

## Making and Breaking of Carbon–Carbon Bonds at a Di-iron or Di-ruthenium Centre: X-Ray Structure of $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{O})\text{C}_2\text{Ph}_2\}(\eta\text{-C}_5\text{H}_5)_2]$

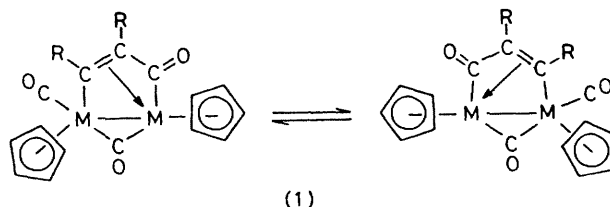
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**Summary** Dimetalloacycles  $[\text{M}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{O})\text{C}_2\text{R}_2\}(\eta\text{-C}_5\text{H}_5)_2]$  ( $\text{M} = \text{Fe}$ ,  $\text{R} = \text{H}$ ,  $\text{Me}$ ,  $\text{Ph}$ ,  $\text{CO}_2\text{Me}$ ,  $\text{M} = \text{Ru}$ ,  $\text{R} = \text{H}$ ,  $\text{Me}$ ,  $\text{Ph}$ ) have been obtained either by  $uv$  irradiation of an alkyne with  $[\{\text{M}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2\}]_2$  or through thermal alkyne exchange with  $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{O})\text{C}_2\text{Ph}_2\}(\eta\text{-C}_5\text{H}_5)_2]$ , the structure of the complexes, whose fluxionality has been shown to involve low energy carbon–carbon bond making and breaking, was established through an X-ray diffraction study of  $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{O})\text{C}_2\text{Ph}_2\}(\eta\text{-C}_5\text{H}_5)_2]$

THERE has been recent speculation that di-nuclear metal centres may be important in catalytic processes<sup>1–3</sup>. Much of this has been concerned with the possible role of such a centre in the cyclo-tetramerisation of alkynes<sup>1,3</sup>. We now describe new dimetalloacycles, derived from reactions of alkynes with di-iron and di-ruthenium complexes, whose chemistry involves unprecedented low energy carbon–carbon bond-making and -breaking processes, lending weight to the general speculation.

Under  $uv$  irradiation (250 W mercury lamp, toluene solution, silica glass flask) the dimers  $[\{\text{M}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2\}]_2$  ( $\text{M} = \text{Fe}$  or  $\text{Ru}$ ) react over several days at room temperature with alkynes  $\text{C}_2\text{R}_2$  to produce brown-red crystalline complexes of formulation  $[\text{M}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{O})\text{C}_2\text{R}_2\}(\eta\text{-C}_5\text{H}_5)_2]$  (**1a–g**) in yields of up to 85%. For ruthenium (**1g**) is formed in this way, but on heating the complex in toluene with ethyne or but-2-yne an alkyne exchange occurs

rapidly (<1 h) and quantitatively, providing (**1e**) and (**1f**) respectively. The structure of (**1g**) [m.p. 170–172 °C,  $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$  1978s, 1803s, and 1731w-m  $\text{cm}^{-1}$ ,  $^1\text{H}$  n.m.r. ( $\text{C}_5\text{D}_5\text{N}$ )  $\tau$  2.70 (m, 10H), 4.44 (s, 5H), and 4.72 (s, 5H)] was determined by X-ray diffraction.



- a,  $\text{M} = \text{Fe}$ ,  $\text{R} = \text{H}$
- b,  $\text{M} = \text{Fe}$ ,  $\text{R} = \text{Me}$
- c,  $\text{M} = \text{Fe}$ ,  $\text{R} = \text{Ph}$
- d,  $\text{M} = \text{Fe}$ ,  $\text{R} = \text{CO}_2\text{Me}$
- e,  $\text{M} = \text{Ru}$ ,  $\text{R} = \text{H}$
- f,  $\text{M} = \text{Ru}$ ,  $\text{R} = \text{Me}$
- g,  $\text{M} = \text{Ru}$ ,  $\text{R} = \text{Ph}$

**Crystal data**  $\text{C}_{27}\text{H}_{20}\text{O}_3\text{Ru}_2$ ,  $M = 594.6$ , orthorhombic, space group  $Pbca$ ,  $a = 14.797(3)$ ,  $b = 17.805(8)$ ,  $c = 16.739(8)$  Å,  $U = 4410(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $F(000) = 2352$ , Mo- $K_\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\mu(\text{Mo-}K_\alpha) = 9.9$   $\text{cm}^{-1}$ .

The structure was solved by conventional heavy atom methods from data collected on a Syntex  $P2_1$  diffractometer to  $2\theta_{\text{max}} = 60^\circ$  at 233 K. For 3726 independent reflections [ $I \geq 3\sigma(I)$ ]  $R$  is 0.033 †. The molecular geometry is shown

† 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.

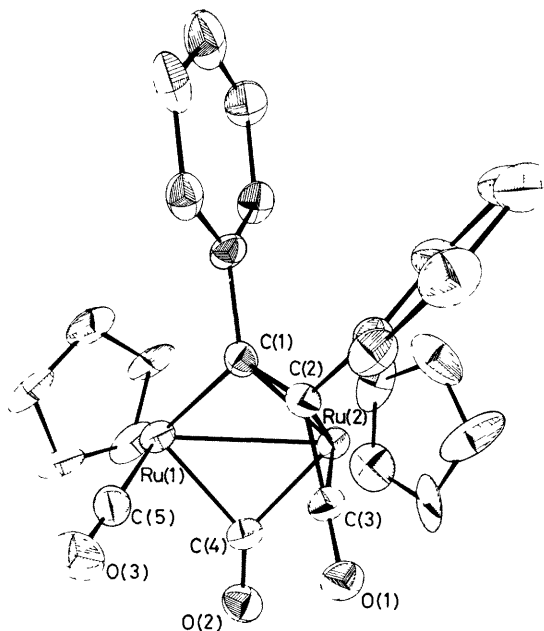
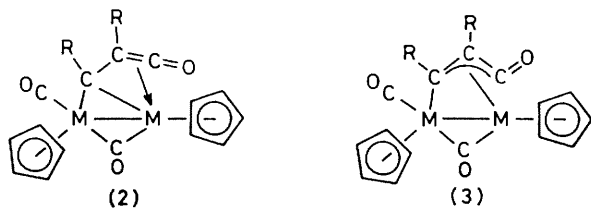


FIGURE. Molecular structure of  $[\text{Ru}_2(\text{CO})(\mu\text{-CO})\{\mu\text{-}\eta^1, \eta^3\text{-C}(\text{O})\text{C}_6\text{Ph}_2\}(\eta\text{-C}_5\text{H}_5)_2]$ . Bond lengths: Ru(1)–Ru(2) 2.729(1), Ru(1)–C(1) 2.080(4), Ru(1)–C(4) 2.039(4), Ru(1)–C(5) 1.865(5), Ru(2)–C(1) 2.158(4), Ru(2)–C(2) 2.219(4), Ru(2)–C(3) 2.011(4), Ru(2)–C(4) 2.005(4), C(1)–C(2) 1.423(6), C(2)–C(3) 1.461(5), C(3)–O(1) 1.198(5), C(4)–O(2) 1.179(5), C(5)–O(3) 1.138(5) Å.

in the Figure. The two ruthenium atoms are at a single bond distance [2.729(1) Å], surmounted by a symmetrically bridging carbonyl and a group derived from the linking of diphenylacetylene and a carbon monoxide ligand. This unusual bridging unit is perhaps best represented as in (1), where C(1) and C(3) are regarded as being  $\eta^1$ -bonded to Ru(1) and Ru(2) respectively, while C(1) and C(2) comprise an olefinic system  $\eta^2$ -bonded to Ru(2). However, the angle C(2)–C(3)–O(1) of 138.1(4)° is somewhat larger than that expected for an  $\text{sp}^2$  carbon atom C(3) and the C(2)–C(3) distance [1.461(5) Å] is shorter than a conventional single bond, indicating a contribution from form (2) towards the overall structure. There are, therefore, grounds for presenting the bonding of C(1)–(3) with Ru(2) in the 'allylic' form (3). Related bonding systems have been observed in iron<sup>4</sup> and molybdenum<sup>5</sup> complexes.

The rapid and quantitative alkyne exchange reaction previously mentioned is extraordinary for the ease with



which a carbon–carbon bond [C(2)–C(3) of (1g)] may be broken and re-formed at the di-nuclear metal centre. This reactivity is matched by the fluxional behaviour of the complexes (1), which involves low energy breaking and re-forming of that same carbon–carbon bond. Each of (1) displays, at room temperature or below, <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra in accord with the solid state structure determined for (1g); i.e. inequivalent C<sub>5</sub>H<sub>5</sub> ligands, inequivalent R groups, and three CO environments. On warming, spectral changes characteristic of fluxional motion ensue, leading to time-average equivalence of the C<sub>5</sub>H<sub>5</sub> ligands, the R groups, and two of the CO groups. For example, the <sup>1</sup>H n.m.r. spectrum of (1d) at 25 °C comprises C<sub>5</sub>H<sub>5</sub> signals at  $\tau$  4.91 and 5.10 and CO<sub>2</sub>Me signals at  $\tau$  5.94 and 6.31, which coalesce at 56 and 67 °C respectively and sharpen at higher temperatures. Clearly, for the two R groups of (1) to become equivalent on the n.m.r. time scale there must be a rapid breaking and regeneration of the 'alkyne–CO' link involving both ends of the 'alkyne'. Coupled with the averaging of C<sub>5</sub>H<sub>5</sub> environments, this suggests the process illustrated, where an ejection of CO from the dimetallocycle (to become a terminal ligand) is accompanied by migration of the other end of the 'alkyne' to the existing terminal CO. Reference to the Figure shows that this unprecedented process requires quite small atomic movements.

The involvement of the two carbon monoxides in the process is confirmed by changes observed in the <sup>13</sup>C n.m.r. spectrum of <sup>13</sup>CO-enriched (1d) over a range of temperatures. At –30 °C in CD<sub>2</sub>Cl<sub>2</sub> there are <sup>13</sup>CO signals at 257.1, 222.3, and 211.3 p.p.m., those at lowest and highest field being characteristic, respectively, of bridging and terminal CO groups on iron. (For [ $\{\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2\}_2$ ] in CD<sub>2</sub>Cl<sub>2</sub> at –100 °C corresponding signals occur at 272.9 and 210.9 p.p.m.). The remaining signal (222.3 p.p.m.) is assigned to the metalcyclic ketonic CO. On warming, the bridging CO signal is unchanged but those due to the terminal and ketonic carbonyls broaden and coalesce at 90 °C, in line with their fluxional exchange. These data provide a free energy of activation of 70.1 kJ mol<sup>–1</sup>, comparable with values of 70.1 (CO<sub>2</sub>Me coalescence) and 71.0 (C<sub>5</sub>H<sub>5</sub> coalescence) kJ mol<sup>–1</sup> obtained from the <sup>1</sup>H n.m.r. spectrum. Similar barriers have been determined for (1f) (69.5) and (1g) (66.7), but for (1a) (84.8) and (1e) (79.4 kJ mol<sup>–1</sup>), derived from ethyne,  $\Delta G^\ddagger$  is substantially higher. Steric factors thus appear to be important, with less crowding in the transition state of the fluxional process than in the ground state.

The involvement of mono-metallocycles in catalytic processes is well documented;<sup>1</sup> the evidence which this communication provides of the lability of dimetallocycles suggests that such species may be equally significant.

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<sup>1</sup> G. Wilke, *Pure Appl. Chem.*, 1978, **50**, 677.

<sup>2</sup> M. H. Chisholm and F. A. Cotton, *Acc. Chem. Res.*, 1978, **11**, 356.

<sup>3</sup> S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1978, 221.

<sup>4</sup> F. A. Cotton, J. D. Jamerson, and B. R. Stults, *Inorg. Chim. Acta*, 1976, **17**, 235.

<sup>5</sup> J. E. Guerschais, F. Le Floch-Perrenou, F. Y. Petillon, A. N. Keith, L. Manojlovic-Muir, K. W. Muir, and D. W. A. Sharp, *J. Chem. Soc., Chem. Commun.*, 1979, 410.