Synthesis of a Hydrido Octaruthenium Cluster: *X*-Ray Analysis of $[H_2Ru_8(CO)_{21}]^{2-}$

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The new octanuclear ruthenium complex $[(Ph_3P)_2N]_2[H_2Ru_8(CO)_{21}]$ has been obtained by reaction of $[H_4Ru_4(CO)_{12}]$ with sodium in refluxing bis-(2-methoxyethyl) ether; *X*-ray analysis shows a structure with a metallic skeleton based on face-to-face condensation of trigonal bipyramidal and octahedral units.

The formation of large metal carbonyl clusters has excited both theoretical[1,2] and synthetic[3] interest. Curiously, however, for the element ruthenium there are few examples of such compounds, although clusters containing seven,[4] eight,[5] and ten[6] ruthenium atoms are known. We report here the synthesis and structure of a hydrido Ru_8 cluster anion, $[H_2Ru_8(CO)_{21}]^{2-}$ (**1**).

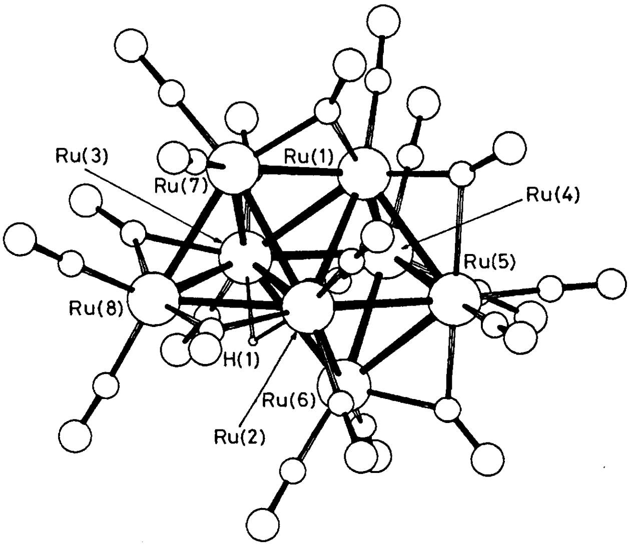

Figure 1. Structure of the anion $[H_2Ru_8(CO)_{21}]^{2-}$ (**1**); one hydrogen atom in the octahedron is not shown. Bond lengths (Å): Ru–Ru (1)–(2) 2.929(1), (1)–(3) 2.875(1), (1)–(4) 2.878(1), (1)–(5) 2.793(1), (1)–(7) 2.645(1), (2)–(3) 2.857(1), (2)–(5) 2.909(1), (2)–(6) 2.931(1), (2)–(7) 2.845(1), (2)–(8) 2.807(1), (3)–(4) 2.854(1), (3)–(6) 2.921(1), (3)–(7) 2.858(1), (3)–(8) 2.783(1), (4)–(5) 2.969(1), (4)–(6) 2.856(1), (5)–(6) 2.840(1), and (7)–(8) 2.778(1); Ru(2)–H(1) 1.69(5); Ru(3)–H(1) 1.97(5).

Heating $[H_4Ru_4(CO)_{12}]$ in bis-(2-methoxyethyl) ether in the presence of sodium, followed by treatment with $(Ph_3P)_2NCl$ afforded $[(Ph_3P)_2N]_2[H_2Ru_8(CO)_{21}]$ as a black crystalline solid, exhibiting i.r. absorptions at 2059w, 2016m, 1996sh, 1990s, 1950sh, 1920w, 1817sh, and 1788m cm^{-1} in CH_2Cl_2. Although the ^1H n.m.r. spectrum shows no resonance peaks attributable to hydrido species at ambient temperature, two peaks appeared below −20 °C: δ (CH_2Cl_2; −50 °C) 6.88 (1H, d, *J* 2.6 Hz) and −12.87 (1H, d, *J* 2.6 Hz). Spin decoupling demonstrated an interaction between these two hydrogen atoms. Although the latter chemical shift value is normal for a metal hydride, the former implies an unusual position.

A black crystal obtained by recrystallization from MeOH was investigated by *X*-ray diffraction.† The molecular struc-

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† *Crystal data:* $[C_{36}H_{30}NP_2]_2[C_{21}H_2O_{21}Ru_8]$, $M = 2473.95$, monoclinic, space group $P2_1/a$, $a = 25.059(7)$, $b = 17.970(6)$, $c = 20.629(9)$ Å, $\beta = 93.75(3)°$, $U = 9269.6$ Å^3, $Z = 4$, $D_x = 1.771$, $D_c = 1.774$ g cm^{-3}, $F(000) = 4856$; $\lambda = 0.71069$ Å, $\mu(Mo\text{-}K_\alpha) = 13.80$ cm^{-1}; 17872 reflections ($0.0° < 2\theta < 50.0°$) were collected by Rigaku four-circle diffractometer using graphite-monochromated Mo-K_α radiation and the ω-scan technique. The data were averaged to give 11030 unique observed reflections $[I > 3\sigma(I)]$. The structure was refined by full-matrix least-square methods. All the non-hydrogen atoms were assigned anisotropic thermal parameters, and a hydrido atom [H(1)] an isotropic thermal parameter. Sixty hydrogen atoms bound to phenyl groups were placed in idealized positions with a common thermal parameter but they were not refined. The weighting scheme $w = 1/(\sigma(I))^2$ was employed. The current residuals are $R = 0.054$ and $R_w = 0.043$. 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.

ture of the dianion (**1**) is shown in Figure 1. The eight Ru atoms constitute a skeleton based on face-to-face condensation of trigonal bipyramidal and octahedral units. The Ru(1),Ru(2),Ru(3) face is common to both units. This type of structure has not been previously reported for homonuclear clusters, although two examples, $[(MeCN)_2Cu_2Ru_6C(CO)_{16}]$[7] and $[Ru_5WC(CO)_{17}(AuPEt_3)_2]$,[8] have been reported for mixed clusters. Five carbonyl groups bridge the Ru–Ru edges. The remaining carbonyl ligands are linear and terminal.

One hydrogen atom [H(1)] in the cluster was revealed by difference Fourier syntheses. This bridges Ru(2) [1.69(5) Å] and Ru(3) [1.97(5) Å]; in addition some interactions with Ru(6) [2.22(5) Å] and Ru(8) [2.12(5) Å] are assumed. This is an unprecedented situation, with a hydrido atom in an open butterfly arrangement of four metal atoms and may be a model for adsorbed hydrogen on a stepped metal (111) surface. This hydrogen atom is responsible for the n.m.r. peak at δ −12.87.

The other hydrogen atom in the cluster was not located by *X*-ray analysis. Its abnormally low field resonance and the production of $[(PPh_3)_2N][HRu_6(CO)_{18}]$[9] on treatment of $[(Ph_3P)_2N]_2[H_2Ru_8(CO)_{21}]$ with CO at atmospheric pressure and room temperature suggest that this particular hydrogen is located at the centre of the octahedron.

In terms of overall electron counting the dianion (**1**) contains 110 valence electrons. This number is in accord with the predictions of the polyhedral skeletal electron pair (PSEP) approach as extended to condensed polyhedra.[10] That is, the dianion (**1**) would be viewed as an octahedron (86 electrons) fused to a trigonal bipyramid (72 electrons) through a triangular face (−48 electrons).

The Ru–Ru distances range from 2.778(1) to 2.969(1) Å, except for Ru(1)–Ru(7) [2.645(1) Å]. In reported ruthenium clusters short Ru–Ru distances are 2.670(1) Å in $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{15}]$,[11] and 2.704(1) Å for a formal ruthenium–ruthenium double bond in $[Ru_5(CO)_{14}(\mu_4\text{-}S)_2]$.[4b] However, Ru(3)–Ru(7) in (**1**) is shorter than these two. The reason is not clear.

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References

1 B. K. Teo, *Inorg. Chem.*, 1985, **24**, 1627.
2 J. W. Lauher, *J. Am. Chem. Soc.*, 1979, **101**, 2604.
3 M. D. Vargas and J. N. Nicholls, *Adv. Inorg. Chem. Radiochem.*, 1986, **30**, 123.
4 F. V. Gastel, N. J. Taylor, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1987, 1049; R. D. Adams, J. E. Babin, and M. Tasi, *Inorg. Chem.*, 1987, **26**, 2807.
5 R. D. Adams, J. E. Babin, and M. Tasi, *Inorg. Chem.*, 1986, **25**, 4460; L. M. Bullock, J. S. Field, R. J. Haines, E. Minshall, D. N. Smit, and G. M. Sheldrick, *J. Organomet. Chem.*, 1986, **310**, C47.
6 C.-M. T. Hayward and J. R. Shapley, *J. Am. Chem. Soc.*, 1982, **104**, 7347.
7 J. S. Bradley, R. L. Pruett, E. Hill, G. B. Ansell, M. E. Leonowicz, and M. A. Modrick, *Organometallics*, 1982, **1**, 748.
8 S. R. Bunkhall, H. D. Holden, B. F. G. Johnson, J. Lewis, G. N. Pain, P. R. Raithby, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1984, 25.
9 C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M. C. Malatesta, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 383.
10 D. M. P. Mingos, *Acc. Chem. Res.*, 1984, **17**, 311.
11 M. I. Bruce and M. L. Williams, *J. Organomet. Chem.*, 1985, **282**, C11.