

**Synthesis, X-Ray Crystal Structure and Reactivity of the Di- μ -carbene
Complex $[\text{Ru}_2(\text{CO})_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$**

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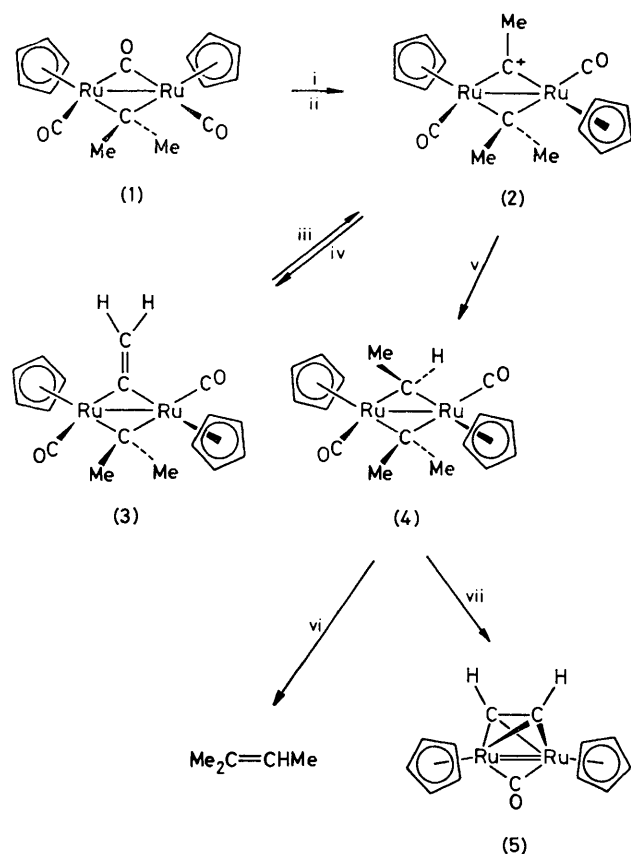
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Summary Treatment of $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ with methyl-lithium and HBF_4 in succession provides the carbyne-carbene-bridged cation $[\text{Ru}_2(\text{CO})_2(\mu\text{-CMe})-$

$(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]^+$ which may be converted into di- μ -carbene complexes $[\text{Ru}_2(\text{CO})_2(\mu\text{-CCH}_2)(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ and $[\text{Ru}_2(\text{CO})_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$; the latter,

whose structure has been determined by X-ray diffraction, releases $\text{Me}_2\text{C}=\text{CHMe}$ at 200 °C as the major volatile product.

BRADY and Pettit have recently revived¹ the original suggestion² of Fischer and Tropsch that hydrocarbon formation during CO hydrogenation arises by combination of methylene groups on the metal surface. Such combination, especially where olefin formation is concerned, could follow simultaneous co-ordination of carbenes at a dinuclear metal centre. Many μ -carbene complexes of transition metals are now known, but those which contain more than one μ -carbene per dinuclear metal centre are rare³⁻⁷ and their chemistry is effectively unexplored. We have sought to prepare model di- μ -carbene complexes and to investigate their chemistry, the preliminary results of which study are described herein.



SCHEME. Reagents: i, MeLi, 25 °C; ii, HBF_4 , -78 °C; iii, H^+ ; iv, H_2O ; v, NaBH_4 , -78 °C; vi, 200 °C; vii, u.v., $\text{HC}=\text{CH}$.

† Compound (2) was obtained as yellow crystals, m.p. 163 °C (decomp.); $\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ 2 000 cm^{-1} ; ^1H n.m.r. (CD_2Cl_2) τ 4.40 (s, 10 H, $2 \times \text{C}_5\text{H}_5$), 5.64 (s, 3 H, CMe), and 6.64 (s, 6 H, CMe_2).

‡ Compound (3) was obtained as yellow crystals, m.p. 177 °C; $\nu(\text{CO})(\text{hexane})$ 1 945 cm^{-1} ; ^1H n.m.r. (CDCl_3) τ 4.12 (s, 2 H, CCH_2), 4.88 (s, 10 H, $2 \times \text{C}_5\text{H}_5$), and 7.16 (s, 6 H, CMe_2); ^{13}C n.m.r. (CDCl_3) δ 244.5 (CCH_2), 201.0 ($2 \times \text{CO}$), 175.6 (CMe_2), 122.2 (CH_2), 92.8 ($2 \times \text{C}_5\text{H}_5$), and 55.3 ($2 \times \text{Me}$) p.p.m..

§ Compound (4) was obtained as yellow crystals, m.p. 161 °C; $\nu(\text{CO})(\text{hexane})$ 1 928 cm^{-1} ; ^1H n.m.r. (CDCl_3) τ 0.60 (q, J 8 Hz, 1 H, CHMe), 4.86 (s, 10 H, $2 \times \text{C}_5\text{H}_5$), 7.20 (s, 3 H, CMe_2), 7.20 (d, J 8 Hz, 3 H, CHMe), and 7.28 (s, 3 H, CMe_2); ^{13}C n.m.r. (CDCl_3) δ 202.6 (CO), 202.5 (CO), 166.8 (CMe_2), 135.3 (CHMe), 92.5 (C_5H_5), 92.1 (C_5H_5), 55.5 (CMe_2), 55.4 (CMe_2), and 44.2 (CHMe) p.p.m.

¶ 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.

The conversion of μ -CO into μ -CMe⁺ at a diruthenium centre is readily achieved by sequential treatment with methyl-lithium at room temperature and HBF_4 at -78 °C.⁸ Application of this procedure to the μ -methylcarbene complex $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CHMe})(\eta\text{-C}_5\text{H}_5)_2]$ failed because of preferential attack of methyl-lithium on the carbene, but the μ -dimethylcarbene complex $[\text{Ru}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ (1) was smoothly and quantitatively converted into the μ -carbyne- μ -carbene species $[\text{Ru}_2(\text{CO})_2(\mu\text{-CMe})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2][\text{BF}_4]$ (2).† The cation was deprotonated on shaking in dichloromethane-water to yield (66%) $[\text{Ru}_2(\text{CO})_2(\mu\text{-CCH}_2)(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ (3),‡ which contains μ -vinylidene and μ -dimethylcarbene ligands, and was attacked by hydride to give $[\text{Ru}_2(\text{CO})_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ (4)§ in 75% yield (see the Scheme). This rare di- μ -carbene complex (4) was subjected to an X-ray diffraction study.

Crystal data: $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Ru}_2$, $M = 458.5$, triclinic, space group $P\bar{1}$, $a = 8.474(2)$, $b = 7.802(3)$, $c = 12.989(5)$ Å, $\alpha = 99.42(3)$, $\beta = 96.96(3)$, $\gamma = 107.73(3)^\circ$, $U = 793.4(4)$ Å³, $D_m = 1.81$, $Z = 2$, $D_c = 1.92$ g cm^{-3} , $F(000) = 452$, $\mu(\text{Mo-K}\alpha) = 18.7$ cm^{-1} . The structure (Figure) was solved by conventional heavy-atom methods and refined to R 0.026 for 4 092 reflections ($2\theta \leq 60^\circ$ at 220 K) on a Nicolet P2₁ diffractometer, using monochromatised radiation.¶

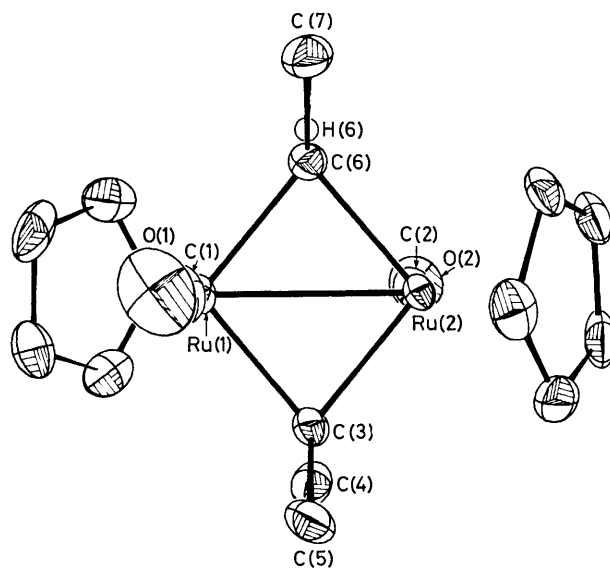


FIGURE. Molecular structure of $[\text{Ru}_2(\text{CO})_2(\mu\text{-CHMe})(\mu\text{-CMe}_2)(\eta\text{-C}_5\text{H}_5)_2]$ (4). Bond lengths: Ru(1)-Ru(2) 2.701(1), Ru(1)-C(3) 2.106(3), Ru(2)-C(3) 2.108(3), Ru(1)-C(6) 2.073(3), and Ru(2)-C(6) 2.086(3) Å. Bond angles: Ru(1)-C(3)-Ru(2) 79.7(1), Ru(1)-C(6)-Ru(2) 81.0(1), C(4)-C(3)-C(5) 107.4(2), C(7)-C(6)-H(6) 104(3), Ru(1)-C(1)-O(1) 175.6(3), and Ru(2)-C(2)-O(2) 175.7(3)°.

The dimethylcarbene and methylcarbene ligands form symmetrical bridges across an Ru(1)–Ru(2) single bond and the dicarbene–metal system is almost planar [the angle between the Ru(1)Ru(2)C(3) and Ru(1)Ru(2)C(6) planes is 177°]. The carbene ligands themselves are mutually coplanar and this plane [C(3)C(4)C(5)C(6)C(7)H(6)] is perpendicular both to the mean Ru(1)Ru(2)C(3)C(6) plane and to the plane which contains the carbonyl ligands. Each ruthenium atom carries a cyclopentadienyl ligand and a carbonyl group, which lie in the *trans* orientations with respect to the Ru₂(carbene)₂ plane.

From the i.r. and n.m.r. spectra of compounds (2)–(4) it is clear that each adopts a uniquely *trans* arrangement of η-C₅H₅ ligands. Up to +135 °C there is no evidence of fluxional *cis* ⇌ *trans* isomerism by compound (4), unlike the μ-dimethylcarbene complex (1),⁹ and any concerted opening of the di-μ-carbene bridge system is evidently a high energy process.

Early results of a study of the reactivity of compounds (3) and (4) suggest that the di-μ-carbene system exhibits significant differences compared with a mono-μ-carbene

complex. Whereas acetylene 'inserts' into a carbene–ruthenium bond of [Ru₂(CO)₂(μ-CO)(μ-CHMe)(η-C₅H₅)₂] or compound (1) to give three-¹⁰ and five-⁸ carbon chains, respectively, both carbenes in compound (4) are ejected by acetylene under the same photochemical conditions to yield [Ru₂(μ-CO)(μ-C₂H₂)(η-C₅H₅)₂] (5). The fate of the carbenes in this reaction is not yet known. However, when compound (4) is decomposed at 200 °C the volatile products include ethylene (*ex* μ-CHMe) and propene (*ex* μ-CMe₂), but the major hydrocarbon product is Me₂C=CHMe, which is *ca.* 70% of the total. The absence of but-2-enes or Me₂C=CMe₂ indicates that Me₂C=CHMe is formed intramolecularly and suggests the viability of carbene combination at a dinuclear metal centre in catalytic processes, such as Fischer–Tropsch synthesis.

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