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Solution and crystal structures of the hydridoruthenium raft clusters $H_2Ru_6(CO)_{15}(L)(C_6H_4O)$ (L = CO, $P(OMe)_3$)

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Abstract

The structures of $H_2Ru_6(CO)_{15}(L)(C_6H_4O)$ (L = CO, $P(OMe)_3$) in solution (as indicated by ^1H NMR studies) and in the solid state (as indicated by X-ray studies) are discussed. The two-dimensional COSEY spectrum of the unsubstituted cluster shows the presence of two isomers in solution, whereas in the solid state only one form is present. There is no evidence for more than one isomer for the phosphite-substituted cluster in solution or in the solid state. Long-range $^{31}P-^{1}H$ coupling differentiates between the ^1H NMR signals of the doubly- and triply-bridging hydrides. Reactions of $Ru_3(CO)_{12}$ with *para*-substituted phenols XC_6H_4OH ($X = NO_2$, NH_2) are also reported.

Introduction

During studies on homogeneous reactions catalysed by $Ru_3(CO)_{12}$ (**1**), we investigated the reactions of **1** with substrates such as phenol, nitrobenzene and aniline [1,2]. The first reaction yielded the hydridoruthenium raft cluster $H_2Ru_6(CO)_{16}(C_6H_4O)$ (**2**), and this was characterised fully by a single crystal X-ray diffraction study [2]. With nitrobenzene and aniline, imido and amido clusters of the type $Ru_3(CO)_{10}(NPh)$ (**3**), $HRu_3(CO)_{10}(NHPh)$ (**4**) and $H_2Ru_3(CO)_9(NPh)$ (**5**) have been isolated [3,4]. The present study had two objectives. First, in the case of **2** we wished to assign unambiguously the ^1H NMR signals from the two hydrides, one doubly- and one triply-bridging, and so a ligand-substituted derivative of **2**, $H_2Ru_6(CO)_{15}[P(OMe)_3](C_6H_4O)$ (**6**) was synthesised; its crystal structure and ^1H NMR spectrum were determined to permit this assignment. Secondly, we wished to investigate the reactions of **1** with bifunctional aromatic compounds such as 4-nitrophenol and 4-aminophenol, for which there is the possibility that both the functional groups might interact with the metal framework.

Results and discussion

(a) NMR spectra of 2 and 6

The ^1H NMR spectrum of the parent cluster (**2**) shows four strong signals of 0–10 ppm with chemical shifts of 6.93–3.64 ppm, and two Ru–H signals, at −11.79 and −21.86 ppm. Substantial differences in the electronic environments of the ring protons are indicated by the observed range of chemical shifts. More interestingly, the NMR spectrum also indicates the presence of a small amount of a second isomer; weak but clear signals are associated with all the ring protons and the metal hydrides. The chemical shifts of the four phenyl protons and the high field Ru–H signals of the two isomers are very close (within 0.1–0.2 ppm) to each other. However, the low field Ru–H signals (ca. −12 ppm) for the two isomers are separated from each other by 1.06 ppm (See Experimental section). The concentration of the minor isomer as judged form the intensity measurements varies between 10–15%.

The similarities in chemical shifts and coupling patterns probably indicate a change in the relative orientation of the OC_6H_4 moiety or the metal hydrides rather than a different skeletal arrangement. In view of the relatively large separations in the chemical shifts between the low field hydrides of the two isomers, it is possible that a difference in the position of these hydrides causes the isomerism. Variable temperature NMR studies (+50 to −50 °C) revealed very little change in the concentrations of the two isomers, indicating that over this temperature range they are not in equilibrium.

To confirm that the two spin systems observed in the NMR are in fact independent of each other, two dimensional-COSEY experiments were carried out. It was found that all the prominent cross-peaks are associated with cross-peaks assignable to the minor isomer. On the basis of the 2D-spectrum the chemical shifts can also be unambiguously assigned to the four ring protons. There is no evidence, however, for the presence of two isomers of **2** in the *solid state*. This is probably because crystal packing forces favour one isomer.

The NMR spectrum of **6**, unlike that of **2**, shows the presence of only one isomer. The chemical shifts of the ring protons and the high field Ru–H signal are close to those of **2**. The other Ru–H signal shows an upfield shift of 1.60 ppm and a coupling of 14 Hz, which we attribute to a long range interaction with the phosphorus atom. The X-ray structure of **6** (see below) shows that the doubly bridging hydrogen atom is considerably (2.8 Å) closer to the phosphorus atom than the μ_3-hydride. The coupled Ru–H signal at −13.39 ppm for **6** and the signal at −11.79 ppm for **2** are therefore assigned to the μ_2-hydrides.

(b) X-ray structure of 6

The atomic coordinates of **6** are given in Table 1. Selected bond lengths and angles are given in the legend to Fig. 1. The structures of **2** and **6** are very similar (Fig. 1). The six ruthenium atoms in both the clusters adopt a raft configuration of the type previously observed for some osmium clusters and an Fe–Pt mixed cluster [5–7]. A ruthenium anionic cluster, $[HRu_6(O{=}CNMe_2)_2(CO)_{18}]^-$ (**7**), containing a cyclic array of six ruthenium atoms has been reported [8], but the absence of transannular Ru–Ru linkages rules out the description of the metal core as a raft. The average metal–metal distances of the inner triangles in the clusters

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq}
Ru(1)	2936.6(4)	6910.4(2)	1986.9(2)	49(1)
Ru(2)	5970.4(4)	7415.8(2)	2355.6(2)	42(1)
Ru(3)	4983.1(4)	6070.9(2)	2822.4(2)	42(1)
Ru(4)	5656.6(3)	8310.3(2)	3472.5(2)	41(1)
Ru(5)	6534.2(3)	6922.6(2)	3940.5(2)	35(1)
Ru(6)	6846.9(4)	5548.0(2)	3933.9(2)	47(1)
H(1)	6565(51)	6664(25)	2964(28)	84(16)
H(2)	5828(53)	7749(24)	4115(27)	80(16)
C(11)	2344(7)	6066(3)	1652(3)	82(2)
O(11)	1926(6)	5579(2)	1414(3)	124(2)
C(12)	3552(6)	6989(3)	1097(3)	69(2)
O(12)	3877(5)	7003(3)	538(2)	105(2)
C(21)	5660(5)	8021(3)	1592(3)	65(2)
O(21)	5510(5)	8379(3)	1124(2)	106(2)
C(22)	7165(5)	6948(3)	1830(3)	60(2)
O(22)	7928(4)	6674(2)	1517(2)	89(2)
C(31)	5714(6)	5620(3)	2119(3)	67(2)
O(31)	6198(5)	5332(2)	1687(3)	110(2)
C(32)	3868(5)	5339(3)	2916(3)	62(2)
O(32)	3193(5)	4875(2)	2983(3)	96(2)
C(41)	5258(6)	9066(2)	2868(3)	65(2)
O(41)	5068(5)	9527(2)	2525(3)	111(2)
C(42)	7119(5)	8790(2)	4070(3)	56(2)
O(42)	7985(4)	9074(2)	4410(3)	86(2)
C(43)	7380(5)	8029(2)	2877(2)	48(2)
O(43)	8546(3)	8205(2)	2879(2)	70(1)
C(51)	8476(5)	7053(2)	4092(2)	51(2)
O(51)	9685(4)	7141(2)	4182(2)	82(2)
C(52)	6620(5)	6805(2)	4916(2)	51(2)
O(52)	6691(5)	6722(2)	5518(2)	80(2)
C(61)	6630(6)	4619(3)	3693(3)	72(2)
O(61)	6464(6)	4078(2)	3564(3)	111(2)
C(62)	8121(6)	5431(3)	4810(3)	69(2)
O(62)	8833(5)	5354(3)	5339(3)	106(2)
C(63)	8311(6)	5735(2)	3352(3)	63(2)
O(63)	9173(5)	5847(2)	3004(3)	87(2)
C(64)	5160(6)	5595(2)	4401(3)	54(2)
O(64)	4167(4)	5625(2)	4667(2)	77(2)
P	3894(1)	8592.2(6)	4139.2(8)	56(1)
C(71)	1219(7)	9040(4)	3730(5)	124(4)
O(71)	2658(4)	8991(2)	3652(3)	95(2)
C(72)	3625(7)	9413(3)	5218(3)	93(3)
O(72)	4463(4)	9080(2)	4752(2)	80(2)
C(73)	3402(9)	7606(4)	4985(3)	117(4)
O(73)	2937(5)	8069(2)	4427(3)	101(2)
C(81)	3463(4)	7103(2)	3209(2)	39(1)
C(82)	2041(4)	6887(2)	3031(2)	49(2)
C(83)	1063(5)	7226(3)	2539(3)	60(2)
C(84)	1495(5)	7784(3)	2196(3)	59(2)
C(85)	2914(5)	7993(2)	2366(2)	50(2)
C(86)	3960(4)	7705(2)	2895(2)	39(1)
O(81)	4318(3)	6707(1)	3647(1)	37(1)

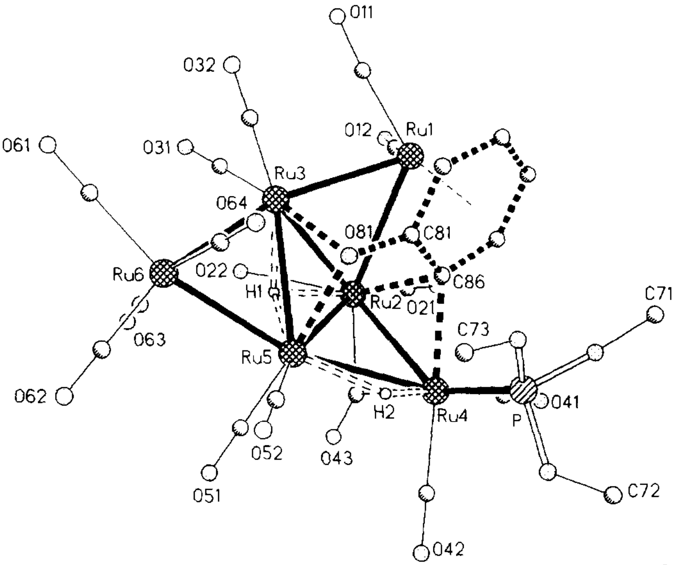


Fig. 1. The molecule of **6** in the crystal (perspective view, radii arbitary). Selected bond lengths (Å): Ru(1)–Ru(2) 3.042, Ru(1)–Ru(3) 2.876, Ru(2)–Ru(3) 3.041, Ru(2)–Ru(4) 2.827, Ru(2)–Ru(5) 3.134, Ru(3)–Ru(5) 2.952, Ru(3)–Ru(6) 2.759, Ru(4)–Ru(5) 3.016, Ru(5)–Ru(6) 2.788 (all ±0.001), Ru(2)–C(86) 2.362(4), Ru(4)–C(86) 2.187(4), Ru(4)–P 2.306(1), Ru(3)–O(81) 2.182(3), Ru(5)–O(81) 2.143(2), Ru(4)–C(43) 2.190(5), C(81)–O(81) 1.338(4).

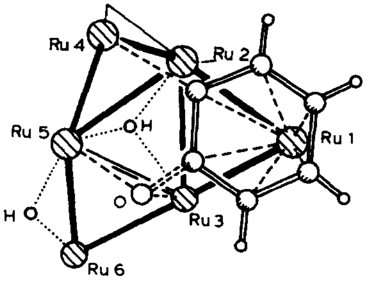
$Os_6(CO)_{17}[P(OMe)_3]_4$ and **2**, **6**, and **7** are 2.842(2), 3.018(2), 3.042(1) and 3.227(2) Å, respectively [6,8].

Based on the reasonable assumption that OC_6H_4 and $O{=}CNMe_2$ moieties donate 10 and 5 valence electrons, the total numbers of valence electrons in the four clusters are 90, 92, 92, and 96, respectively.

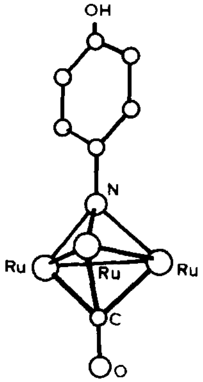
In both **2** and **6** the lengthening of the Ru–Ru distances of the inner triangle must be partly due to the presence of the triply bridging hydride and occupancy of the low-lying antibonding molecular orbital shown to be present by Evans and Mingos in 90-electron raft systems [9]. The hydride positions in **6** are consistent with potential energy calculations [10].

As previously mentioned, the ^1H NMR spectrum of **6** reveals a long range interaction between the phosphorus atom of the $P(OMe)_3$ group and one of the two hydrides. This is also seen in the solid state; the P–H(1) and P–H(2) distances are 5.3 and 2.51 Å, respectively. The doubly bridging hydride is sufficiently close to the phosphorus atom to show through-space coupling. The ligand substitution has very little effect on the rest of the structure.

The substitution of a carbonyl ligand at Ru(4) and not at any other ruthenium centres needs comment. The unique carbonyl that bridges Ru(4) and Ru(2) in cluster **2** has a rather long average Ru–C distance of 2.06(3) Å compared with Ru–C distances for the terminal carbonyl groups, which range from 1.846–1.956 Å. It is possible that this bridging carbonyl ligand is especially labile towards substitution and that the incoming $P(OMe)_3$ appraoches Ru(4) rather than Ru(2) to minimize steric crowding. Subsequently a carbonyl group of **2** adopts a bridging position between Ru(2)–Ru(4) as can be seen in **6** (atoms C(43) and O(43)).



(2)



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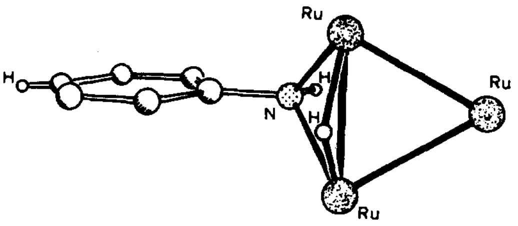

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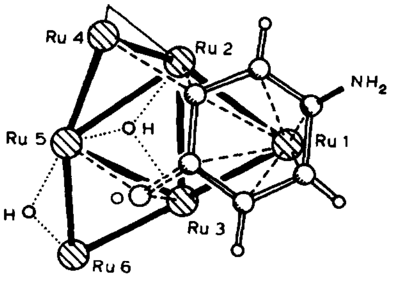

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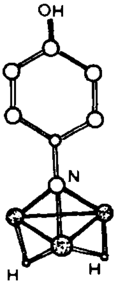

(11)

Proposed structures of **8–11**, terminal CO groups not shown for clarity

The carbonylation behaviours of **2** and **6** are different. Whereas **2** reacts with CO under ambient conditions to give **1** quantitatively, **6** resists carbonylation even at high pressures and temperatures.

(c) Reactions of 1 with p-*XC_6H_4OH ($X = NO_2$, NH_2)*

From the reactions of **1** with 4-nitrophenol and 4-aminophenol, imido and amido clusters $Ru_3(CO)_{10}(NC_6H_4OH)$ (**8**) and $HRu_3(CO)_{10}(HNC_6H_4OH)$ (**9**) were isolated. The reaction with 4-aminophenol also yields a cluster formulated as

$H_2Ru_6(CO)_{16}(p\text{-}NH_2C_6H_3O)$ (**10**). The conversion of **4** into **5** on heating is known [4]. Similarly upon heating **9** is decarbonylated to give **11**. All the complexes **8–11** have been characterised on the basis of their microanalytical and spectroscopic data. The spectral similarities of **8–11** with **3**, **4**, **2** and **5**, respectively, suggest analogous structures [3,4].

Experimental

X-Ray structure determination of compound 6

Crystal data. $C_{24}H_{15}O_{19}PRu_6$, $M_r = 1244.8$, monoclinic, space group $P2_1/n$, $a = 9.496(4)$, $b = 20.164(8)$, $c = 18.929(8)$ Å, $\beta = 98.16(3)°$, $U = 3588$ Å^3, $Z = 4$, $D_x = 2.30$ Mg m^{-3}, $F(000) = 2360$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu = 2.5$ mm^{-1}, $T = 293$ K.

Data collection and reduction. A red-brown prism 0.8 × 0.4 × 0.25 mm was mounted on a glass fibre. 10694 intensities were measured to $2\theta_{max}$ 50° on a Siemens *R*3 diffractometer using monochromated Mo-K_α radiation. An absorption correction based on ψ-scans was applied, with transmission factors 0.68–0.94. Merging equivalents gave 6326 unique reflections (R_{int} 0.024), of which 5304 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL PLUS). Cell constants were refined from setting angles of 50 reflections in the 2θ range 20–24°.

Structure solution and refinement. The Ru atoms were located by direct method and other atoms (including all H atoms) in subsequent difference syntheses. Cluster H (H(1) and H(2)) atoms were refined freely and other H atoms using a riding model. Anisotropic full-matrix refinement on *F* proceeded to *R* 0.026, R_w 0.030 for 459 parameters. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00015F^2$. *S* 1.4; max. Δ/σ 0.01; max. $\Delta\rho$ 1 e Å^{-3}.

Further details of the structure determinations (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft fur Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD 55173.

General comments. All manipulations were carried out under dry nitrogen by use of standard Schlenk and syringe techniques, unless otherwise stated. Solvents were distilled from appropriate drying agents before use. $Ru_3(CO)_{12}$ was synthesised by a published procedure [11]. Infra-red and NMR spectra were recorded on a PE 781 and Bruker 80 and 500 MHz Fourier-Transform instruments. A Carlo–Erba 1106 instrument was used for microanalysis.

Synthesis of 2

A solution of $Ru_3(CO)_{12}$ (32 mg, 0.05 mmol) and phenol (48 mg, 0.5 mmol) in cyclohexane (50 ml) was kept at 80 °C for 16 h. After removal of cyclohexane, the residue was subjected to column chromatography. On elution with hexane a mixture of $H_4Ru_4(CO)_{12}$ (7 mg, 20%), $H_2Ru_4(CO)_{13}$ (7 mg, 20%) was obtained. Subsequent elution with dichloromethane-hexane (1 : 2) gave a dark purple fraction of **2** (14 mg, 40%).

IR ($\nu_{(CO)}$, cyclohexane): 2114m, 2102w, 2076s, 2048s, 2026s, 2018s,sh, 2000w, 2973m, 2952w, 1813m cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.93 (t); 6.12 (t); 4.26 (d); 3.64

(d); −11.79; −21.86 (Ru–H). ^{13}C {^1H} NMR ($CDCl_3$): δ 118.7; 110.73; 105.92; 99.39; 91.30; 82.15. ^1H NMR of the minor isomer ($CDCl_3$): δ 6.83 (t); 5.89 (t); 4.03 (d), 3.83 (d); −12.85 (s); −22.02 (s). Anal. Found: C, 22.92; H, 0.51%. $C_{22}H_6O_{17}Ru_6$ calc.: C, 23.0; H, 0.52%.

*Synthesis of **6***

A solution of $H_2Ru_6(CO)_{16}(OC_6H_4)$ (23 mg, 0.02 mmol) and $P(OMe)_3$ (25 mg, 0.2 mmol) in dichloromethane (25 ml) was stirred at ambient temperature under argon for 19 h. The dark maroon solution was evaporated to dryness under vacuum and then subjected to TLC. Repeated elution with dichloromethane–hexane (1 : 2) gave two purple bands: the first contained **6** (9 mg, ~ 40%), and the species in the other was not identified.

IR ($\nu_{(CO)}$, CH_2Cl_2): 2090m, 2058s, 2034vs, 2020s, 1955m, 1795w,br. ^1H NMR ($CDCl_3$): δ 3.74 (d, Phosphite); 6.65 (t); 5.72 (t); 3.89 (d); −13.39 (d); −21.86 (Ru–H). Anal. Found: C, 23.70, H, 1.15. $C_{24}H_{15}O_{19}PRu_6$ calc.; C, 23.13; H, 1.2%.

*Synthesis of **8***

A solution of $Ru_3(CO)_{12}$ (32 mg, 0.05 mmol) and *p*-nitrophenol (35 mg, 0.25 mmol) in cyclohexane (25 ml) was kept at 80 ° C under argon for 5.5 h. The turbid orange solution obtained was evaporated to dryness and the residue subjected to TLC. Elution with hexane gave a yellow band containing $Ru_3(CO)_{12}$ (9 mg, 30%). Subsequent elution with dichloromethane–hexane (9 : 1) gave a prominent yellow band containing **8** (16 mg, 50%).

IR ($\nu_{(CO)}$, hexane): 2102w, 2070vs, 2030s, 3010w,sh, 1745m. ^1H NMR ($CDCl_3$): A_2B_2, δ 7.02; 6.91; 6.62; 6.51; 4.76 (OH). Anal. Found: C, 27.41; H, 0.69; N, 2.0. $C_{16}H_5NO_{11}Ru_3$ calc.: C, 27.82; H, 0.72; N, 2.02%.

*Synthesis of **9**, **10** and **11***

A solution of $Ru_3(CO)_{12}$ (128 mg, 0.20 mmol) and *p*-aminophenol (436 mg, 4 mmol) in benzene (8 ml) was kept at 78° C under argon for 2.5 h. The turbid dark-brown solution was evaporated to dryness and the residue subjected to TLC. Elution with hexane gave bands containing $H_2Ru_4(CO)_{13}$ (10 mg, 8%) and $H_4Ru_4(CO)_{13}$ (30 mg, 24%), respectively. Subsequent elution with dichloromethane–hexane (9 : 1) gave two prominent bands, one purple and the other yellow: the yellow band contained **9** (25 mg, 20%) and the purple one contained **10** (6 mg, 5%).

9: IR ($\nu_{(CO)}$, hexane): 2099w, 2064vs, 2050s, 2026s, 2010s, 2002m,sh, 1996vw, 1980w. ^1H NMR ($CDCl_3$): A_2B_2, δ 6.68; 6.70; 6.65; 6.63; 6.18 (NH); 4.60 (OH); −12.66 (Ru–H). Anal. Found: C, 27.67; H, 0.99; N, 2.01. $C_{16}H_7NO_{11}Ru_3$ calc.: C, 27.74; H, 1.01; N, 2.02%.

10: IR ($\nu_{(CO)}$, CH_2Cl_2): 2112w, 2098vw, 2072s, 2044vs,br, 2024s, 2014m,sh, 1954m,br; 1790w,br. ^1H NMR (CD_3COCD_3): ABX, δ 6.93 (m); 6.67 (m); 4.41 (m); 6.04 (br, NH_2); −11.69 (s); −21.48 (s, Ru–H). Anal. Found: C, 22.42; H, 0.59; N, 1.18. $C_{22}H_7NO_{17}Ru_6$ calc.: C, 22.69; H, 0.60; N, 1.20%.

When a solution of **9** (7 mg, 0.01 mmol) was kept at 80 ° C in cyclohexane (20 ml) for 12 h there was clean conversion into **11** (6 mg, 0.01 mmol).

11: IR ($\nu_{(CO)}$, hexane): 2114m, 2078s, 2054vs, 2044s,sh, 2018s, 2000s, 1988m. ^1H NMR ($CDCl_3$): A_2B_2, δ 7.14: 7.03; 6.62; 6.51; 4.66 (OH); −16.93 (Ru–H). Anal.

Found: C, 27.0; H, 1.01; N, 2.09. $C_{15}H_7NO_{10}Ru_3$ calc.: C, 27.10; H, 1.05; N, 2.10%.

Acknowledgements

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