
RICHARD L. SHORT, GRAHAM E. TAYLOR, and PETER WOODWARD

(Department of Inorganic Chemistry, The University, Bristol BS8 1TS)

**Summary** Reaction of  $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMe})(\eta\text{-C}_5\text{H}_5)_2]^+$  with  $\text{RCH}=\text{CH}_2$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ) under u.v. radiation provides  $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{Me})\text{C}(\text{R})\text{CH}_2\}(\eta\text{-C}_5\text{H}_5)_2]$  which, for  $\text{R}=\text{H}$ , may also be obtained by treatment of  $[\text{Ru}_2(\text{CO})(\text{C}_2\text{H}_4)(\mu\text{-CO})_2(\eta\text{-C}_5\text{H}_5)_2]$  with  $\text{MeLi}$ ,  $\text{HBF}_4$ , and  $\text{NaBH}_4$  successively; the structure of  $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{Me})\text{C}(\text{Me})\text{CH}_2\}(\eta\text{-C}_5\text{H}_5)_2]$  has been determined by X-ray diffraction.

THE mode of carbon–carbon bond formation during Fischer–Tropsch hydrogenation of carbon monoxide is obscure. Current thought is in favour of dissociative chemisorption of CO and  $\text{H}_2$  on the metal surface and subsequent generation of surface CH,  $\text{CH}_2$ , and  $\text{CH}_3$  species which combine to provide higher hydrocarbons.<sup>1</sup> There is growing evidence that  $\mu$ -carbene species may indeed initiate carbon chain-growth.<sup>2–5</sup> We now report that carbon–carbon bond formation can also be achieved with a  $\mu$ -carbyne, in describing the interaction of olefins with  $\mu$ -methylcarbyne at a diruthenium centre.

When ethylene or propene is bubbled for 3 h through a tetrahydrofuran solution of  $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMe})(\eta\text{-C}_5\text{H}_5)_2][\text{BF}_4]$  (**1**)<sup>6</sup> under u.v. radiation a 40% yield of  $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{Me})\text{C}(\text{R})\text{CH}_2\}(\eta\text{-C}_5\text{H}_5)_2]$  (**2**,  $\text{R} = \text{H}$ ; **3**,  $\text{R} = \text{Me}$ )<sup>†</sup> is obtained. The structure of (**3**) was determined by X-ray diffraction.

**Crystal data:**  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{Ru}_2$ ,  $M = 456.2$ , monoclinic, space group  $P2_1/c$ ,  $a = 14.684(3)$ ,  $b = 9.272(3)$ ,  $c = 12.414(3)$  Å,  $\beta = 114.03(1)^\circ$ ,  $U = 1543.7(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 896$ ,  $\mu(\text{Mo-K}\alpha) = 19.1$  cm<sup>-1</sup>.

The structure was solved by conventional heavy-atom methods and refined to  $R$  0.021 for 3 187 reflections ( $2\theta \leq 55^\circ$  at 230 K) on a Nicolet R3/M diffractometer, using monochromatised Mo- $K\alpha$  X-radiation.‡

The molecular structure (Figure) reveals two ruthenium atoms at a single bond distance, doubly bridged by a carbonyl group and by a  $\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}_2$  moiety. Atoms C(1) of the bridging carbonyl and C(5) of the other bridge are both nearly equidistant from the two metal atoms, though by a small margin C(1) is closer to Ru(2) and C(5) to Ru(1), which atom carries a terminal carbonyl C(2)O(2). Atoms C(4) and C(3) are approximately equidistant from Ru(2) and are significantly further away than is C(5),

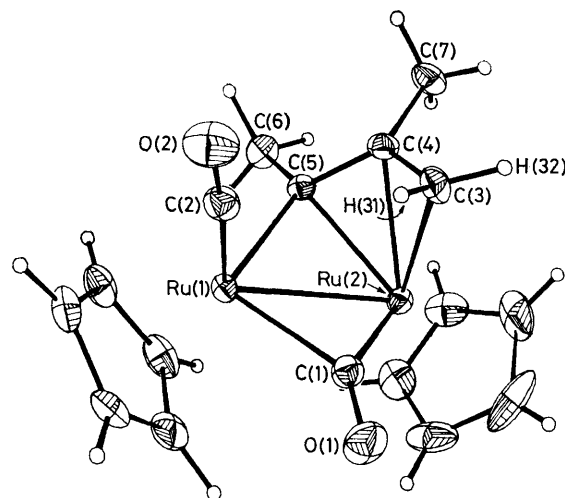


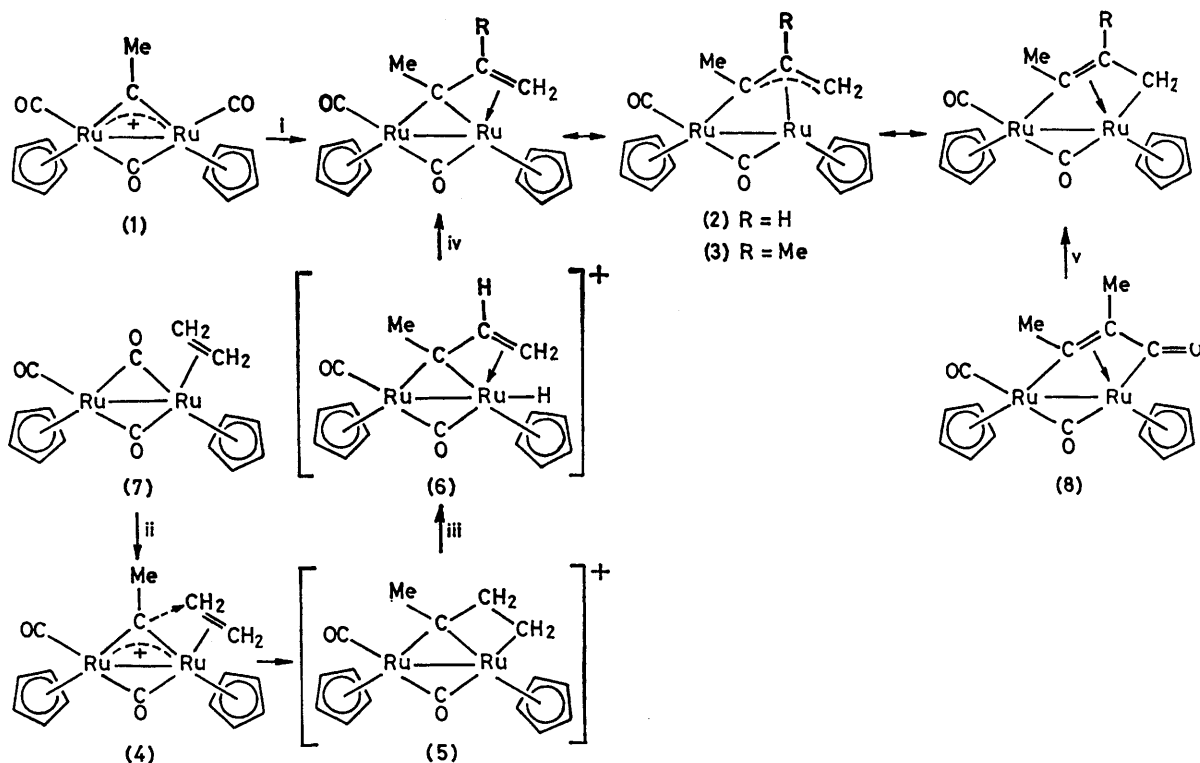
FIGURE. Molecular structure of  $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{Me})\text{C}(\text{Me})\text{CH}_2\}(\eta\text{-C}_5\text{H}_5)_2]$  (**3**). Bond lengths: Ru(1)–Ru(2) 2.719(1), Ru(1)–C(1) 2.081(3), Ru(2)–C(1) 1.974(3), Ru(1)–C(5) 2.083(3), Ru(2)–C(5) 2.125(2), Ru(2)–C(4) 2.168(2), Ru(2)–C(3) 2.180(2), C(3)–C(4) 1.425(5), C(4)–C(5) 1.429(3), C(4)–C(7) 1.526(5), C(5)–C(6) 1.514(4) Å.

suggesting an olefinic C(3)–C(4) interaction with that metal atom. On the other hand, the plane defined by C(4)C(3)H(31)H(32) is at an angle of  $28^\circ$  to that defined by C(3)C(4)C(5)C(7), whereas this latter plane is at an angle of only  $4^\circ$  to the C(4)C(5)C(6) plane, suggesting more twist in the C(3)–C(4) bond than in the C(4)–C(5) bond. Moreover, the carbon–carbon bond lengths within the bridging  $\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}_2$  moiety are not significantly different from one another. The X-ray results do not, therefore, clearly conflict with any of the three representations of (**3**) shown in the Scheme.

Two pathways for the formation of (**2**) and (**3**) seem possible. These involve (a) initial electrophilic attack of the  $\mu$ -carbyne cation (**1**) upon the olefin, followed by coordination, or (b) initial substitution of olefin for CO in the cation (**1**), and then intramolecular electrophilic attack of carbyne upon the co-ordinated olefin. For ethylene path (b) is represented in the Scheme, where substitution to give (**4**) is followed by intramolecular attack to provide (**5**), which is

† (**2**): yellow crystals, m.p.  $180^\circ\text{C}$ ;  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$  1 940 s and 1 773 m cm<sup>-1</sup>;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\tau$  4.78 (s, 5H), 5.16 (s, 5H), 5.74 (dd,  $J$  6 and 8 Hz, 1H), 6.72 (s, 3H), 7.44 (dd,  $J$  2 and 6 Hz, 1H), and 10.08 (dd,  $J$  2 and 8 Hz, 1H); (**3**): yellow crystals, m.p.  $178\text{--}179^\circ\text{C}$ ;  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$  1 936 s and 1 768 m cm<sup>-1</sup>;  $^1\text{H}$  n.m.r. ( $\text{CDCl}_3$ )  $\tau$  4.77 (s, 5H), 5.19 (s, 5H), 6.61 (s, 3H), 7.27 (d,  $J$  3 Hz, 1H), 8.10 (s, 3H), and 10.25 (d,  $J$  3 Hz, 1H).

‡ 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.



SCHEME. i,  $RCH=CH_2$ , u.v.; ii, MeLi,  $HBF_4$ ; iii,  $\beta$ -elimination; iv,  $NaBH_4$  or tetrahydrofuran,  $-H^+$ ; v,  $HBF_4$ ,  $NaBH_4$ .

in turn envisaged to undergo  $\beta$ -elimination to give (6); deprotonation then results in (2). Strong evidence for this path is provided by treating  $[Ru_2(CO)(C_2H_4)(\mu-CO)_2(\eta-C_5H_5)_2]$  (7)<sup>7</sup> with methyl-lithium,  $HBF_4$ , and  $NaBH_4$  in succession, when (2) is formed in 50% yield. It has been established<sup>8</sup> that diruthenium  $\mu$ -CO is converted into  $\mu$ -MeC<sup>+</sup> by MeLi- $HBF_4$  and the intermediacy of (4) in the synthesis from (7) can be assumed with confidence. Deprotonation is achieved by addition of  $NaBH_4$  in this synthesis, where an excess of  $HBF_4$  is present, but in the direct synthesis from (1) deprotonation evidently occurs spontaneously in the tetrahydrofuran solution.

One mechanism proposed for carbon chain growth in Fischer-Tropsch synthesis involved CO 'insertion' into a surface metal alkyl (strictly alkyl migration), followed by conversion of acyl C=O into  $CH_2$ , further CO insertion, and so on.<sup>1</sup> A mechanism based on this idea, but involving CO insertion into a dimetallocycle (which we have shown<sup>9</sup> can be a most favourable process), is suggested by the easy

conversion of  $[Ru_2(CO)(\mu-CO)\{\mu-\eta^1, \eta^3-C(O)C(Me)C(Me)\}(\eta-C_5H_5)_2]$  (8)<sup>9</sup> into (3) when treated with  $HBF_4$  and  $NaBH_4$  in succession.

In view of the variety of products obtainable in Fischer-Tropsch synthesis it is likely that more than one carbon-carbon bond formation process is in operation. This communication provides evidence that not only  $\mu$ -carbene, but also  $\mu$ -carbyne species could be involved, and that discarding the participation of some form of CO insertion may be premature.

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<sup>1</sup> E. L. Muetterties and J. Stein, *Chem. Rev.*, 1979, **79**, 479, and references therein.

<sup>2</sup> C. E. Sumner, P. E. Riley, R. E. Davis, and R. Pettit, *J. Am. Chem. Soc.*, 1980, **102**, 1752.

<sup>3</sup> R. C. Brady and R. Pettit, *J. Am. Chem. Soc.*, 1980, **102**, 6181.

<sup>4</sup> A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Chem. Commun.*, 1980, 803.

<sup>5</sup> K. H. Theopold and R. G. Bergman, *J. Am. Chem. Soc.*, 1981, in the press.

<sup>6</sup> D. L. Davies, A. F. Dyke, A. Endesfelder, S. A. R. Knox, P. J. Naish, A. G. Orpen, D. Plaas, and G. E. Taylor, *J. Organomet. Chem.*, 1980, **198**, C43.

<sup>7</sup> A. F. Dyke, S. A. R. Knox, and P. J. Naish, *J. Organomet. Chem.*, 1980, **199**, C47.

<sup>8</sup> D. L. Davies, A. F. Dyke, J. E. Guerchais, S. A. R. Knox, K. A. Mead, J. Roué, and P. Woodward, to be published.

<sup>9</sup> A. F. Dyke, S. A. R. Knox, P. J. Naish, and G. E. Taylor, *J. Chem. Soc., Chem. Commun.*, 1980, 409.