

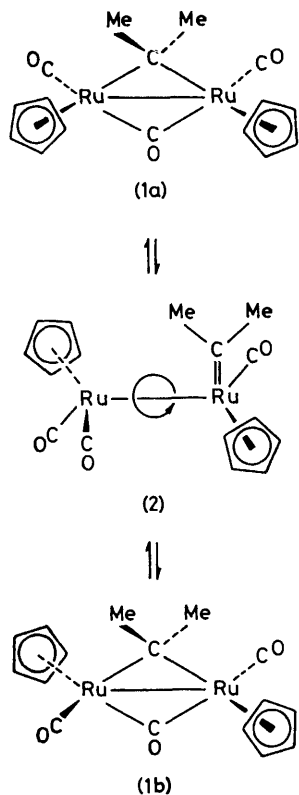
X-Ray Crystal Structure and Molecular Dynamics of the μ -Dimethylcarbene Complex $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$

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Summary X-Ray diffraction has established that $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ exists in the solid state as the *cis*-isomer, but in solution both the *cis*- and *trans*-isomers are present and interconvert rapidly on the n.m.r. time scale above room temperature; the isomerisation is concluded to involve bridge-terminal carbene exchange.

ATTENTION has recently been drawn to the possibility of μ -carbenes being involved in transition-metal catalysed Fischer-Tropsch synthesis and alkyne polymerisation.¹⁻³ The mobility⁴ of surface species is clearly an important feature of such processes, and in this communication we describe studies which indicate that a pathway exists for carbene mobility analogous to that established for carbon monoxide.⁵



The μ -dimethylcarbene complex $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ adopts the *cis*-configuration (**1a**) in the solid state, as shown by an X-ray diffraction study.

Crystal data: $\text{C}_{16}\text{H}_{18}\text{O}_3\text{Ru}_2$, $M = 458.4$, triclinic, space group $P\bar{1}$, $a = 7.124(4)$, $b = 12.373(3)$, $c = 9.494(4)$ Å,

$\alpha = 105.94(3)$, $\beta = 108.61(3)$, $\gamma = 90.60(3)^\circ$, $U = 758.2(4)$ Å³, $Z = 2$, $D_m = 2.06$ g cm⁻³, $D_c = 2.01$ g cm⁻³, $F(000) = 448$, $\mu(\text{Mo-K}\alpha) = 19.6$ cm⁻¹.

The structure was solved by conventional heavy-atom methods and refined to R 0.018 for 2001 reflections ($2\theta \leq 60^\circ$ at 220 K) on a Syntex P3m diffractometer, using monochromatised Mo- $K\alpha$ radiation.†

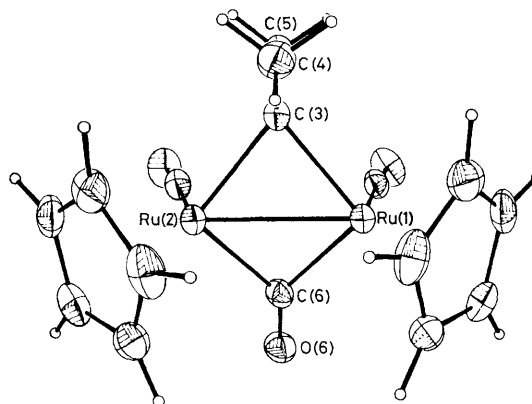


FIGURE 1. Molecular structure of $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ (**1**). Bond lengths: Ru(1)-Ru(2) 2.712(1), Ru(1)-C(3) 2.113(3), Ru(2)-C(3) 2.113(4), Ru(1)-C(6) 2.001(5), and Ru(2)-C(6) 2.031(3) Å. Angles: Ru(1)-C(3)-Ru(2) 79.8(1), Ru(1)-C(6)-Ru(2) 84.3(2), and C(4)-C(3)-C(5) 105.8(3)°.

The structure (Figure 1) is based on two ruthenium atoms at a single bond distance, bridged symmetrically by dimethylcarbene and CO ligands such that the plane C(3)C(4)-C(5) of the carbene makes an angle of 89° with the plane containing the ruthenium atoms and their attendant terminal carbonyl groups. The latter are in a *cis*-arrangement with respect to the Ru_2 unit, as is the pair of cyclopentadienyl ligands. The angle between the planes Ru(1)Ru(2)C(3) and Ru(1)Ru(2)C(6) is 154° which contrasts sharply with that of 177° in the di- μ -carbene complex $[\text{Ru}_2(\text{CO})_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$.⁷

In solution, the ¹H n.m.r. spectrum reveals the presence of both *cis*-(**1a**) [τ 5.32 (s, 10 H), 6.84 (s, 3 H), and 7.22 (s, 3 H)] and *trans*-(**1b**) [5.18 (s, 10 H) and 6.98 (s, 6 H)] isomers, in a *ca.* 1:1 ratio at 39 °C. On warming, as shown in Figure 2, coalescence of the cyclopentadienyl and methyl signals of the two isomers is induced, until at 140 °C sharp singlet signals are observed for each type of proton. These changes, which are reversible, are attributed to a *cis* \rightleftharpoons *trans* interconversion occurring on the n.m.r. time scale and which becomes increasingly rapid as the temperature is raised.

† 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.

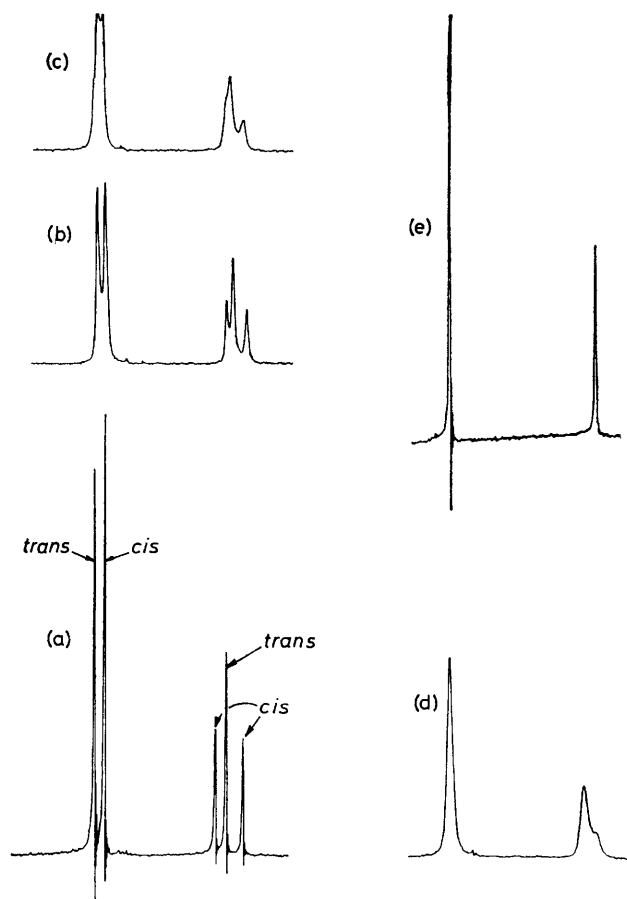


FIGURE 2. ^1H N.m.r. spectrum of $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMe}_2)(\eta\text{-C}_6\text{H}_5)_2]$ (**1**) at various temperatures; (a) 39°C , $[\text{^2H}_8]\text{toluene}$; (b) 91°C , $[\text{^2H}_8]\text{toluene}$; (c) 100°C , $[\text{^2H}_8]\text{toluene}$; (d) 108°C , $[\text{^2H}_8]\text{toluene}$; (e) 140°C , $\text{C}_6\text{H}_4\text{Cl}_2$.

Similar behaviour of the related $[\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-GeMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ has been ascribed to concerted bridge opening, rotation about the metal-metal bond in the non-bridged isomer so-formed, and concerted bridge regeneration.⁸ Convincing evidence and arguments have been presented for such a process occurring generally in dibridged, dinuclear metal systems.⁹ We favour this mechanism for the molecular dynamic behaviour of compound (**1**) for two additional reasons. (i) It requires a transient terminal carbene complex (**2**) of a type for which there is precedent, *e.g.* $[(\text{OC})_5\text{ReRe}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_4]$,¹⁰ and (ii) estimation of the free energy of activation of the process, from coalescence temperatures, provides a value of *ca.* 20 kcal mol^{-1} ($1\text{ cal} = 4.184\text{ J}$). The size of the barrier leads us to discount mechanisms for the isomerisation which involve the carbene remaining as a bridge and CO alone exchanging bridge and terminal sites. In $[\text{Rh}_2(\text{CO})\{\text{P}(\text{OPh})_3\}(\mu\text{-CO})(\eta\text{-C}_5\text{H}_5)_2]$ ¹¹ and $[\text{Ru}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$,¹² closely related to compound (**1**), isomerisation by purely CO migration faces a much lower energy barrier of *ca.* 9 kcal mol^{-1} .

We conclude that bridge \rightleftharpoons terminal carbene exchange is involved in the isomerisation of compound (**1**) and suggest that, like carbon monoxide, this variation in co-ordination mode provides a pathway for carbene mobility on metal surfaces and in complexes in catalysis.

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