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Preliminary communication

SEQUENTIAL CONVERSION OF ETHYNE INTO μ-VINYLIDENE, μ-METHYLCARBYNE AND μ-METHYLCARBENE AT A DI-RUTHENIUM CENTRE: X-RAY STRUCTURES OF $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ AND $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)(\eta\text{-}C_5H_5)_2][BF_4]$

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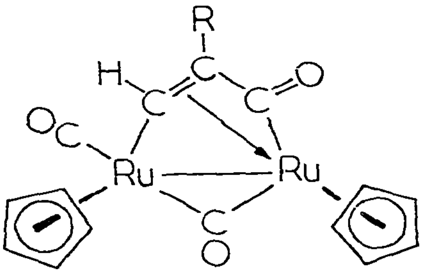
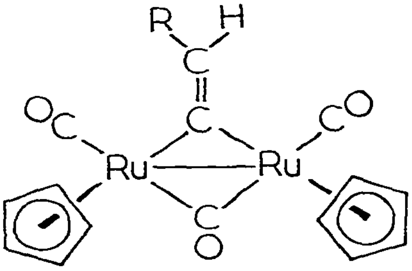
Summary. The ethyne-derived dimetallocycle $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2H_2\}(\eta\text{-}C_5H_5)_2$ isomerises in boiling toluene to yield the μ-vinylidene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$, which on protonation with dry HBF_4 provides the μ-carbyne complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)(\eta\text{-}C_5H_5)_2][BF_4]$; the structure of each product has been determined by X-ray diffraction. The μ-carbyne cation is attacked by hydride to produce the μ-methylcarbene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)(\eta\text{-}C_5H_5)_2]$.

In a recent article we described how ethyne may be converted to μ-methylcarbene or ethene at a di-iron or di-ruthenium centre [1]. The process involved protonation of the ethyne-derived dimetallocycle $[Ru_2(CO)(\mu\text{-}CO)\{\mu\text{-}C(O)C_2H_2\}(\eta\text{-}C_5H_5)_2]$ (Ia) or its iron analogue to form a μ-vinyl cation, followed by treatment with sodium borohydride. We have now discovered that (Ia), which at up to ca. 100 °C undergoes fluxional breaking and re-forming of the 'carbonyl-alkyne' carbon-carbon bond, suffers irreversible cleavage of that bond in boiling toluene



Ia, R=H
Ib, R=Ph



IIa, R=H
IIb, R=Ph

(111 °C). The result is an unprecedented isomerisation to yield the μ-vinylidene complexes *cis* (IIa)- and *trans*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$. Protonation of these latter yields the μ-methylcarbyne complex *cis*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)(\eta\text{-}C_5H_5)_2][BF_4]$ (IIIa), which in turn gives the μ-methylcarbene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)(\eta\text{-}C_5H_5)_2]$ [2] with $NaBH_4$. It has been suggested that ethyne on platinum [3,4] and nickel [5] surfaces converts to $CHCH_3$ or CCH_3 species, perhaps *via* a CCH_2 intermediate. This article describes an interesting parallel with this contention and comparative X-ray diffraction studies on (IIa) and (III).

Heating (Ia) in boiling toluene for 1 day provides the yellow crystalline vinylidene complexes *cis*(IIa)- and *trans*-$[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$* in 35 and 30 % yields respectively. The isomers are separable by chromatography but slowly convert in

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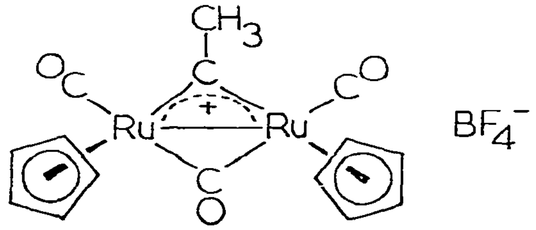
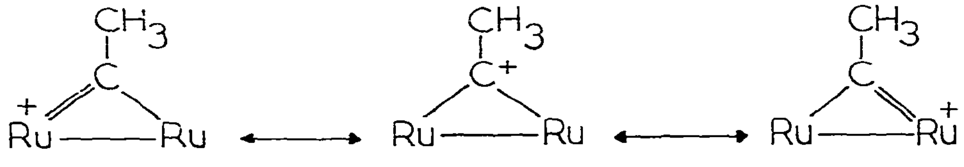
* (IIa): m.p. 178-180 °C; $\nu(CO)(CH_2Cl_2)$ 1 994s, 1 951m, 1 788m cm^{-1}; ^1H n.m.r. $(CDCl_3)$ δ 5.20 (s, 10H, 2 x C_5H_5), 6.27 (s, 2H, CH_2); ^{13}C n.m.r. (CD_2Cl_2) 249.1 ($\underline{C}CH_2$), 245.2(μ-CO), 199.6(2 x CO), 122.7(CH_2), 90.3(2 x C_5H_5) p.p.m.



III



IVa V IVb

solution at room temperature to give an equilibrium mixture of the two forms. A similar rearrangement occurs when (Ib), derived from phenylacetylene, is heated to produce (IIb). An insight into the mechanism of the process was obtained by thermolysis of deuteriated (Ib) (88 % D by mass spectrometry) prepared from PhC_2D. This gave (IIb) containing 74 % of deuterium in the vinylidene ligand, suggesting that the rearrangement is substantially intramolecular in character

Addition of <u>dry</u> HBF_4 in ether to a mixture of *cis*- and *trans*-[$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2$] provides the μ-carbyne complex *cis*-[$Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)(\eta\text{-}C_5H_5)_2$][$BF_4$] (III)[†] quantitatively.

[†] (III): m.p. 170-172 °C(decomp.); $\nu(CO)(CH_2Cl_2)$ 2 049s, 2 014m, 1 854m cm^{-1}; ^1H n.m.r. $(CD_2Cl_2)\delta 5.72$ (s, 10H, 2 x C_5H_5), 4.62 (s, 3H, CH_3); ^{13}C n.m.r. (CD_2Cl_2) 469.7 ($\underline{C}CH_3$), 227.1 (μ-CO), 195.8 (2 x CO), 94.1 (2 x C_5H_5), 68.2 (CH_3) p.p.m.

There has been a very brief report [6] of the iron analogue of (III), derived by sequential addition of methyllithium and HBF_4 to $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$, and recently a dimanganese μ-CCH_2 complex was acidified to give a μ-CCH_3 cation in solution, identified by n.m.r. spectroscopy [7]. Complex (III), which is readily obtained as stable yellow crystals, is surprisingly acidic; when a dichloromethane solution is shaken with water H^+ is lost rapidly and (IIa) is regenerated. However, when the μ-carbyne cation is treated with $NaBH_4$ the known μ-methylcarbene complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)(\eta\text{-}C_5H_5)_2]$ [1] is formed quantitatively, completing a sequence in which ethyne is converted, *via* the dimetallocycle (I), into μ-CCH_2 then μ-CCH_3 and finally μ-$CHCH_3$.

The availability of (IIa) and (III) presented an ideal opportunity for a comparative X-ray diffraction study of the important μ-CCH_2 and μ-CCH_3 ligands.

Crystal data. (IIa): $C_{13}H_{12}O_3Ru_2$, M 418.1, monoclinic, space group $P2_1/n$, a = 8.620(6), b = 15.712(9), c = 10.844(8) Å, β = 92.57(4)°, U = 1 467(1) $Å^3$, Z = 4, D_c = 1.893g cm^{-3}, $F(000)$ = 856, $\mu(Mo\text{-}K_\alpha)$ = 20.2 cm^{-1}. Current R 0.052 (R' 0.053) for 2 503 absorption-corrected, observed [$I > 2\sigma(I)$] intensities.

(III): $C_{13}H_{13}O_3BF_4Ru_2$, M 505.9, monoclinic, space group $P2_1/n$, a = 9.121(2), b = 9.724(3), c = 20.666(6) Å, β = 106.42(3)°, U = 1 758(1) $Å^3$, Z = 4, D_c = 1.911g cm^{-3}, $F(000)$ = 1 044, $\mu(Mo\text{-}K_\alpha)$ = 17.36 cm^{-1}. Current R 0.026(R' 0.029) for 3 019 absorption-corrected, observed [$I > 2.5\sigma(I)$] intensities.

Full quadrants of intensity data were collected at room temperature on a Syntex $P2_1$ diffractometer for $3 < 2\theta < 55°$ using $Mo\text{-}K_\alpha$ X-radiation (λ = 0.710 69 Å). The structures were solved and refined by conventional heavy atom Fourier and least squares techniques, all hydrogen atoms being located and incorporated in the final models.

The structures of (IIa) and the cation in (III) are shown in

Figures 1 and 2 respectively. The metal-metal distances are typical of singly bonded, bridged ruthenium atoms and differ only slightly [2.695(1) Å in (IIa); 2.714(1) Å in (III)]. There are more marked effects of protonation however. On passing from (IIa) to (III) the C(1)-C(2) bond length increases from 1.325(11) to 1.462(6) Å, to be expected of a bond order change from two to one, whereas the Ru-C(1) distances decrease from mean 2.029(7) to 1.937(4) Å and the Ru(1)-C(1)-Ru(2) angle consequently opens from 83.2(3) to 89.0(1)°. Carbon C(1) is almost perfectly trigonal in both (IIa) (Σ angles = 359.8°) and (III) (Σ angles = 359.6°), and the CH_2 group in (IIa) is

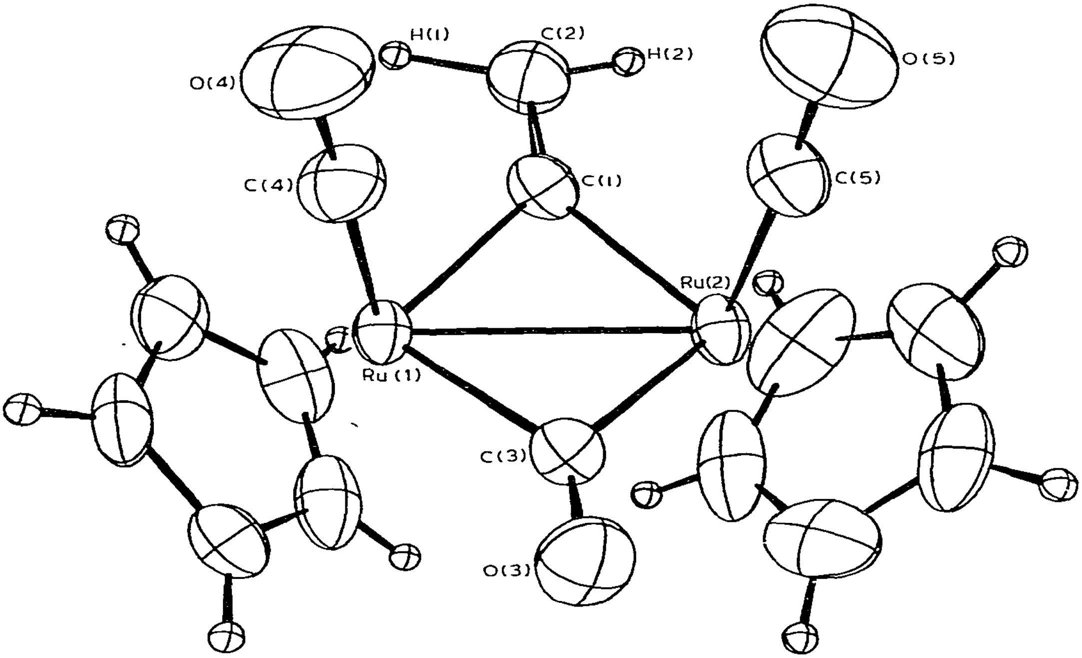


Figure 1. Molecular structure of $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2)(\eta\text{-}C_5H_5)_2]$ (IIa)
Bond lengths: Ru(1)-Ru(2) 2.695(1), Ru(1)-C(1) 2.033(7), Ru(1)-C(3) 2.036(7), Ru(1)-C(4) 1.847(8), Ru(2)-C(1) 2.025(7), Ru(2)-C(3) 2.047(7), Ru(2)-C(5) 1.839(7), C(1)-C(2) 1.325(11), C(3)-O(3) 1.172(8), C(4)-O(4) 1.136(10), C(5)-O(5) 1.155(9) Å.
Angles: Ru(1)-C(1)-Ru(2) 83.2(3), Ru(1)-C(3)-Ru(2) 82.6(2)°.

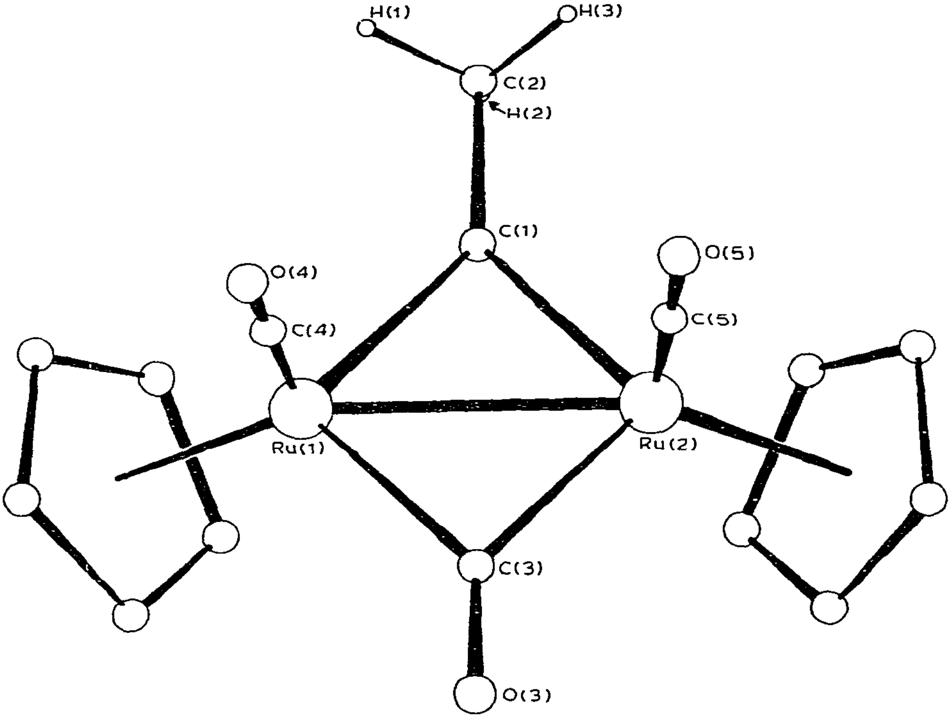


Figure 2. Structure of the cation in $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)(\eta\text{-}C_5H_5)_2][BF_4]$ (III)
Bond lengths: Ru(1)-Ru(2) 2.714(1), Ru(1)-C(1) 1.933(4), Ru(1)-C(3) 2.053(5), Ru(1)-C(4) 1.901(5), Ru(2)-C(1) 1.941(5), Ru(2)-C(3) 2.070(4), Ru(2)-C(5) 1.896(6), C(1)-C(2) 1.462(7), C(3)-O(3) 1.164(5), C(4)-O(4) 1.142(7), C(5)-O(5) 1.134(6) Å.
Angles: Ru(1)-C(1)-Ru(2) 89.0(2), Ru(1)-C(3)-Ru(2) 82.3(2)°.

co-planar (to within ca. 5°) with $C(1)Ru_2$. The angle [8] between the $C(1)Ru_2$ and $C(3)Ru_2$ planes decreases from 20.6° in (IIa) to 15.1° in (III). The Ru-CO distances in (III) are longer than those in (IIa), reflecting the lower π back-donation expected for the cation.

On the basis of the above data the structure of the µ-carbyne cation is probably best represented by (III), the hybrid of (IV) and (V), indicating both the symmetry of the molecule and the delocalisation of positive change to the metal atoms, resulting in the short Ru-C(1) bond lengths. The very low field ^{13}C n.m.r. shift (469.7 p.p.m.) of the bridging carbyne carbon suggests that the contribution from the carbonium ion (V) is substantial.

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