A Trigonal Bipyramidal Pentaruthenium Cluster, $[Ru_5(CO)_3(\mu_3\text{-}CO)_3(\eta\text{-}C_5H_5)_4]$ *

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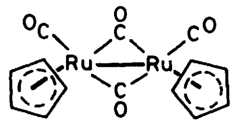
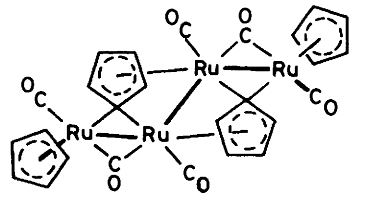
Heating $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ in boiling decalin gives $[Ru_5(CO)_3(\mu_3\text{-}CO)_3(\eta\text{-}C_5H_5)_4]$, containing the first trigonal bipyramidal cluster of ruthenium atoms.

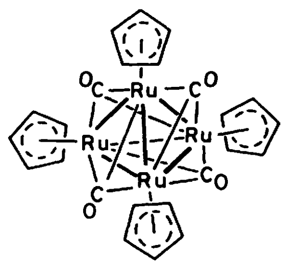
We have observed that prolonged photolysis of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (1) results in the formation of $[Ru_4(CO)_4(\mu\text{-}CO)_2(\mu_3\text{-}C_5H_4)_2(\eta\text{-}C_5H_5)_2]$ (2), containing a linear tetraruthenium skeleton.[1] Thermolysis of (1) in xylene (b.p. 140 °C), on the other hand, has been found to give a low yield of tetrahedrally based $[Ru_4(\mu_3\text{-}CO)_4(\eta\text{-}C_5H_5)_4]$ (3) and a trace of tentatively identified square-pyramidal $[Ru_5(CO)_3(\mu\text{-}CO)_4(\eta\text{-}C_5H_5)_4]$ (4).[2] We now report that heating compound (1) at a higher temperature in decalin (decahydronaphthalene) (b.p. 190 °C) affords the cluster complex $[Ru_5(CO)_3(\mu_3\text{-}CO)_3(\eta\text{-}C_5H_5)_4]$ (5), containing an unprecedented trigonal-bipyramidal arrangement of ruthenium atoms.



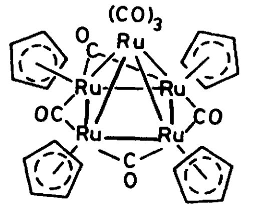
(1)



(2)



(3)



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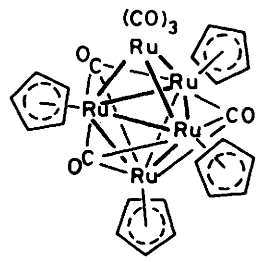

(5)

Results and Discussion

Heating a yellow decalin solution of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (1) at reflux for 48 h caused a colour change to dark red. Subsequent column chromatography produced three easily separable bands, the first of which contained unchanged (1). The second band was due to the new compound $[Ru_5(CO)_3(\mu_3\text{-}CO)_3(\eta\text{-}C_5H_5)_4]$ (5), isolated as a brown air-stable solid in 17% yield. The third band gave (14%) the dark red-purple tetramer (3). The latter was originally characterised by i.r and mass spectra and microanalysis;[2] a more complete spectroscopic characterisation is included in the Experimental section.

The presence of five ruthenium atoms in the new compound is indicated by elemental analyses and by the mass spectrum, which displays a heaviest ion with a characteristic Ru_5 isotope pattern centred on m/z 851, corresponding to $[Ru_5(CO)_3(\eta\text{-}C_5H_5)_4]^+$, *i.e.* $[M - 3CO]^+$. Ready loss of the three terminal carbonyl groups in (5) would not be unexpected.

The spectroscopic properties of (5) clearly show that the molecule has effective C_{3v} symmetry, consistent only with the ruthenium atoms forming a trigonal bipyramid. Thus, a single 'axial' and three 'equatorial' cyclopentadienyl ligands are seen in the ^1H n.m.r. spectrum as singlets at δ 5.38 and 5.06, integrating in the required 1:3 ratio. Moreover, the i.r. spectrum exhibits at 2 020 and 1 939 cm^{-1} the two active carbonyl stretching frequencies ($A_1 + E$) expected for an 'axial' $Ru(CO)_3$ group under the C_{3v} regime. The face-bridging μ_3-CO ligands provide an absorption at 1 628 cm^{-1}, similar to that of 1 634 cm^{-1} for (3). The ^{13}C n.m.r. spectrum echoes the above observations in showing two cyclopentadienyl signals [δ 90.2 (3 C_5H_5) and 96.5 (C_5H_5)] and two carbonyl signals [δ 249.4 (μ_3-CO) and 194.0 (CO) p.p.m.]. Electron-counting and symmetry considerations place the three μ_3-CO ligands on the three $Ru_3(\eta\text{-}C_5H_5)_3$ faces of the trigonal bipyramid, an arrangement strongly supported by the almost identical ^{13}C shifts of the μ_3-CO ligands in (3) and (5) (δ 248.7 and 249.4 p.p.m. respectively).

Attempts to confirm the molecular structure of compound (5) by *X*-ray diffraction failed. Crystals grown from dichloromethane–hexane had a high level of disorder which, together with other crystallographic problems, prevented the successful solution and refinement of the structure, but ruthenium atom positions within the unit cell were consistent with the trigonal-bipyramidal formulation.[3] No suitable crystals could be obtained from a variety of other solvents and attempts to prepare a phosphine-substituted derivative for a structural investigation were unsuccessful.

As a 72-electron cluster with five skeletal metal atoms, the trigonal-bipyramidal *closo* structure of (5) is in agreement with Wade's rules.[4] The compounds $[Os_5(CO)_{16}]^5$ and $[Os_5H_2$-

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* 1,2,3;1,2,4;1,3,4-Tri-μ_3-carbonyl-5,5,5-tricarbonyl-1,2,3,4-tetra(η-cyclopentadienyl)-*cyclo*-pentaruthenium (9 *Ru–Ru*).

Non-S.I. unit employed: atm = 101 325 Pa.

$(CO)_{15}]$,[6] together with anions derived from the latter, are the only other homonuclear examples of clusters with this electron count and geometry. Complex (**5**) is unique among pentaruthenium clusters in that those previously characterised have all contained more open geometries (*e.g.* square pyramid, bridged butterfly, or fused triangles) stabilised by a variety of multicentre bridging ligands. These include carbide in $[Ru_5(\mu_5\text{-}C)(CO)_{15}]$ and its derivatives,[7] phosphide in $[Ru_5(CO)_{16}(\mu\text{-}PPh_2)(\mu_5\text{-}P)]$,[8] isocyanide in $[Ru_5(CO)_{15}(\mu_5\text{-}CNBu^t)(CNBu^t)]$,[9] phosphinidenes,[10,11] and acetylides.[11,12]

The clusters (**3**) and (**5**) are closely related. Each contains a tetrahedron of cyclopentadienylruthenium units with three faces bridged by μ_3-CO ligands; in (**3**) the fourth face also bears a carbonyl whereas in (**5**) it is capped by an $Ru(CO)_3$ group. This view emphasises the isolobal[13] relationship between μ_3-CO and the $Ru(CO)_3$ moiety. It also raises the intriguing, but as yet unrealised possibility of obtaining Ru_6, Ru_7, and Ru_8 clusters through further $Ru(CO)_3$-capping of the $Ru_4(\eta\text{-}C_5H_5)_4$ unit.

The formation of compound (**5**) involves an unusual, but not unknown[14] loss of a cyclopentadienyl ligand from one metal atom and is obscure. Despite the structural relationship between (**3**) and (**5**) it is unlikely that the former is an intermediate since the complex is very unreactive; it survives heating to 600 °C and treatment with CO (100 atm, 100 °C), H_2 (150 atm, 100 °C), KOH, or methyl-lithium. Heating (**3**) with $[Ru_3(CO)_{12}]$ in decalin did not yield (**5**) (or any higher nuclearity cluster) through exchange of μ_3-CO for 'μ_3-$Ru(CO)_3$'. Neither did addition of $[Ru_3(CO)_{12}]$ to a boiling decalin solution of (**1**) result in any increase in the yield of (**5**).

In the earlier work on the thermolysis of compound (**1**) a trace of an unstable *green* compound was isolated and tentatively characterised as $[Ru_5(CO)_3(\mu\text{-}CO)_4(\eta\text{-}C_5H_5)_4]$ (**4**) on the basis of i.r. and mass spectral data.[2] This compound was not observed during the present work, but loss of one CO could induce rearrangement of the metal-atom skeleton to produce (**5**). Interestingly, the solid formed upon decomposition of (**4**) was reported to be brown, like (**5**), but no further details were given.

Experimental

General techniques and instrumentation were as described in a recent paper from this Laboratory;[15] in addition, a Nicolet 5-MX Fourier-transform spectrometer was used to record the i.r. spectra. The complex $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ was prepared by a modification[16] of the literature method.[17] Decalin was degassed by bubbling nitrogen through it but was not distilled.

Preparation of $[Ru_5(CO)_3(\mu_3\text{-}CO)_3(\eta\text{-}C_5H_5)_4]$ (**5**).—A solution of $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (0.25 g, 0.56 mmol) in decalin (150 cm^3) was heated at reflux for 48 h, the colour changing to dark red. The decalin was removed by vacuum distillation while the solution was still hot. The residue was dissolved in dichloromethane and subjected to chromatography on an alumina column. Elution with dichloromethane–hexane (1:1) gave a yellow band of unreacted starting material (0.097 g, 39% recovery). Elution with dichloromethane–acetone (9:1) then developed a brown band which yielded $[Ru_5(CO)_3(\mu_3\text{-}CO)_3(\eta\text{-}C_5H_5)_4]$ (**5**) (0.035 g, 17%), m.p. > 250 °C (Found: C, 33.7; H, 2.4. $C_{26}H_{20}O_6Ru_5$ requires C, 33.4; H, 2.1%); ν(CO) (in CH_2Cl_2) 2 020, 1 939, and 1 628 cm^{-1}. N.m.r.: ^1H (in $CDCl_3$), δ 5.06 (s, 15 H) and 5.38 (s, 5 H); ^{13}C (in CH_2Cl_2–CD_2Cl_2), δ 90.2 (3 C_5H_5), 96.5 (C_5H_5), 194.0 (CO), and 249.4 (μ_3-CO) p.p.m. Mass spectrum: *m/z* 851 $[M - 3CO]^+$.

Further elution with dichloromethane–acetone (4:1) provided the dark red-purple complex $[Ru_4(\mu_3\text{-}CO)_4(\eta\text{-}C_5H_5)_4]$ (**3**) (0.030 g, 14%), m.p. > 250 °C (Found C, 37.4; H, 2.6. $C_{24}H_{20}O_4Ru_4$ requires C, 37.0; H, 2.6%); ν(CO) (in CH_2Cl_2) 1 634 cm^{-1}. N.m.r.: ^1H (in $CDCl_3$), δ 5.23 (s); ^{13}C (in CH_2Cl_2–CD_2Cl_2), δ 97.6 (C_5H_5) and 248.7 (μ_3-CO) p.p.m. Mass spectrum: *m/z* 778 (M^+).

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