compounds; however, previous studies[6] suggest that cobalt atoms react initially with cyclopentadiene at low temperatures to give the reactive cobalt hydride species (η^1-C_5H_5)Co-H or (η^5-C_5H_5)Co-H, which can then undergo insertion or dehydroinsertion reactions with polyhedral borane fragments. For more stable cage systems, simple metal insertion is generally observed; however, as the reactivity of the cage increases, more extensive decomposition can occur. Owing principally to the highly reactive nature of the CpCo–H hydrogen fragments, the selectivity and yields of metal complexes obtained in the reactions reported herein are quite low, especially when compared to the corresponding reactions[1] involving metal atom generated (η^6-arene)iron fragments. Furthermore, the distribution and type of products obtained are probably mainly determined by their relative stabilities with respect to further reaction. Thus, while this work has resulted in the production of several new cobaltathiaborane complexes, alternative syntheses or improvements in the metal vapor technique will be required before these complexes can be produced selectively on reasonable scales.

Acknowledgment. We thank the National Science Foundation for support of this research.

Supplementary Material Available: A table of infrared data for compounds I–VII and tables of atomic positional parameters, general temperature factors, intramolecular distances and angles, molecular planes, and dihedral angles for IV and V (21 pages); listings of observed and calculated structure factors for IV and V (20 pages). Ordering information is given on any current masthead page.

Contribution from The Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama 351-01, Japan, and Institute for Protein Research, Osaka University, Suita-shi, Osaka 565, Japan

Synthesis and X-ray Structure Analysis of the Tetracapped Octahedral Ruthenium Carbido Cluster $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$

Teiji Chihara,*,† Ryuhei Komoto,† Kimiko Kobayashi,† Hiroshi Yamazaki,*,† and Yoshiki Matsuura‡

Received July 22, 1988

It has been reported[1] that treatment of $Ru_3(CO)_{12}$ with sodium in refluxing bis(2-methoxyethyl) ether (162 °C) gives $[Ru_6C(CO)_{16}]^{2-}$ (**1**) quantitatively. Similar treatment of $Os_3(CO)_{12}$, however, gives only the non-carbido cluster $[Os_6(CO)_{18}]^{2-}$. Thermolysis of this osmium cluster in 2,5,8,11,14-pentaoxapentadecane (230 °C) gives a carbido dianion, $[Os_{10}C(CO)_{24}]^{2-}$ (**2**), having a tetracapped octahedral metal framework. Thermolysis of the same compound in bis(2-methoxyethyl) ether (162 °C) followed by oxidation under a CO atmosphere gives $Os_6C(CO)_{17}$ in a small yield (2%); hence, $[Os_6C(CO)_{16}]^{2-}$ is believed to be an intermediate in the formation of the decanuclear cluster **2**. On the other hand, thermolysis of **1** in 2,5,8,11,14-pentaoxapentadecane (210–230 °C) failed to give the dianionic carbido ruthenium cluster $[Ru_{10}C(CO)_{24}]^{2-}$ (**3**) but gave the dianionic dicarbido cluster $[Ru_{10}C_2(CO)_{24}]^{2-}$,[2] whose metallic structure has been shown to consist of two edge-sharing octahedra. There seems to be no reason for the absence of the tetracapped octahedral ruthenium cluster **3**, which is analogous to the known osmium cluster **2**.[3] We have examined a "redox condensation" reaction[4] of **1** with the neutral ruthenium compound $Ru_3(CO)_{12}$ for the direct synthesis of **3**. Here we report the successful preparation of this compound and the X-ray structure analysis.

* To whom correspondence should be addressed.
† The Institute of Physical and Chemical Research.
‡ Institute for Protein Research.

Table I. Crystallographic Data for $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$

chem formula: $C_{97}H_{60}N_2O_{24}P_4Ru_{10}$	fw: 2772.1
a = 17.520 (5) Å	space group: $P\bar{1}$ (No. 2)
b = 27.102 (9) Å	T = 19 °C
c = 10.444 (2) Å	λ = 0.71073 Å
α = 100.61 (3)°	ρ_{calcd} = 1.90 g cm^{-3}
β = 96.28 (3)°	μ = 16.24 cm^{-1}
γ = 85.74 (6)°	$R(F_o)$ = 0.050
V = 4838 (2) Å^3	$R_w(F_o)$ = 0.043
Z = 2	

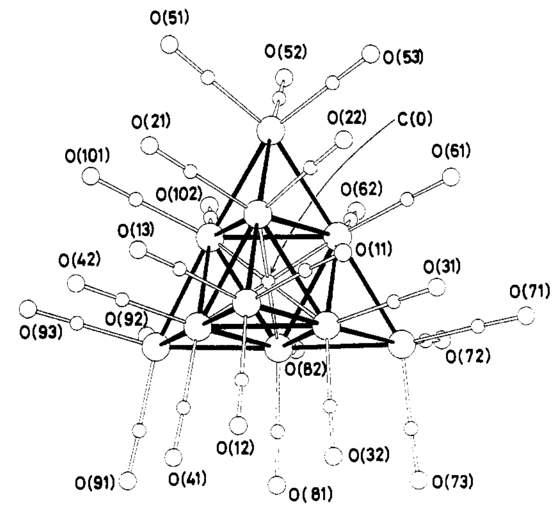

Figure 1. Structure of $[Ru_{10}C(CO)_{24}]^{2-}$ (**3**) with the numbering of the oxygen atoms corresponding to that of the relevant carbonyl carbon atoms. The first digit of each oxygen number is the number of the osmium atom to which the carbonyl is attached.

Experimental Section

Preparation of $[Ru_{10}C(CO)_{24}]^{2-}$ (3). A solution of $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$[1] (402 mg, 0.188 mmol) and $Ru_3(CO)_{12}$ (180 mg, 0.282 mmol) in 12 mL of dry bis(2-methoxyethyl) ether was refluxed for 3 h under an argon atmosphere. The color of the solution changed from orange to brown to deep green. Then the solvent was removed under vacuum, and the residue was dissolved in a minimum quantity of CH_2Cl_2 and applied to a 10% water-containing alumina column. Elution with a benzene–CH_2Cl_2 (1:1) solvent mixture separated a deep green band. Crystallization from CH_2Cl_2–MeOH provided deep green crystals of $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$ (422 mg, 0.152 mmol, 81% yield based on $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$): IR ($\nu$(CO) in CH_2Cl_2): 2066 (sh), 2026 (s), 1997 (w), 1984 (s) cm^{-1}. ^{1}H NMR (acetone-d_6): δ 7.5–7.9 (phenyl protons, m). Anal. Calcd for $C_{97}H_{60}N_2O_{24}P_4Ru_{10}$: C, 42.02; H, 2.18; N, 1.01. Found: C, 42.06; H, 2.11; N, 1.01. $[NEt_4]_2[Ru_{10}C(CO)_{24}]$ was also obtained from the $[NEt_4]^+$ salt by the same procedure.

Crystallographic Analysis. A deep green crystal of **3** was mounted in a thin-walled glass capillary. Diffraction measurements were made at 19 °C on a Rigaku AFC4 automatic diffractometer using graphite-monochromatized Mo Kα radiation from a rotating anode generator operated at 40 kV and 200 mA. Unit cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with 20° < 2θ < 25°. Crystal data, data collection parameters, and results of the analyses are listed in Table I. Absorption correction was not made, because deviations of F_0 for axial reflections at χ = 90° were within ±5%. The structure was solved by direct methods by use of the program MULTAN,[5] which located 10 ruthenium atoms. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and refined by the block-diagonal least-squares method[6] with anisotropic

(1) Hayward, C.-M. T.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816.
(2) Hayward, C.-M. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1982**, *104*, 7347.
(3) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Nelson, J. H.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1982**, 2099.
(4) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 123.
(5) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J.-P.; Woolfson, M. M. "MULTAN 78"; University of York: York, England, 1978.
(6) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69.

0020-1669/89/1328-0964$01.50/0

Table II. Atomic Coordinates (×10[5]) and Equivalent Temperature Factors (Å[2]) for $[Ru_{10}C(CO)_{24}]^{2-}$ (**3**) with Esd Values in Parentheses

atom	x	y	z	B_{eq}[a]
Ru(1)	24360 (4)	35001 (3)	20676 (7)	3.0
Ru(2)	19404 (4)	28476 (2)	−1893 (6)	2.5
Ru(3)	34916 (4)	31655 (2)	2712 (6)	2.5
Ru(4)	29908 (4)	25086 (2)	18281 (6)	2.4
Ru(5)	15239 (4)	21624 (3)	−24487 (7)	3.1
Ru(6)	30134 (4)	24739 (2)	−20619 (6)	2.4
Ru(7)	45034 (4)	27660 (3)	−15915 (7)	3.5
Ru(8)	40552 (4)	21436 (3)	−339 (7)	2.7
Ru(9)	35375 (5)	15041 (3)	14108 (7)	3.5
Ru(10)	25193 (4)	18274 (2)	−5083 (6)	2.6
O(11)	10678 (39)	33660 (24)	34470 (65)	5.5
O(12)	18909 (43)	45149 (23)	14106 (65)	6.0
O(13)	35033 (35)	39118 (23)	44319 (59)	4.8
O(21)	4300 (38)	26754 (29)	7784 (73)	6.7
O(22)	12957 (45)	37517 (24)	−13550 (69)	6.5
O(31)	32388 (52)	41368 (26)	−8041 (75)	7.9
O(32)	47847 (37)	35642 (26)	22694 (59)	5.6
O(41)	18349 (40)	22477 (24)	35021 (64)	5.5
O(42)	41743 (37)	27527 (24)	41558 (59)	5.3
O(51)	−559 (41)	18646 (28)	−20843 (78)	7.2
O(52)	8882 (42)	29122 (27)	−41671 (69)	6.5
O(53)	17353 (43)	12916 (26)	−46824 (67)	6.4
O(61)	26459 (40)	32251 (24)	−38718 (64)	5.4
O(62)	34908 (41)	16824 (25)	−43148 (60)	5.8
O(71)	44195 (49)	36194 (32)	−31009 (75)	8.4
O(72)	53179 (49)	19930 (32)	−35129 (80)	9.1
O(73)	59922 (40)	30645 (26)	−527 (73)	6.7
O(81)	48144 (57)	12521 (32)	−16778 (93)	11.0
O(82)	54857 (39)	23146 (29)	18371 (69)	6.5
O(91)	41552 (55)	4951 (28)	813 (81)	9.4
O(92)	23464 (46)	10632 (28)	26695 (80)	7.5
O(93)	47708 (40)	15483 (28)	36783 (66)	6.4
O(101)	30423 (42)	8975 (23)	−23711 (65)	6.0
O(102)	11440 (40)	14133 (26)	3868 (67)	6.0
C(0)	29992 (39)	24963 (26)	−1141 (62)	1.5
C(11)	16045 (55)	34159 (31)	29580 (88)	4.1
C(12)	21010 (54)	41269 (33)	16214 (79)	4.0
C(13)	30954 (50)	37514 (32)	35574 (83)	3.7
C(21)	10185 (54)	27416 (34)	4089 (96)	4.7
C(22)	15465 (54)	34106 (33)	−9008 (78)	3.9
C(31)	33250 (57)	37661 (35)	−3984 (83)	4.4
C(32)	42936 (50)	34150 (31)	15196 (83)	3.6
C(41)	22777 (51)	23492 (30)	28850 (83)	3.6
C(42)	37216 (50)	26655 (30)	32915 (82)	3.5
C(51)	5555 (55)	19806 (33)	−22039 (90)	4.4
C(52)	11424 (53)	26318 (36)	−35075 (86)	4.3
C(53)	16718 (54)	16184 (36)	−38241 (87)	4.4
C(61)	27865 (51)	29361 (32)	−31538 (81)	3.7
C(62)	33105 (50)	19798 (32)	−34465 (79)	3.5
C(71)	44439 (56)	32936 (41)	−25530 (90)	5.2
C(72)	49933 (61)	22855 (42)	−28051 (99)	6.0
C(73)	54197 (55)	29511 (34)	−6305 (96)	4.6
C(81)	45098 (61)	15953 (40)	−10383 (100)	5.9
C(82)	49475 (52)	22507 (35)	11225 (97)	4.5
C(91)	39200 (69)	8809 (38)	5714 (91)	5.9
C(92)	27987 (59)	12353 (35)	22081 (100)	5.0
C(93)	42947 (55)	15427 (34)	28384 (90)	4.3
C(101)	28252 (54)	12464 (32)	−16359 (81)	4.0
C(102)	16777 (52)	15689 (31)	462 (86)	3.9

[a] $B_{eq} = {}^4/_3(\sum_i\sum_j B_{ij}a_ib_j)$.

thermal parameters for all non-hydrogen atoms. As refinement proceeded, 60 hydrogen atoms attached to the phenyl rings of the countercation $[N(PPh_3)_2]^+$ were added in their idealized positions for the structure factor calculations, but their positions were not refined.

Results

The reaction of $[N(PPh_3)_2]_2[Ru_6C(CO)_{16}]$ and $Ru_3(CO)_{12}$ in refluxing bis(2-methoxyethyl) ether proceeds with release of CO gas, and deep green crystals are obtained after alumina chromatography. The IR spectrum (ν(CO) 2026 (s) and 1984 (s) cm^{-1}) shows the presence of only terminal carbonyl groups. The similarity of the IR patterns with those of $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$ (ν(CO) 2033 (s) and 1986 (s) cm^{-1}) and the elemental analysis suggested the formation of $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$.

Table III. Selected Interatomic Distances (Å) and Esd Values for $[Ru_{10}C(CO)_{24}]^{2-}$ (**3**)

(a) Metal–Metal			
(i) Within Octahedron			
Ru(2)–Ru(3)	2.876 (1)	Ru(3)–Ru(8)	2.843 (2)
Ru(2)–Ru(4)	2.878 (1)	Ru(4)–Ru(8)	2.837 (1)
Ru(2)–Ru(6)	2.860 (1)	Ru(4)–Ru(10)	2.859 (1)
Ru(2)–Ru(10)	2.847 (1)	Ru(6)–Ru(8)	2.869 (1)
Ru(3)–Ru(4)	2.862 (1)	Ru(6)–Ru(10)	2.834 (1)
Ru(3)–Ru(6)	2.874 (1)	Ru(8)–Ru(10)	2.849 (1)
(ii) From Capping Ru Atoms			
Ru(1)–Ru(2)	2.772 (1)	Ru(7)–Ru(3)	2.792 (1)
Ru(1)–Ru(3)	2.765 (1)	Ru(7)–Ru(6)	2.751 (1)
Ru(1)–Ru(4)	2.765 (1)	Ru(7)–Ru(8)	2.756 (1)
Ru(5)–Ru(2)	2.786 (1)	Ru(9)–Ru(4)	2.790 (1)
Ru(5)–Ru(6)	2.767 (1)	Ru(9)–Ru(8)	2.757 (1)
Ru(5)–Ru(10)	2.764 (1)	Ru(9)–Ru(10)	2.757 (1)
(b) Metal–Carbido			
Ru(2)–C(0)	2.022 (7)	Ru(6)–C(0)	2.027 (7)
Ru(3)–C(0)	2.021 (7)	Ru(8)–C(0)	2.019 (7)
Ru(4)–C(0)	2.024 (7)	Ru(10)–C(0)	2.010 (7)
(c) Metal–Ligand			
(i) From Ru Atoms of the Octahedron			
Ru(2)–C(21)	1.854 (10)	Ru(6)–C(61)	1.839 (9)
Ru(2)–C(22)	1.872 (9)	Ru(6)–C(62)	1.872 (8)
Ru(3)–C(31)	1.878 (10)	Ru(8)–C(81)	1.837 (10)
Ru(3)–C(32)	1.884 (8)	Ru(8)–C(82)	1.874 (9)
Ru(4)–C(41)	1.877 (10)	Ru(10)–C(101)	1.867 (8)
Ru(4)–C(42)	1.889 (8)	Ru(10)–C(102)	1.868 (10)
(ii) From Capping Ru Atoms			
Ru(1)–C(11)	1.861 (10)	Ru(7)–C(71)	1.884 (10)
Ru(1)–C(12)	1.879 (9)	Ru(7)–C(72)	1.872 (10)
Ru(1)–C(13)	1.885 (8)	Ru(7)–C(73)	1.849 (9)
Ru(5)–C(51)	1.858 (10)	Ru(9)–C(91)	1.867 (10)
Ru(5)–C(52)	1.876 (10)	Ru(9)–C(92)	1.870 (11)
Ru(5)–C(53)	1.884 (9)	Ru(9)–C(93)	1.878 (9)
(d) C–O			
(i) Bonded to Ru Atoms of the Octahedron			
C(21)–O(21)	1.177 (12)	C(61)–O(61)	1.176 (11)
C(22)–O(22)	1.153 (11)	C(62)–O(62)	1.152 (10)
C(31)–O(31)	1.154 (13)	C(81)–O(81)	1.171 (13)
C(32)–O(32)	1.142 (10)	C(82)–O(82)	1.140 (11)
C(41)–O(41)	1.140 (12)	C(101)–O(101)	1.171 (10)
C(42)–O(42)	1.137 (10)	C(102)–O(102)	1.168 (12)
(ii) Bonded to Capping Ru Atoms			
C(11)–O(11)	1.146 (12)	C(71)–O(71)	1.133 (15)
C(12)–O(12)	1.140 (11)	C(72)–O(72)	1.143 (13)
C(13)–O(13)	1.136 (10)	C(73)–O(73)	1.145 (11)
C(51)–O(51)	1.164 (12)	C(91)–O(91)	1.145 (12)
C(52)–O(52)	1.152 (12)	C(92)–O(92)	1.140 (14)
C(53)–O(53)	1.147 (11)	C(93)–O(93)	1.141 (11)

In order to confirm the structure, a single-crystal X-ray diffraction analysis has been undertaken. Figure 1 shows the structure of the dianionic cluster species **3**. Final positional parameters are given in Table II. Selected intramolecular distances and intramolecular angles are listed in Tables III and IV, respectively.

Discussion

$[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$ is isomorphous with the corresponding osmium cluster $[N(PPh_3)_2]_2[Os_{10}C(CO)_{24}]$.[3] The lattice constants of these two are almost the same; those of the ruthenium cluster are 0.1–0.2% smaller than those of osmium. As Figure 1 shows, the molecular structure of the dianionic ruthenium cluster **3** is also the same as that of the osmium cluster **2**, and this similarity is a unique example for high-nuclearity clusters.

The metal core of **3** constitutes a large tetrahedron, which is made of four fused small tetrahedrons. As Figure 2 shows, the ruthenium atoms of **3** may be regarded as constituting a face-centered cubic unit cell of metal atoms without four tetrahedrally related corner atoms. In the case of ruthenium clusters a hexagonal close-packed (hcp) array, which is characterized by a trigonal-bipyramidal array, has been reported for two cases in $[Ru_8H_2(CO)_{21}]^{2-}$[7] and $[Ru_5C(CO)_3(\mu_3\text{-}CO)_3(\eta\text{-}C_5H_5)_4]$,[8] and

Table IV. Selected Interatomic Angles (deg) and Esd Values for $[Ru_{10}C(CO)_{24}]^{2-}$ (3)

(a) Angles between Metal Atoms							
Ru(2)–Ru(1)–Ru(3)	62.58 (4)	Ru(2)–Ru(3)–Ru(7)	117.71 (4)	Ru(2)–Ru(6)–Ru(3)	60.20 (4)	Ru(4)–Ru(8)–Ru(9)	59.82 (4)
Ru(2)–Ru(1)–Ru(4)	62.64 (4)	Ru(2)–Ru(3)–Ru(8)	89.91 (5)	Ru(2)–Ru(6)–Ru(5)	59.33 (4)	Ru(4)–Ru(8)–Ru(10)	60.37 (3)
Ru(3)–Ru(1)–Ru(4)	62.34 (5)	Ru(4)–Ru(3)–Ru(6)	89.86 (4)	Ru(2)–Ru(6)–Ru(7)	119.66 (4)	Ru(6)–Ru(8)–Ru(7)	58.52 (4)
Ru(1)–Ru(2)–Ru(3)	58.60 (4)	Ru(4)–Ru(3)–Ru(7)	118.15 (4)	Ru(2)–Ru(6)–Ru(8)	89.73 (4)	Ru(6)–Ru(8)–Ru(9)	118.31 (4)
Ru(1)–Ru(2)–Ru(4)	58.56 (4)	Ru(4)–Ru(3)–Ru(8)	59.63 (3)	Ru(2)–Ru(6)–Ru(10)	60.00 (4)	Ru(6)–Ru(8)–Ru(10)	59.42 (3)
Ru(1)–Ru(2)–Ru(5)	176.73 (3)	Ru(6)–Ru(3)–Ru(7)	58.07 (4)	Ru(3)–Ru(6)–Ru(5)	119.52 (5)	Ru(7)–Ru(8)–Ru(9)	176.61 (3)
Ru(1)–Ru(2)–Ru(6)	118.73 (4)	Ru(6)–Ru(3)–Ru(8)	60.23 (4)	Ru(3)–Ru(6)–Ru(7)	59.47 (4)	Ru(7)–Ru(8)–Ru(10)	117.94 (5)
Ru(1)–Ru(2)–Ru(10)	118.47 (4)	Ru(7)–Ru(3)–Ru(8)	58.55 (4)	Ru(3)–Ru(6)–Ru(8)	59.36 (4)	Ru(9)–Ru(8)–Ru(10)	58.89 (4)
Ru(3)–Ru(2)–Ru(4)	59.66 (3)	Ru(1)–Ru(4)–Ru(2)	58.80 (4)	Ru(3)–Ru(6)–Ru(10)	89.84 (4)	Ru(4)–Ru(9)–Ru(8)	61.52 (4)
Ru(3)–Ru(2)–Ru(5)	118.82 (5)	Ru(1)–Ru(4)–Ru(3)	58.83 (4)	Ru(5)–Ru(6)–Ru(7)	177.75 (4)	Ru(4)–Ru(9)–Ru(10)	62.04 (5)
Ru(3)–Ru(2)–Ru(6)	60.15 (3)	Ru(1)–Ru(4)–Ru(8)	118.67 (5)	Ru(5)–Ru(6)–Ru(8)	119.07 (4)	Ru(8)–Ru(9)–Ru(10)	62.22 (4)
Ru(3)–Ru(2)–Ru(10)	89.55 (5)	Ru(1)–Ru(4)–Ru(9)	176.29 (3)	Ru(5)–Ru(6)–Ru(10)	59.13 (4)	Ru(2)–Ru(10)–Ru(4)	60.59 (4)
Ru(4)–Ru(2)–Ru(5)	118.68 (4)	Ru(1)–Ru(4)–Ru(10)	118.28 (4)	Ru(7)–Ru(6)–Ru(8)	58.69 (4)	Ru(2)–Ru(10)–Ru(5)	59.52 (4)
Ru(4)–Ru(2)–Ru(6)	89.82 (4)	Ru(2)–Ru(4)–Ru(3)	60.12 (4)	Ru(7)–Ru(6)–Ru(10)	118.63 (5)	Ru(2)–Ru(10)–Ru(6)	60.45 (3)
Ru(4)–Ru(2)–Ru(10)	59.92 (4)	Ru(2)–Ru(4)–Ru(8)	89.98 (4)	Ru(8)–Ru(6)–Ru(10)	59.94 (4)	Ru(2)–Ru(10)–Ru(8)	90.38 (5)
Ru(5)–Ru(2)–Ru(6)	58.68 (4)	Ru(2)–Ru(4)–Ru(9)	117.89 (5)	Ru(3)–Ru(7)–Ru(6)	62.46 (4)	Ru(2)–Ru(10)–Ru(9)	120.14 (5)
Ru(5)–Ru(2)–Ru(10)	58.77 (4)	Ru(2)–Ru(4)–Ru(10)	59.49 (4)	Ru(3)–Ru(7)–Ru(8)	61.67 (4)	Ru(4)–Ru(10)–Ru(5)	120.11 (4)
Ru(6)–Ru(2)–Ru(10)	59.55 (4)	Ru(3)–Ru(4)–Ru(8)	59.85 (4)	Ru(6)–Ru(7)–Ru(8)	62.79 (4)	Ru(4)–Ru(10)–Ru(6)	90.73 (4)
Ru(1)–Ru(3)–Ru(2)	58.83 (3)	Ru(3)–Ru(4)–Ru(9)	118.48 (4)	Ru(3)–Ru(8)–Ru(4)	60.52 (4)	Ru(4)–Ru(10)–Ru(8)	59.61 (4)
Ru(1)–Ru(3)–Ru(4)	58.83 (4)	Ru(3)–Ru(4)–Ru(10)	89.57 (4)	Ru(3)–Ru(8)–Ru(6)	60.41 (4)	Ru(4)–Ru(10)–Ru(9)	59.56 (4)
Ru(1)–Ru(3)–Ru(6)	118.47 (4)	Ru(8)–Ru(4)–Ru(9)	58.66 (4)	Ru(3)–Ru(8)–Ru(7)	59.79 (4)	Ru(5)–Ru(10)–Ru(6)	59.23 (4)
Ru(1)–Ru(3)–Ru(7)	176.01 (4)	Ru(8)–Ru(4)–Ru(10)	60.02 (4)	Ru(3)–Ru(8)–Ru(9)	120.31 (4)	Ru(5)–Ru(10)–Ru(8)	119.86 (4)
Ru(1)–Ru(3)–Ru(8)	118.45 (5)	Ru(9)–Ru(4)–Ru(10)	58.40 (4)	Ru(3)–Ru(8)–Ru(10)	90.15 (5)	Ru(5)–Ru(10)–Ru(9)	178.74 (4)
Ru(2)–Ru(3)–Ru(4)	60.21 (4)	Ru(2)–Ru(5)–Ru(6)	61.99 (4)	Ru(4)–Ru(8)–Ru(6)	90.47 (4)	Ru(6)–Ru(10)–Ru(8)	60.64 (4)
Ru(2)–Ru(3)–Ru(6)	59.65 (4)	Ru(2)–Ru(5)–Ru(10)	61.71 (4)	Ru(4)–Ru(8)–Ru(7)	120.27 (4)	Ru(6)–Ru(10)–Ru(9)	119.52 (4)
		Ru(6)–Ru(5)–Ru(10)	61.64 (4)			Ru(8)–Ru(10)–Ru(9)	58.89 (4)
(b) Metal–Carbido–Metal							
Ru(2)–C(0)–Ru(3)	90.7 (3)	Ru(2)–C(0)–Ru(10)	89.8 (3)	Ru(3)–C(0)–Ru(10)	179.4 (4)	Ru(6)–C(0)–Ru(8)	90.3 (3)
Ru(2)–C(0)–Ru(4)	90.7 (3)	Ru(3)–C(0)–Ru(4)	90.1 (2)	Ru(4)–C(0)–Ru(6)	179.2 (4)	Ru(6)–C(0)–Ru(10)	89.2 (3)
Ru(2)–C(0)–Ru(6)	89.9 (3)	Ru(3)–C(0)–Ru(6)	90.5 (3)	Ru(4)–C(0)–Ru(8)	89.1 (3)	Ru(8)–C(0)–Ru(10)	90.0 (3)
Ru(2)–C(0)–Ru(8)	179.8 (4)	Ru(3)–C(0)–Ru(8)	89.5 (3)	Ru(4)–C(0)–Ru(10)	90.3 (3)		
(c) Metal–Metal–Carbon							
(i) At Capping Ru Atoms							
Ru(2)–Ru(1)–C(11)	94.5 (3)	Ru(2)–Ru(5)–C(51)	104.2 (3)	Ru(3)–Ru(7)–C(71)	99.9 (3)	Ru(4)–Ru(9)–C(91)	160.7 (3)
Ru(2)–Ru(1)–C(12)	101.5 (2)	Ru(2)–Ru(5)–C(52)	97.4 (3)	Ru(3)–Ru(7)–C(72)	158.6 (4)	Ru(4)–Ru(9)–C(92)	98.8 (3)
Ru(2)–Ru(1)–C(13)	157.4 (2)	Ru(2)–Ru(5)–C(53)	156.2 (3)	Ru(3)–Ru(7)–C(73)	99.1 (3)	Ru(4)–Ru(9)–C(93)	98.1 (3)
Ru(3)–Ru(1)–C(11)	152.8 (2)	Ru(6)–Ru(5)–C(51)	164.0 (3)	Ru(6)–Ru(7)–C(71)	100.5 (3)	Ru(8)–Ru(9)–C(91)	101.4 (4)
Ru(3)–Ru(1)–C(12)	101.1 (3)	Ru(6)–Ru(5)–C(52)	95.4 (3)	Ru(6)–Ru(7)–C(72)	101.2 (3)	Ru(8)–Ru(9)–C(92)	155.0 (3)
Ru(3)–Ru(1)–C(13)	100.7 (3)	Ru(6)–Ru(5)–C(53)	97.6 (3)	Ru(6)–Ru(7)–C(73)	157.8 (3)	Ru(8)–Ru(9)–C(93)	101.8 (3)
Ru(4)–Ru(1)–C(11)	95.0 (3)	Ru(10)–Ru(5)–C(51)	105.7 (3)	Ru(8)–Ru(7)–C(71)	158.9 (3)	Ru(10)–Ru(9)–C(91)	103.0 (3)
Ru(4)–Ru(1)–C(12)	160.5 (2)	Ru(10)–Ru(5)–C(52)	153.8 (3)	Ru(8)–Ru(7)–C(72)	99.3 (4)	Ru(10)–Ru(9)–C(92)	95.7 (3)
Ru(4)–Ru(1)–C(13)	96.7 (3)	Ru(10)–Ru(5)–C(53)	98.9 (3)	Ru(8)–Ru(7)–C(73)	98.4 (3)	Ru(10)–Ru(9)–C(93)	158.4 (3)
(ii) At Ru Atoms of the Octahedron							
Ru(1)–Ru(2)–C(21)	94.4 (3)	Ru(7)–Ru(3)–C(31)	91.8 (3)	Ru(3)–Ru(6)–C(61)	97.6 (2)	Ru(7)–Ru(8)–C(82)	91.7 (3)
Ru(1)–Ru(2)–C(22)	88.0 (2)	Ru(7)–Ru(3)–C(32)	92.8 (3)	Ru(3)–Ru(6)–C(62)	147.1 (3)	Ru(9)–Ru(8)–C(81)	88.8 (4)
Ru(3)–Ru(2)–C(21)	151.2 (3)	Ru(8)–Ru(3)–C(31)	149.3 (3)	Ru(5)–Ru(6)–C(61)	92.3 (3)	Ru(9)–Ru(8)–C(82)	91.7 (3)
Ru(3)–Ru(2)–C(22)	94.4 (3)	Ru(1)–Ru(4)–C(41)	92.9 (2)	Ru(5)–Ru(6)–C(62)	91.5 (3)	Ru(10)–Ru(8)–C(81)	97.4 (3)
Ru(4)–Ru(2)–C(21)	99.3 (3)	Ru(1)–Ru(4)–C(42)	91.6 (2)	Ru(7)–Ru(6)–C(61)	89.9 (3)	Ru(10)–Ru(8)–C(82)	148.5 (3)
Ru(4)–Ru(2)–C(22)	144.6 (3)	Ru(8)–Ru(3)–C(32)	95.7 (3)	Ru(7)–Ru(6)–C(62)	89.2 (3)	Ru(2)–Ru(10)–C(101)	148.2 (3)
Ru(5)–Ru(2)–C(21)	87.8 (3)	Ru(2)–Ru(4)–C(41)	99.3 (3)	Ru(8)–Ru(6)–C(61)	147.0 (3)	Ru(2)–Ru(10)–C(102)	96.8 (3)
Ru(5)–Ru(2)–C(22)	94.3 (2)	Ru(2)–Ru(4)–C(42)	148.7 (3)	Ru(8)–Ru(6)–C(62)	97.3 (3)	Ru(4)–Ru(10)–C(101)	143.5 (3)
Ru(6)–Ru(2)–C(21)	145.1 (3)	Ru(3)–Ru(4)–C(41)	150.4 (3)	Ru(10)–Ru(6)–C(61)	149.9 (3)	Ru(4)–Ru(10)–C(102)	99.5 (2)
Ru(6)–Ru(2)–C(22)	97.6 (3)	Ru(3)–Ru(4)–C(42)	97.4 (3)	Ru(10)–Ru(6)–C(62)	97.9 (3)	Ru(5)–Ru(10)–C(101)	92.6 (3)
Ru(1)–Ru(3)–C(31)	90.7 (3)	Ru(8)–Ru(4)–C(41)	146.9 (2)	Ru(3)–Ru(8)–C(81)	149.1 (4)	Ru(5)–Ru(10)–C(102)	88.0 (3)
Ru(1)–Ru(3)–C(32)	90.1 (3)	Ru(8)–Ru(4)–C(42)	97.0 (3)	Ru(3)–Ru(8)–C(82)	96.6 (3)	Ru(6)–Ru(10)–C(101)	93.3 (3)
Ru(2)–Ru(3)–C(31)	98.2 (3)	Ru(9)–Ru(4)–C(41)	89.3 (2)	Ru(4)–Ru(8)–C(81)	147.4 (4)	Ru(6)–Ru(10)–C(102)	146.1 (3)
Ru(2)–Ru(3)–C(32)	146.7 (3)	Ru(9)–Ru(4)–C(42)	91.4 (2)	Ru(4)–Ru(8)–C(82)	96.6 (3)	Ru(8)–Ru(10)–C(101)	91.4 (3)
Ru(4)–Ru(3)–C(31)	148.4 (3)	Ru(10)–Ru(4)–C(41)	97.7 (2)	Ru(6)–Ru(8)–C(81)	98.1 (3)	Ru(8)–Ru(10)–C(102)	150.5 (3)
Ru(4)–Ru(3)–C(32)	94.8 (3)	Ru(10)–Ru(4)–C(42)	148.1 (2)	Ru(6)–Ru(8)–C(82)	148.2 (3)	Ru(9)–Ru(10)–C(101)	87.4 (3)
Ru(6)–Ru(3)–C(31)	98.7 (2)	Ru(2)–Ru(6)–C(61)	98.8 (3)	Ru(7)–Ru(8)–C(81)	90.6 (4)	Ru(9)–Ru(10)–C(102)	93.2 (3)
Ru(6)–Ru(3)–C(32)	148.5 (2)	Ru(2)–Ru(6)–C(62)	149.1 (3)				
(d) Carbonyl–Metal–Carbonyl							
(i) At Capping Ru Atoms							
C(11)–Ru(1)–C(12)	97.6 (4)	C(51)–Ru(5)–C(52)	94.3 (4)	C(71)–Ru(7)–C(72)	96.6 (5)	C(91)–Ru(9)–C(92)	94.7 (5)
C(11)–Ru(1)–C(13)	96.6 (4)	C(51)–Ru(5)–C(53)	93.9 (4)	C(71)–Ru(7)–C(73)	94.5 (4)	C(91)–Ru(9)–C(93)	94.2 (4)
C(12)–Ru(1)–C(13)	96.5 (4)	C(52)–Ru(5)–C(53)	96.5 (4)	C(72)–Ru(7)–C(73)	93.1 (4)	C(92)–Ru(9)–C(93)	95.9 (4)
(ii) At Ru Atoms of the Octahedron							
C(21)–Ru(2)–C(22)	94.2 (4)	C(41)–Ru(4)–C(42)	91.4 (4)	C(81)–Ru(8)–C(82)	92.5 (4)	C(101)–Ru(10)–C(102)	97.1 (4)
C(31)–Ru(3)–C(32)	93.6 (4)	C(61)–Ru(6)–C(62)	91.6 (4)				
(e) Metal–Carbon–Oxygen							
Ru(1)–C(11)–O(11)	176.4 (8)	Ru(2)–C(21)–O(21)	179.4 (9)	Ru(3)–C(32)–O(32)	179.4 (8)	Ru(5)–C(51)–O(51)	178.3 (8)
Ru(1)–C(12)–O(12)	176.8 (7)	Ru(2)–C(22)–O(22)	178.8 (7)	Ru(4)–C(41)–O(41)	178.5 (7)	Ru(5)–C(52)–O(52)	177.9 (9)
Ru(1)–C(13)–O(13)	177.8 (9)	Ru(3)–C(31)–O(31)	178.6 (9)	Ru(4)–C(42)–O(42)	178.4 (7)	Ru(5)–C(53)–O(53)	177.5 (8)

Table IV (Continued)

Ru(6)-C(61)-O(61)	178.7 (7)	Ru(7)-C(72)-O(72)	177.3 (9)	Ru(8)-C(82)-O(82)	179.2 (9)	Ru(9)-C(92)-O(92)	178.5 (8)
Ru(6)-C(62)-O(62)	178.7 (8)	Ru(7)-C(73)-O(73)	179.0 (9)	Ru(9)-C(91)-O(91)	178.5 (9)	Ru(9)-C(93)-O(93)	177.1 (8)
Ru(7)-C(71)-O(71)	178.0 (8)	Ru(8)-C(81)-O(81)	178.4 (10)				

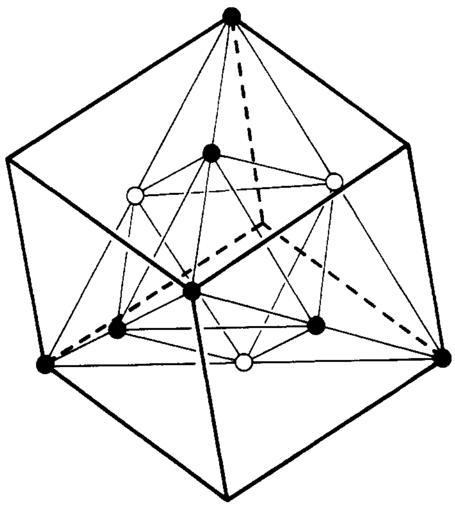

Figure 2. Relationship between the Ru_{10} core and the fcc unit cell.

cluster **3** is the first example in which the ruthenium atom has a cubic close-packed (ccp) metal array. The structure of the metal core of **3** may be seen as a tetracapped octahedron. A carbido atom is placed at the center of the octahedron.

There is a difference between the Ru-Ru bond lengths within the central octahedron (2.834 (1)-2.878 (1) Å) and those from the capping ruthenium atoms (2.751 (1)-2.792 (1) Å). The former relatively long Ru-Ru bond lengths are seen in a wide range of ruthenium clusters, that is 2.8512 (4)-2.8595 (4) Å in $Ru_3(CO)_{12}$,[9] 2.85 (±0.02)-2.90 (±0.10) Å in **1**,[10,11] 2.832 (2)-2.927 (2) Å in $[HRu_6(CO)_{18}]^-$,[12] 2.80-2.89 Å in $[Ru_6(CO)_{18}]^{2-}$,[13] 2.827 (5)-3.034 (5) Å in $Ru_6C(CO)_{17}$,[14] and 2.858 (3)-2.959 (2) Å in $H_2Ru_6(CO)_{18}$.[15] On the other hand, the latter short Ru-Ru bond lengths are reported in those participating with capping ruthenium atoms without or virtually without bridging ligands, that is, 2.778 (1)-2.807 (1) Å in $[Ru_8H_2(CO)_{21}]^{2-}$[7] and 2.787 (1) Å in $[Ru_4H_3(CO)_{12}]^-$ of C_{3v} symmetry.[16] Consequently, those short Ru-Ru bond lengths in **3** may be attributable to the capping structure.

When the structure of **3** is compared with that of **2**, the Ru-Ru bonds are 0.8% shorter than the corresponding Os-Os bonds, and the Ru-carbido bonds are 0.7% shorter than the Os-carbido bonds.[3] These findings are in agreement with the fact that the metallic radius of ruthenium is 0.9% smaller than that of osmium.[17] Similar tendencies are seen in related cases: Ru-Ru bonds of $Ru_3(CO)_{12}$[9] and $[Ru_6(CO)_{18}]^{2-}$[13] are 0.8% and 0.6% shorter than the corresponding bonds of $Os_3(CO)_{12}$[18] and $[Os_6(CO)_{18}]^{2-}$,[19] respectively.

There are two kinds of terminal carbonyl ligands in **3**; two CO's coordinate to each ruthenium atom of the carbido-centered octahedron, and three CO's coordinate to each capping ruthenium atom. Although there are no differences in the bond angles of Ru-C-O (176.4 (8)-179.4 (9)°) among these carbonyl ligands, there is a slight difference in the bond lengths. The C-O bonds coordinating to the capping Ru atoms are 0.02 Å (mean) longer than those to the carbido-centered octahedron.

There is a relatively large difference between **2** and **3** in the bond lengths where carbonyl ligands are concerned. The Ru-CO bonds of **3** are 1.3% longer than the Os-CO bonds of **2**, and the C-O bonds of **3** are, in contrast, 2.7% shorter than those of **2**,[3] which suggests less metal-CO back-bonding interactions in the ruthenium cluster than those in the osmium cluster. A similar trend can be seen in the equatorial CO groups of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ of the same structure.[9,18]

Acknowledgment. We thank Ken-ichi Sakaguchi for help with the X-ray diffraction experiments. The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 62115004) from the Ministry of Education, Science and Culture.

Supplementary Material Available: Complete listings of crystallographic data, atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles and a packing diagram of the unit cell (18 pages); a listing of structure factors (44 pages). Ordering information is given on any current masthead page.

(7) Chihara, T.; Matsuura, Y.; Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1988**, 886.
(8) Knox, S. A. R.; Morris, M. J. *J. Chem. Soc., Dalton Trans.* **1987**, 2087.
(9) (a) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655. (b) Mason, R.; Rae, A. I. M. *J. Chem. Soc. A* **1968**, 778.
(10) Ansell, G. B.; Bradley, J. S. *Acta Crystallogr.* **1980**, *B36*, 726.
(11) Johnson, B. F. G.; Lewis, J.; Sankey, S. W.; Wong, K.; McPartlin, M.; Nelson, W. J. H. *J. Organomet. Chem.* **1980**, *191*, C3.
(12) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980**, 383.
(13) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Chem. Commun.* **1979**, 735.
(14) Sirigu, A.; Bianchi, M.; Benedetti, E. *J. Chem. Soc., Chem. Commun.* **1969**, 596.
(15) Churchill, M. R.; Wormald, J. *J. Am. Chem. Soc.* **1971**, *93*, 5670.
(16) Jackson, P. E.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1978**, 920.
(17) Hume-Rothery, W.; Lonsdale, K. *International Tables for X-Ray Crystallography*; Reidel: Dordrecht, Holland, 1985; Vol. III, Table 4.3.
(18) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.
(19) McPartlin, M.; Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1976**, 883.

Contribution from the Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Electron-Transfer Series of Gold Clusters: $PtAu_8(PPh_3)_8^{2+/+/0}$, $Au_9[P(p\text{-}MeOC_6H_4)_3]_8^{3+/2+/+}$, and $Au_9(PPh_3)_8^{3+/2+/+}$

Johannes G. M. van der Linden,* Annie M. Roelofsen, and Gerard H. W. Ipskamp

Received April 26, 1988

Continuous interest in metal cluster redox chemistry results in large part from the observed structural differences effected by changes in the oxidation states of these compounds.[1-5] Gold-phosphine clusters show a fluxional behavior in solution, even at low temperatures,[6] and they exhibit an interesting electrochemical behavior. We reported the electrochemical behavior in acetone of the gold cluster $Au_9(PPh_3)_8^{3+}$, which could be reduced at a platinum electrode in two consecutive one-electron steps.[7] Re-

(1) Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 337.
(2) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 114.
(3) Lemoine, P. *Coord. Chem. Rev.* **1988**, *83*, 169.
(4) Zanello, P. *Coord. Chem. Rev.* **1988**, *83*, 199.
(5) Barley, M. H.; Drake, S. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1657.
(6) Steggerda, J. J.; Bour, J. J.; Van der Velden, J. W. A. *Recl.: J. R. Neth. Chem. Soc.* **1982**, *101*, 164.
(7) Van der Linden, J. G. M.; Paulissen, M. L. H.; Schmitz, J. E. J. *J. Am. Chem. Soc.* **1983**, *105*, 1903.

