Synthesis of Trimethylenemethane by Combination of Methylene with Allene at a Diruthenium Centre: *X*-Ray Structure of $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}CH_2C(CH_2)_2\}(\eta\text{-}C_5H_5)_2]$

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Carbon–carbon bond formation is rapid when the μ-methylene complex $[Ru_2(CO)(MeCN)(\mu\text{-}CH_2)(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ is treated with allene at room temperature, affording the μ-trimethylenemethane complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}CH_2C(CH_2)_2\}(\eta\text{-}C_5H_5)_2]$, structurally characterised by *X*-ray diffraction; the fluxionality and isomerisation of the complex, and its reactivity towards H^+ and CO, are described.

The ways in which hydrocarbons rearrange and combine at metal centres continue to be a subject of great importance in organometallic chemistry. We recently described the synthesis of the complex $[Ru_2(CO)(C_2H_4)(\mu\text{-}CH_2)(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$, *via* the displacement of labile acetonitrile from $[Ru_2(CO)(MeCN)(\mu\text{-}CH_2)(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ (**1**), and showed that combination of the methylene and ethene ligands occurs only at high temperatures (>200 °C).[1] In contrast, we now report that combination of methylene and allene takes place rapidly at room temperature in this system, producing a μ-trimethylenemethane ligand with reactivity quite different from that associated with a mononuclear metal centre.

Condensation (−196 °C) of allene into a dichloromethane solution of the acetonitrile complex [Ru₂(CO)(MeCN)(μ-

$CH_2)(\mu\text{-}CO)(\eta\text{-}C_5H_5)_2]$ (**1**),[1] followed by warming to 25 °C, affords the μ-trimethylenemethane complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}CH_2C(CH_2)_2\}(\eta\text{-}C_5H_5)_2]$ (**3**)† in 50% yield. The structure of the product in the solid state was established as (**3a**) by an *X*-ray diffraction study, the results of which are summarised in Figure 1 and in its caption.‡ The structure consists of two ruthenium atoms at a single bond distance [2.818(1) Å], bridged by a carbonyl ligand; each bears an η^5-cyclopentadienyl group and one carries a terminal CO. A trimethylenemethane ligand bridges the two metal atoms so that it is η^3-allyl bound to one and $\eta^1(\sigma)$-bound to the other, with the four carbons of the ligand forming an approximate plane oriented such that C(1)–C(2) lies parallel to the Ru–Ru bond. The delocalisation of the trimethylenemethane is partly disrupted by the σ–π bonding, seen in the long C(1)–C(2) bond [1.460(7) Å] *cf.* C(2)–C(3) [1.406(7)] and C(2)–C(4) [1.433(8) Å]. A similar structure has been proposed, on spectroscopic grounds, for related complexes obtained from hydrocarbons containing a pre-formed C_4 skeleton.[2,3]

It is likely that, as for ethene, allene reacts with (**1**) to first displace MeCN, forming the transient η^2-allene complex (**2**) as shown in Scheme 1. No spectroscopic evidence for this species was obtained, suggesting that carbon–carbon bond formation occurs rapidly between the μ-CH_2 and the central carbon of the allene, followed by the co-ordination of the remaining allenic carbon to relieve electronic unsaturation at the diruthenium centre. In accord, the reaction of the μ-CD_2 analogue of (**1**) with allene gave (**3**) with CD_2 uniquely as the σ-bound group. The great difference in energy barriers between methylene–ethene and methylene–allene combinations at a dinuclear metal centre is undoubtedly attributable to the additional π-system associated with the central carbon of η^2-allene. In this connection, it is noteworthy that C–C bond formation occurs rapidly at room temperature when (**1**) reacts with alkynes, which also contain a second available π-system.[4]

The ^1H NMR spectrum of (**3**) at −60 °C shows six intense signals for the trimethylenemethane protons, indicating that the asymmetric solid state structure is retained in solution. On warming, however, the signals broaden and coalesce pair-wise to give three signals of equal intensity at +70 °C, consistent with the onset of a fluxional process (ΔG° = 56 kJ mol^{-1}) which interconverts the enantiomers (**3a**) and (**3b**) as shown in Scheme 1. This exchange of bridging and terminal CO ligands generates a time-averaged mirror plane, and consequently three proton environments. The expected intermediate (**3c**), with two semi-bridging carbonyls and an inherent mirror plane, is sufficiently stable to be detected both in the IR [ν(CO) at 1860 w, br. cm^{-1}] and ^1H NMR spectra [weak signals at δ 1.37 (s, 2H), 1.86 (s, 2H), and 3.20 (s, 2H) at −60 °C]. Interestingly, when the μ-$CH(CO_2Et)$ analogue of (**1**) is treated with allene to give $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}CH(CO_2Et)C(CH_2)_2\}(\eta\text{-}C_5H_5)_2]$, the isomer corresponding to (**3c**) is the major species in solution.

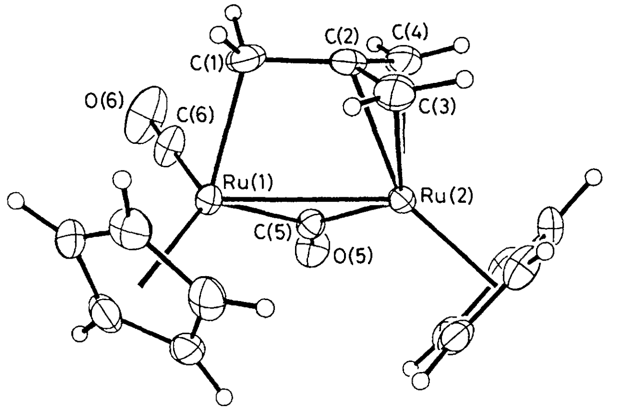

Figure 1. Molecular structure of (**3a**). Important bond lengths: Ru(1)–Ru(2) 2.818(1), Ru(1)–C(1) 2.154(5), Ru(1)–C(5) 2.052(4), Ru(1)–C(6) 1.833(4), Ru(2)–C(2) 2.183(5), Ru(2)–C(3) 2.204(5), Ru(2)–C(4) 2.186(5), Ru(2)–C(5) 1.996(4), C(1)–C(2) 1.460(7), C(2)–C(3) 1.406(7), C(2)–C(4) 1.433(8) Å; bond angles: C(1)–C(2)–C(3) 120.1(5), C(1)–C(2)–C(4) 122.8(5), C(3)–C(2)–C(4) 115.2(5)°.

Trimethylenemethane is known to rotate at a mononuclear metal centre, albeit with a high barrier.[5] The NMR data for (**3**) between −60 and +70 °C eliminate the possibility of a similar propellor-like rotation occurring on the NMR time scale for μ-trimethylenemethane, since the process would interchange the σ- and π-bound methylene groups and generate a single time-averaged proton environment. Moreover, the labelling study described above also rules it out on the chemical time scale. In an attempt to induce such a rotation, (**3**) was heated to >70 °C; instead, isomerisation to the μ-allylidene complex $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}\eta^1,\eta^3\text{-}CHC(Me)CH_2\}(\eta\text{-}C_5H_5)_2]$ (**4**)[6] occurred. In refluxing toluene the rearrangement is complete within 1 h, but it also occurs smoothly upon UV irradiation of (**3**) for *ca.* 17 h. Isomerisation of $[Ru_2(CO)(\mu\text{-}CO)\{(\mu\text{-}\eta^1,\eta^3\text{-}CD_2C(CH_2)_2\}(\eta\text{-}C_5H_5)_2]$ gave (**4**) with deuterium and proton scrambling among all the sites of the μ-allylidene, indicating a reversible 1,3-shift encompassing all three methylene groups. It appears that the process is initiated by heterolytic Ru–Ru bond cleavage, creating 18- and 16-electron centres, since when CO is bubbled through a refluxing toluene solution of (**3**) the η^3-allyl complex (**5**)† is formed quantitatively.

The μ-trimethylenemethane ligand is evidently prone to 1,3-hydrogen shift rearrangement. Thus, when (**3**) is protonated with HBF_4 in the presence of CO the product is $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CMe_2)(\eta\text{-}C_5H_5)_2]^+$ (**6**),† containing a μ-dimethylvinyl ligand. Hydride attack on (**6**) yields a 50 : 50 mixture of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCHMe_2)(\eta\text{-}C_5H_5)_2]$ and $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CMe_2)(\eta\text{-}C_5H_5)_2]$, completing the

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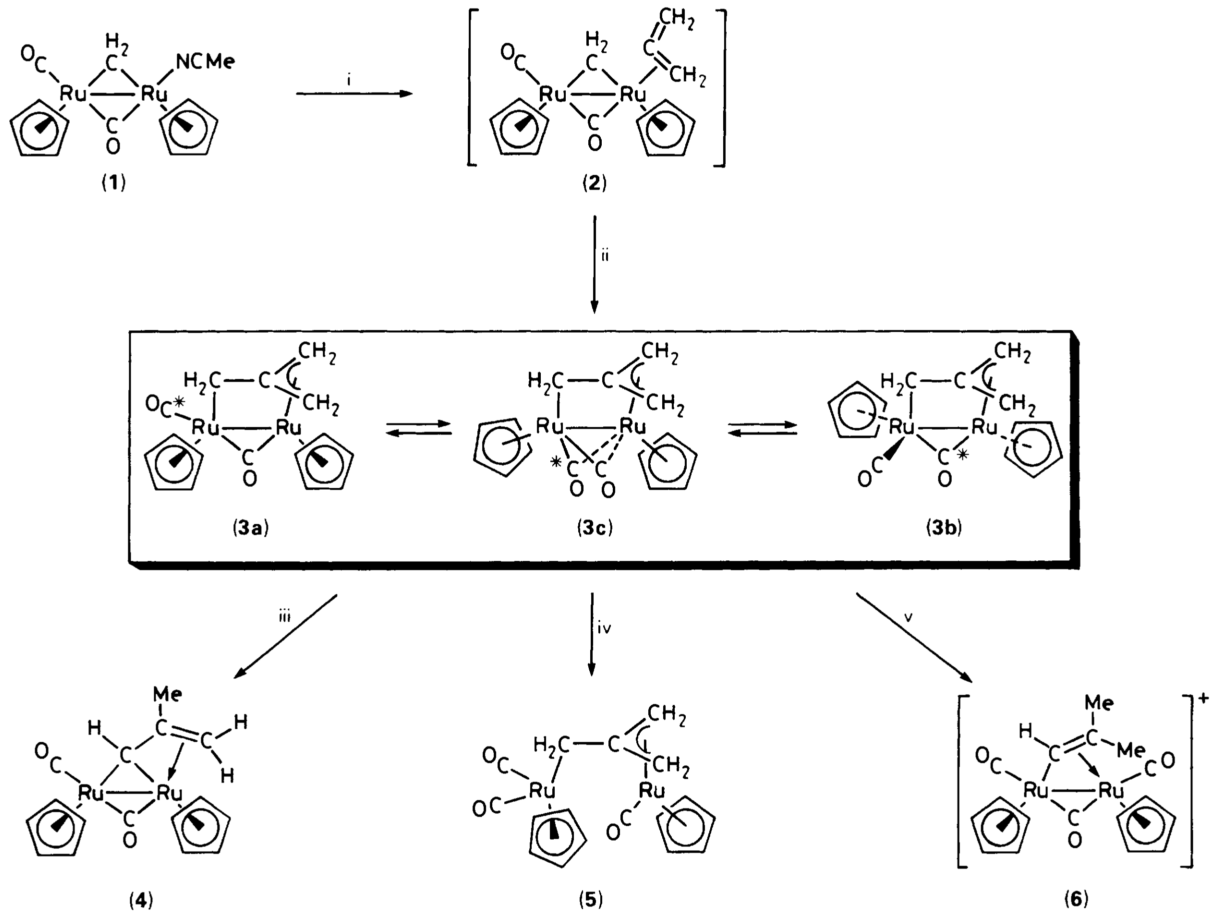
† The new complexes were identified by elemental analyses and by mass, IR, and NMR (^1H and ^{13}C) spectroscopy. *Selected data* (IR in CH_2Cl_2, NMR in CD_2Cl_2, coupling constants in Hz): (**3**) (red crystals): ν(CO) at 1965s and 1733m cm^{-1}; ^1H NMR (a) at −60 °C; δ 0.66 (dd, *J* 3.0, 6.4, 1H), 1.12 (d, *J* 2.8, 1H), 1.18 (d, *J* 2.4, 1H), 2.08 (dd, *J* 6.4, 2.4, 1H), 2.18 (d, *J* 2.8, 1H), 3.46 (d, *J* 3.0, 1H), 4.87 (s, 5H), and 5.06 (s, 5H), (b) at +70 °C (in C_6D_6); δ 1.61 (s,br., 2H), 1.72 (s, 2H), 2.70 (s, 2H), 4.52 (s, 5H), and 4.69 (s, 5H); $^{13}C\{^1H\}$ NMR (at −55 °C); δ 25.9 (σ-CH_2), 44.1 (η^3-CH_2), 47.1 (η^3-CH_2), 84.7 (C_5H_5), 85.6 (C_5H_5), 108.1 [$C(CH_2)_3$], 201.9 (CO), and 251.9 (μ-CO). (**5**) (colourless crystals): data for the major of two rotamers, ν(CO) (in hexane) at 2025s, 1969s, and 1949s cm^{-1}; ^1H NMR δ 1.22 (s, 2H), 2.30 (s, 2H), 2.90 (s, 2H), 5.05 (s, 5H), and 5.28 (s, 5H); $^{13}C\{^1H\}$ NMR (in CD_2Cl_2) δ 5.3 (σ-CH_2), 32.5 (η^3-CH_2), 83.6 (C_5H_5), 89.3 (C_5H_5), 121.0 [$C(CH_2)_3$], 202.4 (CO), and 203.1 (CO). (**6**) (yellow powder): ν(CO) at 2022s, 1996m, and 1864m cm^{-1}; ^1H NMR (fluxional molecule) δ 1.90 (s, 3H), 2.24 (s, 3H), 5.69 (s, 10H), 10.63 (s, 1H); $^{13}C\{^1H\}$ NMR δ 30.2 (Me), 37.6 (Me), 92.8 ($2C_5H_5$), 115.1 ($CHCMe_2$), and 156.8 ($CHCMe_2$).

‡ *Crystal data* for (**3a**): $C_{16}H_{16}O_2Ru_2$, *M* = 442.5, monoclinic, space group $P2_1/n$ (No. 14), *a* = 9.163(2), *b* = 13.867(3), *c* = 11.916(3) Å, β = 103.80(2)°, *U* = 1470.7(5) Å^3, *T* = 295 K, *Z* = 4, D_c = 2.00 g cm^{-1}, *F*(000) = 864, graphite-monochromated Mo-K_α *X*-radiation (λ = 0.71069 Å), μ(Mo-K_α) = 20.14 cm^{-1}. The structure was solved by heavy atom methods and refined by least squares to *R* = 0.027 for 2176 unique, observed [$I > 1.5\sigma(I)$], absorption-corrected intensities with $4 < 2\theta < 50°$, collected on a Nicolet P3m diffractometer. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1. *Reagents and conditions:* i, $CH_2=C=CH_2$; ii, C–C formation; iii, toluene, reflux or UV; iv, CO, toluene, reflux; v, H^+, CO.

unprecedented transformation of trimethylenemethane to μ-isobutylidene and μ-dimethylvinylidene.

We are grateful to the S.E.R.C. for the award of Research Studentships (to M. J. F., M. L. T., and M. I. Y.) and for support, to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work, and Johnson Matthey p.l.c. for a loan of ruthenium trichloride.

Received, 10th August 1989; Com. 9/03426I

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