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Preliminary communication

THE μ_3-CYCLOPENTADIENYLIDENE LIGAND: X-RAY STRUCTURE OF $[Ru_4(CO)_5\{P(OMe)_3\}(\mu_3\text{-}C_5H_4)_2(\eta\text{-}C_5H_5)_2]$

NEIL D. FEASEY, NIGEL J. FORROW, GRAEME HOGARTH, SELBY A.R. KNOX, KIRSTY A. MACPHERSON, MICHAEL J. MORRIS, and A. GUY ORPEN
Department of Inorganic Chemistry, The University, Bristol BS8 1TS, (Great Britain)

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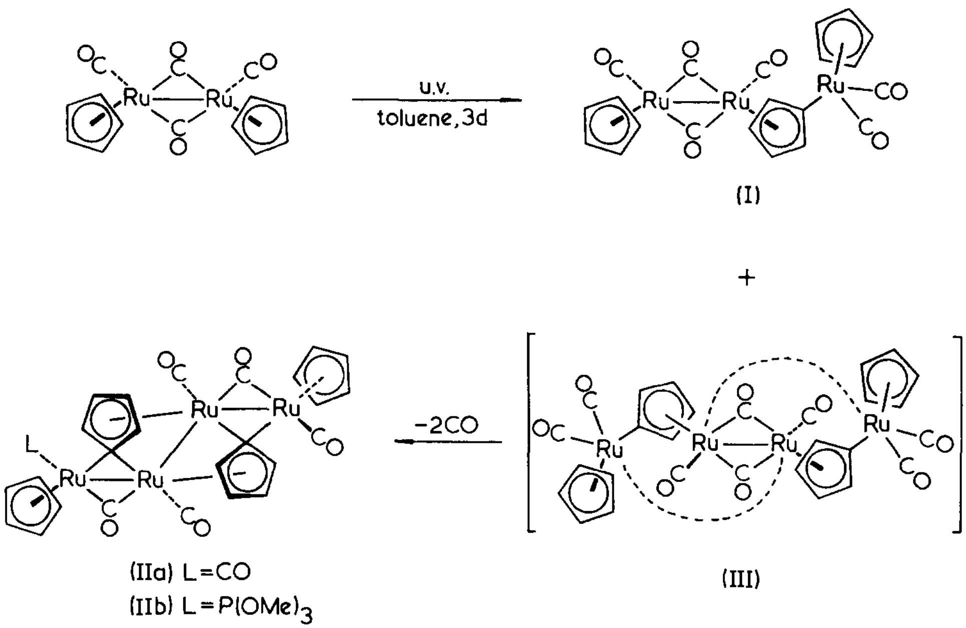
Summary

UV irradiation of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ yields the tri- and tetra-ruthenium complexes $[Ru_2(CO)_4(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4Ru(CO)_2(\eta\text{-}C_5H_5)\}]$ and $[Ru_4(CO)_6(\mu_3\text{-}C_5H_4)_2(\eta\text{-}C_5H_5)_2]$. The μ_3-C_5H_4 ligand in the latter has been characterised through an X-ray diffraction study on $[Ru_4(CO)_5\{P(OMe)_3\}(\mu_3\text{-}C_5H_4)_2(\eta\text{-}C_5H_5)_2]$.

It has been established that upon UV irradiation dimeric $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ undergoes Ru—Ru bond fission to generate $Ru(CO)_2(\eta\text{-}C_5H_5)$ radicals [1]. We now report that these radicals attack cyclopentadienyl rings and that after extended irradiation the major product is a tetraruthenium complex containing the cyclopentadienylidene ligand, observed for the first time bridging three transition metal atoms.

UV irradiation (250 W mercury lamp, silica flask) of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in toluene solution for 3 d gives $[Ru_2(CO)_4(\eta\text{-}C_5H_5)\{\eta\text{-}C_5H_4Ru(CO)_2(\eta\text{-}C_5H_5)\}]$ (I) (4%) and $[Ru_4(CO)_6(\mu_3\text{-}C_5H_4)_2(\eta\text{-}C_5H_5)_2]$ (IIa) (45%).

The former, which has been previously described [2] as a side-product of the photochemical reaction of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with diphenylacetylene, clearly results from $Ru(CO)_2(\eta\text{-}C_5H_5)$ radical attack upon one cyclopentadienyl ring of the diruthenium compound. Further attack on the second ring would lead to the unobserved complex (III) which, through loss of two CO ligands and Ru—Ru bond formation as indicated, can be seen as the precursor of the isolated product (IIa). This yellow, air-stable complex gave no crystals suitable for an X-ray diffraction study, but on treatment with trimethylphosphite under UV irradiation an orange mono-substituted derivative (IIb) was obtained which did yield such a crystal.



(I)

(IIa) L=CO
(IIb) L=P(OMe)$_3$

(III)

Crystal data: $C_{28}H_{27}O_8PRu_4$, M = 927, triclinic, space group $P\bar{1}$, a 12.557(4), b 15.818(4), c 8.294(2) Å, α 104.70(2), β 103.60(2), γ 105.95(2)°, U 1447.5(6) Å^3, Z = 2, D_x 2.13 g cm^{-3}, $F(000)$ = 900, Mo-K_α X-radiation, $\bar{\lambda}$ 0.710 69 Å, μ(Mo-K_α) 21.1 cm^{-1} ; R = 0.063 for 4678 unique, observed ($I > 2\sigma(I)$) absorption-corrected diffracted intensities, measured for $4 < 2\theta < 55°$ at 295 K on a Nicolet $P3m$ diffractometer.

The molecular geometry of IIb is illustrated in Fig. 1. The molecule has an Ru_4 chain which can be considered as two Ru_2 units joined by the central Ru(2)—Ru(3) bond, the longest of the three Ru—Ru bonds. The Ru(1)—Ru(2) and Ru(3)—Ru(4) bonds are bridged by carbonyl ligands, and each Ru atom carries a terminal CO or P(OMe)$_3$ ligand (Ru(1) only). The terminal Ru atoms each bear a conventional η^5-C_5H_5 ligand, but the other C_5 rings bind in a most unusual manner, bridging three ruthenium atoms η^5 to one and η^1 to each of the other two. Cyclopentadienylidene has been observed bound to $AlTi_2$ [3], Al_2Mo [4] and $FeAu_2$ [5] units, but not to three transition metal atoms. The triply-bridging carbons C(21) and C(31) show highly asymmetric Ru—C distances (see caption of Fig. 1) being more closely linked to the terminal atoms of the Ru_4 chain, and are also displaced out of the plane of their C_5 rings (by 0.11 and 0.06 Å, respectively) towards these atoms. The bonding of the C_5H_4 ligands is evidently highly delocalised and not satisfactorily described by any single Valence Bond representation, but that shown as IV clearly contributes significantly.

The ligands are disposed about the Ru(3)Ru(4) unit so that the terminal carbonyls are *trans*, and about Ru(1)Ru(2) so that the terminal CO and P(OMe)$_3$ ligands are *cis* to one another. If the same *cis—trans* situation arose in IIa then the η-C_5H_5 ligands would be inequivalent, and this is indeed the case, two signals of equal intensity being observed at δ 5.01 and 5.42 ppm

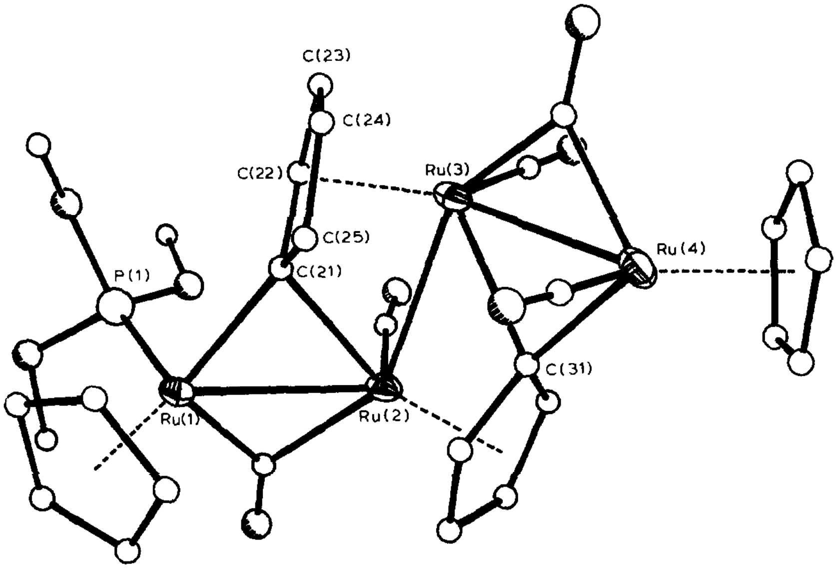
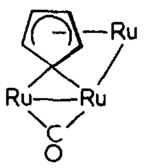
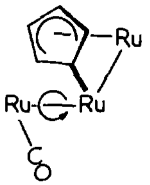


Fig. 1. Molecular structure of IIb. Selected bond lengths (Å): Ru(1)—Ru(2) 2.755(1), Ru(2)—Ru(3) 2.887(1), Ru(3)—Ru(4) 2.767(1), Ru(1)—P(1) 2.217(3), Ru(1)—C(21) 2.119(7), Ru(2)—C(21) 2.281(10), Ru(3)—C(21) 2.386(8), Ru(3)—C(22) 2.207(10), Ru(3)—C(23) 2.196(12), Ru(3)—C(24) 2.242(13), Ru(3)—C(25) 2.251(9), Ru(2)—C(31) 2.320(11), Ru(3)—C(31) 2.331(10), Ru(4)—C(31) 2.117(10). Bond angles (°): Ru(1)—Ru(2)—Ru(3) 101.7(1), Ru(2)—Ru(3)—Ru(4) 99.6(1), Ru(1)—C(21)—Ru(2) 77.4(3), Ru(2)—C(21)—Ru(3) 76.4(3), Ru(2)—C(31)—Ru(3) 76.8(3), Ru(3)—C(31)—Ru(4) 76.8(3).

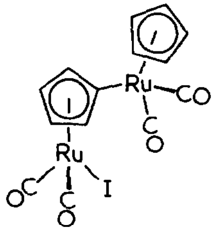
in the ^{1}H NMR spectrum. However, another isomer is present in greater amount (ca. 2.5/1 in $CDCl_3$ at 30°C), and this displays a single η-C_5H_5 resonance at δ 5.41 ppm, as expected when both Ru_2 units have the same stereochemistry. This is so for either the *cis-cis* or the *trans-trans* isomer, but inspection of a molecular model indicates that on steric grounds the *trans-trans* form is the most favoured of the three possible isomers, and it therefore appears likely that it is this species which is also present in solution. For the *trans-trans* symmetrical isomer the ^{1}H NMR spectrum shows the μ_3-C_5H_4 signals as multiplets at δ 2.42 (2 H), 4.92 (2 H), 5.19 (2 H), and 5.97 (2 H) ppm, while the ^{13}C NMR spectrum reveals alkylidene character in the μ_3-carbon, emphasised by the representation IV, in its low field shift of 122.1 ppm.



(IV)



(V)



(VI)

The isomers of IIa may be partially separated by chromatography, but interconvert slowly on heating such that at 60°C in pyridine-d_5 the *trans-trans/cis-trans* ratio is reversed to reach ca. 1/2. In accord with an earlier study [6] of the *cis*$\rightleftharpoons$*trans* isomerisation of μ-alkylidene complexes $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CR_2)(\eta\text{-}C_5H_5)_2]$, the interconversion of the isomers of IIa requires that the μ-CO and μ_3-C_5H_4 ligands temporarily adopt the situation shown in V, thereby allowing rotation about an exterior Ru—Ru bond to exchange the terminal CO and η-C_5H_5 environments. Such bridging of a dimetal centre by C_5H_4 has been observed [7].

Complex IIa does not convert to III even under 50 atm of CO at 125°C, but reacts with hydrogen under UV irradiation to yield $[Ru_3(CO)_3(\mu\text{-}H)_3(\eta\text{-}C_5H_5)_3]$ (18%) [8]. Ruthenium—ruthenium bonds in IIa are cleaved by iodine in chloroform to afford $[RuI(CO)_2\{\eta\text{-}C_5H_4Ru(CO)_2(\eta\text{-}C_5H_5)\}]$ VI in good yield.

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