suitable single crystals of complex **1** with other anions had failed.[25]

Although the present structure seems significantly different than that of the sulfide-bridged analogue **3** with respect to crowding of the "active" site, it is believed that this is a consequence more of solid-state effects than of chemical differences. Any differences in the chemistries of these two species that might occur are more likely a consequence of the difference in the bridging ligands (S^{2-} and Cl^-) and the overall charge of the species. In this regard it will be of obvious interest to compare the chemistries of these species.

The present structure is a significant contribution to the understanding of the chemistry of "A-frame" complexes since it verifies that the "active" site in DPM-bridged species *is* accessible to small molecules and hence it is not unexpected that SO_2 is capable of attack at this site, as the experimental evidence suggests. It is not directly obvious, however, why CO should prefer terminal attack, whereas SO_2 appears to attack the bridging site. It is hoped that further work in this area will shed light on this problem.

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Registry No. $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2][BF_4]$, 67202-35-1.

Supplementary Material Available: Tables VII and VIII, showing the idealized hydrogen parameters and the root-mean-square amplitudes of vibration of the individual atoms, respectively, and a listing of the observed and calculated structure amplitudes (28 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959.

(2) Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628.

(3) Cowie, M. *Inorg. Chem.* **1979**, *18*, 286 and references therein.

(4) Cowie, M.; Dwight, S. K.; Sanger, A. R. *Inorg. Chim. Acta* **1978**, *31*, L407.

(5) Cowie, M.; Dwight, S. K., submitted for publication.

(6) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1979**, *18*, 1209.

(7) Abbreviations used: DPM = bis(diphenylphosphino)methane; Ph = C_6H_5; TCNE = tetracyanoethylene.

(8) Mague, J. T.; Sanger, A. R. *Inorg. Chem.*, in press.

(9) Cowie, M.; Dwight, S. K., to be submitted for publication.

(10) Sanger, A. R., private communication.

(11) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 6129.

(12) The cell reduction was performed by using a modification of TRACER II by S. L. Lawson. See: Lawson, S. L.; Jacobson, R. A. "The Reduced Cell and Its Crystallographic Applications", Ames Laboratory Report IS-1141; USAEC: Iowa State University, Ames, Iowa, April 1965.

(13) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

(14) Besides local programs and some kindly supplied by Professor J. A. Ibers, the following were used in solution and refinement of the structure: FORDAP, the Fourier summation program by A. Zalkin; AGNOST, the absorption and extinction program from Northwestern University; SFLS-5, structure factors and least-squares refinement by C. J. Prewitt; ORFFE for calculating bond lengths angles and associated standard deviations by W. Busing and H. A. Levy; ORTEP, plotting program by C. K. Johnson.

(15) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

(16) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(17) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(18) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(19) Supplementary material.

(20) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 1369. Ittel, S. D.; Ibers, J. A. *Ibid.* **1975**, *14*, 636. Davis, P. H.; White, L. K.; Belford, R. L. *Ibid.* **1975**, *14*, 1753. Crommer, R. E.; Van Doorne, W.; Dubois, R. *Ibid.*, **1975**, *14*, 2462. Milbraith, D. S.; Springer, J. P.; Clardy, J. C.; Verkade, J. G. *Ibid.* **1975**, *14*, 2665.

(21) Dahl, L. F.; Martell, C.; Wampler, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 1761.

(22) Ibers, J. A.; Snyder, R. G. *Acta Crystallogr.* **1962**, *15*, 923.

(23) Bonnet, J. J.; Jeanin, Y.; Kalck, P.; Maisonnat, A.; Poilblanc, R. *Inorg. Chem.* **1975**, *14*, 743.

(24) Coetzer, J.; Gafner, G. *Acta Crystallogr., Sect. B* **1970**, *26*, 985.

(25) Mague, J. T.; Sanger, A. R., private communications.

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(Pentamethylcyclopentadienyl)rhodium and -iridium Complexes. 24.[1] Preparation, X-ray Crystal Structure, and Properties of $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4]^{2+}$

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Reaction of $[Rh_2(\mu\text{-}OH)_3(\eta^5\text{-}C_5Me_5)_2]Cl\cdot 4H_2O$ in water with hydrogen (90 °C, 1 atm) gives the green tetranuclear dication $[Rh_4H_4(C_5Me_5)_4]^{2+}$, $2Y^-$ ($Y^- = Cl^-$, PF_6^-, or BF_4^-; $2Y^- = PtCl_4^{2-}$). The BF_4^- salt was characterized by X-ray crystallography (tetragonal unit cell with $a = 11.763$ (5) Å and $c = 15.522$ (6) Å, space group $I\bar{4}$), the structure was solved by Patterson and Fourier techniques and gave a final R of 0.039. The dication contains four rhodium atoms, each bearing a $\eta^5\text{-}C_5Me_5$ ligand, arranged in a distorted tetrahedral manner (D_{2d} symmetry) with two short (2.655 (1) Å) and four long (2.829 (1) Å) Rh–Rh bonds. The presence of four hydride ligands in the cation has been shown by NMR spectroscopy; they do not take part in any major fluxional process. It is proposed that the four hydrides bridge the four long Rh–Rh bonds.

Introduction

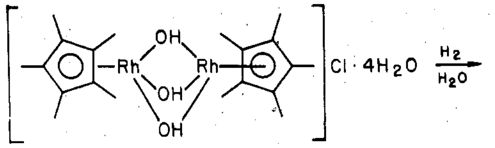
We have previously reported on (pentamethylcyclopentadienyl)rhodium and -iridium hydrides obtained from $[M_2(\eta^5\text{-}C_5Me_5)_2X_4]$ (M = Rh, X = Cl, Br, $OCOCH_3$, $OCOCF_3$; M = Ir, X = Cl, Br, I, $OCOCH_3$, $OCOCF_3$),[2,3] by reaction with hydrogen or 2-propanol in the presence of base. These complexes appear for the most part to be binuclear and a general characteristic is that the hydride(s) always occupy bridging positions. This has been shown by spectroscopic means[2,3] and by X-ray diffraction studies of $[Rh_2(C_5Me_5)_2HCl_3]$,[4] $[Ir_2(C_5Me_5)_2HCl_3]$,[5] $[Ir_2(C_5Me_5)_2H_3][PF_6]$,[6] and $[Ir_2(C_5Me_5)_2H(OCOCH_3)_2][PF_6]$.[7]

These investigations have now been extended to an examination of the reaction of the tri-μ-hydroxy complex (**1**)[8] with hydrogen.

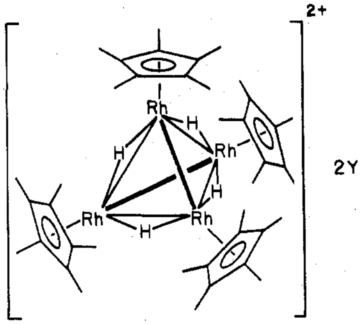
Results and Discussion

Under certain conditions we have observed that, when hydrogenation of benzene and other aromatic molecules is carried out in water with **1** as catalyst, the aqueous layer at the end of the reaction is dark green and shows a band at 624 nm in the visible spectrum.[9]

The same characteristic green color and absorption spectrum were observed when the tri-μ-hydroxy complex **1** was reacted with hydrogen (1 atm, 90 °C) in water. An impure chloride complex (**2a**) was obtained as a glassy solid on evaporation of the filtered solution; however, it proved more convenient to precipitate the salts (**2b–d**) with large anions (PF_6^-, BF_4^-, or $PtCl_4^{2-}$). All of these were very dark green, almost black, solids which had identical spectroscopic properties apart from any bands originating from the anion. The $PtCl_4^{2-}$ salt **2d** was quite insoluble but the PF_6^- and BF_4^- salts were soluble in acetone and the BF_4^- salt **2c** was also moderately soluble in water, and it was possible to obtain small crystals of **2c** suitable for an X-ray diffraction study from this solvent.



1



2a, Y = Cl
b, Y = PF_6
c, Y = BF_4
d, Y_2 = $PtCl_4$

The ^1H NMR spectra of **2a**, **2b**, and **2c** were very similar; they each showed a sharp singlet at approximately δ 2.0, arising from equivalent C_5Me_5 protons and a multiplet at δ −15.3 due to metal hydrides. Integration established that the ratio of C_5Me_5 to hydride intensities was 15:1.0 (±0.1), and analytical data on **2a–c** were consistent with the formula $[\{Rh(C_5Me_5)H_x\}_y][Y]_{y/2}$. Taken together with the NMR integrations, therefore, the ratio Rh:H:C_5Me_5 is 1:1:1 (i.e., x = 1) and the green cluster must contain an even number of rhodium atoms. The X-ray structure determination (see below) later showed the complex to be tetranuclear (y = 4).

Further support for this formulation has come from the field desorption mass spectrum of **2c**. The expected molecular ion for the dication of formula weight 956 is at m/e 478 and this was observed; in addition weak peaks due to $[Rh_4(C_5Me_5)_4H_4]^{2+}$ containing ^{13}C and/or ^2D were observed at m/e 478.5, 479, and 479.5. We thank Drs. D. and M. L. Games of University College, Cardiff, for this measurement.

There were no peaks in the IR spectra of **2a–d** which could be ascribed to terminal ν(Rh–H) and therefore we presume the hydrides to be bridging, as is the case in the previously described binuclear complexes.[2,3] For the mono-μ-hydrido-trichlorodirhodium complex $[Rh_2(C_5Me_5)_2HCl_3]$ we observed a band at 1151 cm^{-1} which we ascribed to a bridging ν(Rh–H). A weak band at 1153 cm^{-1} in the IR spectrum of complex **2b** may again arise from a bridging ν(Rh–H).

At first sight the ^1H NMR spectrum of the hydrides appeared to be a quartet; closer inspection, however, revealed that the outer lines were weaker than expected and that the two inner lines were broad and appeared as doublets under optimum resolution (see Figure 1). The pattern observed was common to all three soluble salts **2a–c**, in both D_2O and $(CD_3)_2CO$ solvents; it was also unchanged over the temperature range −60 to +50 °C in $(CD_3)_2CO$ and was the same at 60, 100, and 220 MHz.

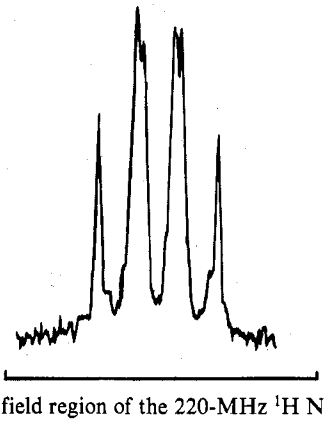


Figure 1. High-field region of the 220-MHz ^1H NMR spectrum of complex **2b** (220 Hz width).

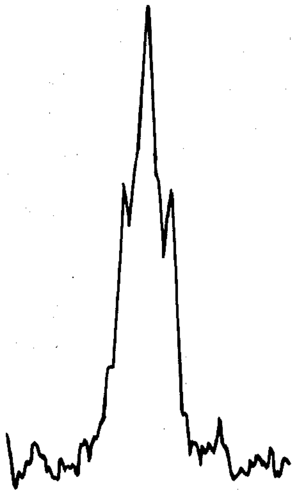


Figure 2. $^{13}C\{^1H\}$ NMR spectrum of complex **2b** in the C_5Me_5 region.

We are indebted to Dr. R. J. Goodfellow of Bristol University for a $^1H\{^{103}Rh\}$ INDOR NMR measurement on **2b**. This showed the presence of only one type of rhodium [at δ +585 to high frequency of 3.16 MHz = 0 ppm]; irradiation at the rhodium frequency collapsed the multiplet to a singlet.

These results indicate (i) that the multiplet arises only through coupling of the hydrides to the rhodiums, (ii) that there is only one type of hydride present, since the invariance of the spectrum with field strength indicates the complex pattern to arise from the couplings of one type of H to ^{103}Rh (100%, $I = {}^1/_2$) rather than from inequivalent hydrides, and (iii) that the hydrides are not taking part in any major fluxional process. If the hydride ligands were able to move freely about the framework, then the ^1H spectrum should show a regular quintet of intensities 1:4:6:4:1 arising from the coupling of the four hydrides (which would be equivalent on the NMR time scale) to all four rhodiums.[10]

The pattern of the multiplet suggests that it may arise from an $[AX]_4$ spin system. The ^{13}C spectrum of **2b** shows a singlet for the C_5Me_5 methyl carbons and a multiplet due to the ring carbons which presumably arises from an [AXX′X″X‴] spin system (Figure 2).

The X-ray structure of the tetrafluoroborate salt **2c** shows the cation to contain a tetrarhodium cluster with each rhodium being π bonded to a C_5Me_5 ligand as shown in Figure 3. The four rhodiums do not, however, form a regular tetrahedron but rather a distorted one with crystallographic $\bar{4}$ symmetry. This gives two independent sets of Rh–Rh distances; of the six Rh–Rh edges the two between the rhodiums related by the crystallographic twofold axis are short (2.655 (1) Å) and the other four are longer (2.829 (1) Å).

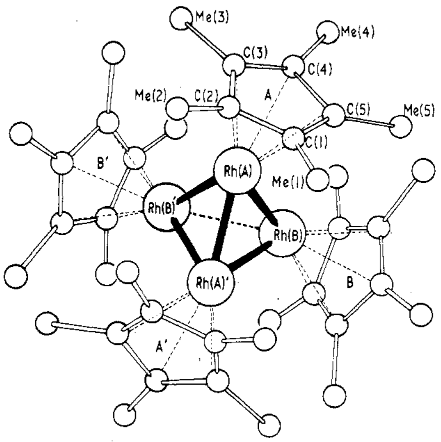


Figure 3. View of the dication of complex **2c** with hydrogens omitted.

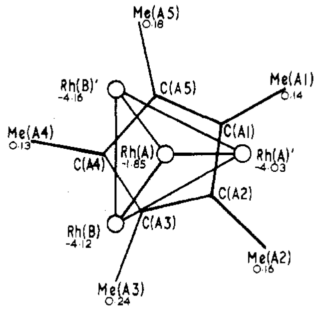


Figure 4. View of the Rh_4 tetrahedron projected onto the C_5 ring (A); perpendicular distances from the best plane of C(Al)–C(A5) in Å. The equation of this plane is $0.3100X + 0.7584Y + 0.5733Z = 3.542$, in the form $lX + mY + nZ = d$ where X, Y, and Z are coordinates, in Å, referred to the axes a, b, and c.

The C_5Me_5 ligands are, within experimental error, symmetrically η^5 bonded to rhodium (Rh–C(average) = 2.215 (14) Å), and the ring C–C bonds are also equal (average = 1.440 (19) Å) (Table II). The five ring carbons form a plane, which is 1.846 Å above the rhodium to which the ring is bonded and which is approximately symmetrically arranged with respect to the other three rhodiums (perpendicular distances 4.034, 4.117, and 4.158 Å) (see Figure 4).

The Rh–C ring distances in **2c** are somewhat longer than in other C_5Me_5Rh complexes; for example, in $[Rh_2(C_5Me_5)_2Cl_4]$ the Rh–C bonds average 2.127 (4) Å and the perpendicular distance from the metal to the center of the ring is 1.756 Å.[11] This implies a rather weaker Rh–C_5Me_5 binding in **2c**, which arises from the crowding experienced by the four C_5Me_5 rings around the tetranuclear core. This effect can also be seen in short intramolecular contacts between some of the methyl C's of one ring and those of another (e.g., Me(Al)–Me(A2′) = 3.455 Å and Me(A3)–Me(B5′) = 3.392 Å).

Another effect of the molecular crowding is that the methyl groups are bent away from the rhodium to a much larger extent (average distance from the C_5 plane is 0.17 Å) than has been found for other C_5Me_5Rh and -Ir complexes where the methyl groups are typically 0.032–0.060 Å away from the C_5 plane.[5,11]

One of the BF_4^- ions behaved well in the refinement but the other was disordered over two sites; this accounts for the large number of ν(B–F) bands observed in the IR spectrum. It may also be noted that four of the five methyl groups on each C_5Me_5 have short (BF_4^-) fluorine to (CH_3) carbon contacts (3.33–3.50 Å); since the estimated van der Waals contact C—H···F is about 3.6 Å, it is possible that the BF_4^- and the CH_3 groups are interleaved.

Attempts to definitively locate the hydrides have not been successful, but we note that many workers have found that, in polynuclear hydride clusters, the hydrides bridge the longer M–M bonds.[12] Since by NMR integration and mass spectrometry we find four hydrides in the tetranuclear cluster and also four long and two short Rh–Rh bonds, we suggest that the hydrides indeed bridge these four longer bonds. Support for this proposal comes from the observation that the Rh–Rh distance in the dinuclear mono-μ-chloro complex $[Rh_2(C_5Me_5)_2HCl_3]$ is 2.906 (1) Å,[4] reasonably close to that observed here (2.829 (1) Å) for the longer Rh–Rh bonds. Since the dinuclear complex has both H and Cl bridging the two rhodiums, the Rh–Rh distance might well be anticipated to be a little longer than in a complex where only H's bridge. The existence of a H bridge on the Rh–Rh bonds of length 2.829 Å in **2c** is also quite consistent with the suggestion by Day et al.[10b] that one hydride bridges each of the three Rh–Rh bonds of length 2.824 Å in the triangular trinuclear cluster $[Rh_3H_3\{P(OMe)_3\}_6]$.

The structure determined for **2c** shows an interesting similarity to those found for $[Ru_4H_4(CO)_{12}]$ and some phosphine- or phosphite-substituted derivatives.[13] The molecular geometry of the major isomer of $[Ru_4H_4(CO)_{12}]$ has D_{2d} symmetry and the Ru_4 core has two short (2.786 Å) and four long (2.950 Å) Ru–Ru bonds, the latter bearing the bridging hydrides. The differences, (Ru–Ru) – (Rh–Rh) = 0.121 Å, between the longer bonds and 0.131 Å between the shorter bonds of $[Ru_4H_4(CO)_{12}]$ and **2c** are probably largely due to the smaller size of Rh compared with Ru.[14] It is surprising that the two complexes, which are 60- and 58-electron species, respectively, are structurally so similar.

A feature of the substituted tetraruthenium hydride clusters is that the hydrides are highly fluxional;[18] for example, in the ^1H NMR spectrum of $[Ru_4H_4(CO)_8\{P(OMe)_3\}_4]$ the hydride signal appears as a regular quintet as if all the hydrides were equivalently coupled to all four ^{31}P nuclei. The contrast to the apparently static system in complex **2** is interesting.

Hoffmann et al.[19] have carried out a theoretical analysis of the bonding in tetranuclear hydride clusters from which it appears that a cluster of the type $[Rh_4H_4(C_5R_5)_4]^{2+}$ would be expected to be high spin (paramagnetic) with two unpaired electrons and face-bridging hydrides if the molecular skeleton had T_d symmetry.[20] Since the low-spin diamagnetic form is evidently preferred, this is accompanied by a distortion away from T_d toward D_{2d}.

Complex **2** is rather unreactive except toward acid where breakdown of the cluster quickly occurs. The complex is inert to CO (at 90 °C and 1 atm) over some hours and is a relatively poor hydrogenation catalyst. Both the lack of reactivity toward CO and the low reactivity as a hydrogenation catalyst could have been anticipated since we have previously found that even dinuclear complexes, such as $[Ir_2(\mu\text{-}H)_3(C_5Me_5)_2]^+$, are very unreactive.[21] This presumably stems from the high degree of shielding afforded by the C_5Me_5 ligands and the strengths of the metal–metal bonds.[22] As is clear from the X-ray structure (Figure 3), the metal atoms in complex **2** are very strongly shielded.

The crystal structures of some four tetranuclear tetrahydrido complexes are now known and it may be noted that whereas our $[Rh_4(C_5Me_5)_4H_4]^{2+}$ (58 electrons) and the $[Ru_4H_4(CO)_{12}]$ (60 electrons) clusters are both of D_{2d} symmetry, the 56-electron cluster $[Re_4H_4(CO)_{12}]^{23}$ and the 60-electron cluster $[Co_4H_4(C_5H_5)_4]^{2+}$ are both of T_d symmetry with face-bridging hydrides. The reasons for these variations are not clear.

Experimental Section

$[Rh_4(C_5Me_5)_4H_4]^{2+}$ Salts. Hydrogen (1 atm) was slowly bubbled, with stirring, through a solution of $[Rh_2(C_5Me_5)_2(OH)_3]Cl\cdot 4H_2O$ (0.700 g) in water (20 mL) for 10 min at 20 °C; the temperature of the solution was then raised to 90 °C and the bubbling of hydrogen continued for 9 h at a rate of ca. 1 L h^{-1}. The solution darkened, becoming first red and then black. The solution was then left to cool

Table I. Atomic Coordinates and Anisotropic[a] Thermal Parameters (×10^4, except Those for Rh Which Are ×10^5)

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Rh	4079 (7)	10520 (7)	6817 (5)	293 (7)	217 (6)	126 (3)	−57 (9)	−30 (9)	−54 (11)
Me(01)	1639 (15)	828 (14)	2652 (10)	78 (14)	75 (14)	25 (6)	35 (16)	−36 (16)	−3 (23)
Me(02)	−831 (14)	1991 (15)	2527 (11)	69 (13)	92 (16)	33 (7)	−24 (18)	61 (17)	−5 (24)
Me(03)	−849 (13)	3657 (14)	927 (11)	45 (11)	65 (12)	52 (10)	−29 (17)	−25 (16)	47 (19)
Me(04)	1607 (14)	3460 (13)	−36 (9)	75 (13)	52 (12)	23 (5)	19 (14)	10 (14)	−37 (19)
Me(05)	3136 (12)	1780 (14)	1103 (10)	28 (9)	65 (12)	39 (7)	−18 (16)	5 (13)	−1 (18)
C(01)	1209 (11)	1576 (12)	1916 (9)	44 (10)	51 (10)	19 (5)	−13 (12)	−24 (12)	−25 (17)
C(02)	134 (12)	2059 (11)	1851 (8)	59 (11)	39 (10)	21 (5)	−31 (12)	16 (14)	12 (17)
C(03)	108 (12)	2826 (11)	1121 (9)	46 (10)	37 (9)	26 (5)	−23 (12)	−6 (13)	10 (17)
C(04)	1208 (11)	2762 (9)	678 (11)	59 (10)	24 (8)	32 (5)	−12 (15)	6 (18)	−32 (15)
C(05)	1880 (11)	2002 (11)	1209 (8)	44 (10)	32 (9)	20 (5)	−17 (12)	−12 (12)	−7 (15)
B(A)	5000 (0)	0 (0)	2500 (0)	63 (0)	63 (0)	28 (0)	0 (0)	0 (0)	0 (0)
F(A)	4430 (7)	785 (5)	3020 (0)	68 (8)	167 (14)	51 (5)	−103 (16)	19 (12)	−40 (17)
B(B)	0 (0)	0 (0)	5000 (0)	174 (0)	173 (0)	12 (0)	0 (0)	0 (0)	0 (0)
F(B)	36 (37)	970 (2)	4480 (0)	395 (65)	256 (42)	93 (17)	187 (47)	250 (59)	352 (91)
B(C)	0 (0)	0 (0)	5000 (0)	174 (0)	173 (0)	12 (0)	0 (0)	0 (0)	0 (0)
F(C)	827 (77)	−508 (117)	4480 (0)	536 (99)	1106 (99)	332 (99)	−1046 (99)	−233 (99)	657 (99)

[a] The expression for the temperature factor is $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + klB_{23} + hlB_{13} + hkB_{12})]$.

Table II. Selected Interatomic Distances (Å)[a] and Bond Angles (deg)[a]

Rh(A)–Rh(B)	2.829 (1)	C(A3)–C(A4)	1.467 (19)
Rh(A)–Rh(A′)	2.655 (1)	C(A4)–C(A5)	1.450 (19)
Rh(A)–C(A1)	2.223 (14)	C(A5)–C(A1)	1.442 (19)
Rh(A)–C(A2)	2.191 (14)	C–C av	1.440
Rh(A)–C(A3)	2.224 (13)	C(A1)–Me(A1)	1.528 (21)
Rh(A)–C(A4)	2.221 (14)	C(A2)–Me(A2)	1.548 (22)
Rh(A)–C(A5)	2.217 (13)	C(A3)–Me(A3)	1.521 (21)
Rh(A)–C(A) av	2.215	C(A4)–Me(A4)	1.457 (21)
C(A1)–C(A2)	1.391 (19)	C(A5)–Me(A5)	1.509 (20)
C(A2)–C(A3)	1.449 (19)	C–Me av	1.513
Rh(B)Rh(A)Rh(B′)	55.96 (3)	C(A3)C(A4)C(A5)	104 (1)
Rh(B)Rh(A)Rh(A′)	62.02 (3)	C(A4)C(A5)C(A1)	110 (1)
C(A1)C(A2)C(A3)	109 (1)	C(A5)C(A1)C(A2)	107 (1)
C(A2)C(A3)C(A4)	108 (1)		

[a] Esd's in parentheses. Atoms related by the twofold axis are primed; thus Rh(A)–Rh(B) = Rh(A)–Rh(B′) = Rh(A′)–Rh(B) = Rh(A′)–Rh(B′) and Rh(A)–Rh(A′) = Rh(B)–Rh(B′); Rh(B)Rh(A)Rh(B′) = Rh(A)Rh(B)Rh(A′) and Rh(B)Rh(A)Rh(A′) = Rh(A′)Rh(A)Rh(B′), etc.

(18 h) under hydrogen and centrifuged to remove a black tarry precipitate and the supernatant dark green liquid filtered through a short cellulose column under nitrogen. The green solution obtained in this way could be evaporated to dryness to give a glassy blackish solid (**2a**, 30%). This material contained water of crystallization (IR, ν(OH) 1630, 3300 cm^{-1}, both strong and broad) and was contaminated by a yellow chloride-containing impurity from which it could not be purified. Anal. Calcd for $[Rh_4(C_5Me_5)_4H_4]\cdot 2Cl\cdot 8H_2O$: C, 41.0; H, 6.9; Cl, 6.1. Found: C, 39.7; H, 5.3; Cl, 10.2.

More usefully, the dication could be precipitated as the green microcrystalline $[Rh_4(C_5Me_5)_4H_4][PF_6]_2$ (**2b**, 50%) (Anal. Calcd for $C_{40}H_{64}F_{12}P_2Rh_4$: C, 38.5; H, 5.2. Found: C, 38.8; H, 4.8.), the black crystalline $[Rh_4(C_5Me_5)_4H_4][BF_4]_2$ salt (**2c**, 37%) (Anal. Calcd for $C_{40}H_{64}B_2F_8Rh_4$: C, 42.5; H, 5.7. Found: C, 42.6; H, 5.9.) or the dark green microcrystalline $[Rh_4(C_5Me_5)_4H_4][PtCl_4]\cdot H_2O$ (**2d**, 50%) (Anal. Calcd for $C_{40}H_{66}Cl_4OPtRh_4$: C, 36.6; H, 5.0; Cl, 10.8. Found: C, 36.4; H, 4.6; Cl, 10.8.) by addition of an excess of NH_4PF_6, $NaBF_4$, or K_2PtCl_4 dissolved in the minimum of water to the green solution of **2a**.

Spectroscopic data for **2a**: ^{1}H NMR (in D_2O) δ 1.85 (s, C_5Me_5), −15.33 (m, H); visible spectrum, λ_{max} 626 nm (H_2O). Spectroscopic data for **2b**: ^{1}H NMR (in $(CD_3)_2CO$) δ 2.02, −15.28; (in $(CD_3)_2CO/D_2O$) δ 1.94, −15.34; ^{13}C NMR (in $(CD_3)_2CO$) δ 12.1 (s, $C_5\mathit{Me}_5$), 102.4 (m, C_5Me_5); ^{19}F NMR δ 72.0 (d, *J*(P–F) = 707 Hz, PF_6^-); IR $\nu(PF_6)$ 834 (vs) cm^{-1}. Spectroscopic data for **2c**: ^{1}H NMR (in $(CD_3)_2CO/D_2O$) δ 1.94, −15.32; IR $\nu(BF_4)$ 1011 (s), 1036 (s), 1052 (vs), 1073 (s), and 1092 (s) cm^{-1}.

The PF_6^- salt (**2b**) was insoluble in water but was soluble in acetone; a solution in acetone–water (7:3 v/v) when allowed to evaporate slowly gave small crystals. Much better crystals were, however, obtained by allowing a saturated aqueous solution of the BF_4^- salt (**2c**) to evaporate slowly over 2 weeks in a N_2-filled desiccator over P_4O_{10}. One of these crystals was used in the structure determination.

Crystal data: $C_{40}H_{64}Rh_4(BF_4)_2$, mol wt 1130.2; tetragonal, a = 11.763 (5) Å, c = 15.522 (6) Å, U = 2147.8 Å^3, Z = 2, space group $I\bar{4}$ (from systematic absences), ρ_{calcd} = 1.747, ρ_{obsd} = 1.71 g cm^{-3}, Mo Kα radiation, λ 0.710 69 Å. The crystal used was tetrahedral with edges of 0.038 cm. (The cell constants were determined from a least-squares fit to the setting angles of 122 reflections centered manually.)

Three-dimensional X-ray data ($6.5 < 2\theta < 50°$) were collected by using a Stoe STADI-2 diffractometer in the moving crystal–stationary counter mode. Preliminary photographs showed the crystal mounted along a nonunique axis, with tetragonal $4/m$ diffraction symmetry. In each layer of data collected along the b axis, only reflections with $l > 0$ and $|h| \geq k$ were collected. Variable-width scans were measured by using ω steps of 0.01°, and background was measured at each end of the scan. A total of 1061 independent reflections were collected with $I_{obsd} \geq 3\sigma(I_{obsd})$; the data were corrected for Lorentz, polarization, and absorption (μ(Mo Kα) = 16.64 cm^{-1}) and no allowance was made for extinction. The position of the rhodium atom was obtained from a Patterson function, and structure factors based on this position alone gave R = 0.145. The remaining nonhydrogen atoms were obtained from Fourier syntheses; one of the tetrafluoroborate ions was well behaved, and the other was disordered over two sites such that the boron atom (0, 0, 0.5) lay at the center of two tetrahedra of fluorine atoms. All nonhydrogen atoms were allowed to refine as individual atoms initially and then the tetrafluoroborate ions were restricted to groups of idealized tetrahedral geometry with a B–F distance of 1.398 Å (the mean of values obtained from individual atom refinement). The populations of the disordered tetrafluoroborate ion were manually adjusted until the isotropic thermal parameters of the fluorine atoms from each set were the same—at this stage the populations were found to be in the ratio (0.65:0.35). Full-matrix least-squares refinement with anisotropic thermal parameters for all the atoms reduced R to 0.039. Atomic scattering factors were taken from ref 25. Programs used were part of the Sheffield X-ray system and calculations were performed on the Sheffield University ICL 1906S computer. Atomic coordinates and thermal parameters are given in Table I and selected interatomic distances and bond angles in Table II.

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Registry No. **1**, 12609-94-8; **2a**, 71204-91-6; **2b**, 71250-45-8; **2c**, 71250-46-9; **2d**, 71250-47-0.

Supplementary Material Available: Complete listing of bond lengths and bond angles as well as calculated and observed structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 23: A. Nutton and P. M. Maitlis, *J. Organomet. Chem.*, **166**, C21 (1979).

(2) C. White, A. J. Oliver, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1901 (1973).

(3) D. S. Gill and P. M. Maitlis, *J. Organomet. Chem.*, **87**, 359 (1975).

(4) M. R. Churchill and S. W. Y. Ni, *J. Am. Chem. Soc.*, **95**, 2150 (1973).

(5) M. R. Churchill and S. A. Julis, *Inorg. Chem.*, **16**, 1488 (1977).

(6) R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, **99**, 3872 (1977).

(7) P. M. Bailey and P. M. Maitlis, unpublished results.

(8) J. W. Kang and P. M. Maitlis, *J. Organomet. Chem.*, **30**, 127 (1971).

(9) A. Millan and P. M. Maitlis, unpublished results.

(10) See, for example, (a) S. Martinengo, B. T. Heaton, R. J. Goodfellow, and P. Chini, *J. Chem. Soc., Chem. Commun.*, 39 (1977); (b) V. W. Day, M. F. Fredrich, G. S. Reddy, A. J. Sivak, W. R. Pretzer, and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 8091 (1977).

(11) M. R. Churchill, S. A. Julis, and F. J. Rotella, *Inorg. Chem.*, **16**, 1137 (1977).

(12) R. G. Teller, R. D. Wilson, R. K. McMullan, R. F. Koetzle, and R. Bau, *J. Am. Chem. Soc.*, **100**, 3071 (1978), and references therein; M. R. Churchill, F. J. Hollander, J. R. Shapley, and D. S. Foose, *J. Chem. Soc., Chem. Commun.*, 534 (1978); A. F. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *ibid.*, 723 (1978).

(13) R. D. Wilson, S. M. Wu, R. A. Love, and R. Bau, *Inorg. Chem.*, **17**, 1271 (1978), and references therein.

(14) Useful comparisons of the sizes of Ru and Rh are difficult to make, particularly when they bear π-bonding ligands, since the geometric environments and electronic states of the metals are never identical. An approximate value of 0.136–0.139 Å for (Ru–Ru) – (Rh–Rh) can be estimated from the Ru–Ru distances in $Ru_3(CO)_{12}$ (average 2.854 Å)[15] and the nonbridged Rh–Rh distances in $Rh_4(CO)_{12}$ (2.715 Å)[16] or $[Rh_4(CO)_8\{P(OMe)_3\}_4]$ (2.718 Å).[17]

(15) M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, **16**, 2655 (1977).

(16) C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969).

(17) G. Ciani, L. Garlaschelli, M. Manassero, U. Sartorelli, and V. Albano, *J. Organomet, Chem.*, **129**, C25 (1977).

(18) S. A. R. Knox and H. D. Kaesz, *J. Am. Chem. Soc.*, **93**, 4594 (1971); J. R. Shapley, S. I. Richter, M. R. Churchill, and R. A. Lashewycz, *ibid.*, **99**, 7384 (1977), and references therein.

(19) R. Hoffmann, B. E. R. Schilling, R. Bau, H. D. Kaesz, and D. M. P Mingos, *J. Am. Chem. Soc.*, **100**, 6088 (1978).

(20) R. Hoffmann, personal communication.

(21) D. S. Gill, C. White, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 617 (1978).

(22) P. M. Maitlis, *Acc. Chem. Res.*, **11**, 301 (1978).

(23) R. Saillant, G. Barcelo, and H. D. Kaesz, *J. Am. Chem. Soc.*, **92**, 5739 (1970); R. D. Wilson and R. Bau, *ibid.*, **98**, 4687 (1976).

(24) J. Müller and H. Dorner, *Angew. Chem., Int. Ed. Engl.*, **12**, 843 (1973); G. Huttner and H. Lorenz, *Chem. Ber.*, **108**, 973 (1975).

(25) "International Tables for X-ray Crystallography", Vol. 4, Kynoch Press, Birmingham, England, 1974.

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Preparation of the Oxotetrabromo- and Oxotetraiodomolybdenum(V) Ions from Dimolybdenum Tetraacetate. Structures by X-ray Crystallography

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The $[MoOBr_4(H_2O)]^-$ ion has long been known, but its structure has been determined only roughly. We have found that a number of compounds containing this ion are formed when $Mo_2(O_2CCH_3)_4$ reacts in the presence of oxygen with aqueous HBr. These preparative reactions are reported in detail and the crystal structures of two compounds, one of which contains two crystallographically independent $[MoOBr_4(H_2O)]^-$ ions, reported. The structurally characterized compounds and their crystallographic properties are as follows. **1**, $(C_5H_5NH)_5[MoOBr_4(H_2O)]_3Br_2$: space group *Pmma*; $a = 21.875$ (3), $b = 8.487$ (1), $c = 13.724$ (2) Å; $V = 2547.9$ (1) Å^3; the unit cell contains six $[MoOBr_4(H_2O)]^-$ ions, four with *m* symmetry and two with *mm* symmetry. **2**, $(Et_4N)[MoOBr_4(H_2O)]$: space group *Pnma*; $a = 11.202$ (2), $b = 12.957$ (3), $c = 11.523$ (2) Å; $V = 1672.5$ (1) Å^3; $Z = 4$. The compound $(Et_4N)[MoOI_4(H_2O)]$ (**3**), the first reported compound containing the oxoiodo ion, is prepared in a similar way. It is isomorphous with **2** with $a = 11.592$ (3) Å, $b = 13.623$ (3) Å, $c = 11.898$ (3) Å, and $V = 1879$ (1) Å^3. The Mo=O distances in **1** are 1.61 (2) and 1.62 (2) Å, while those in **2** and **3** are 1.65 (1) and 1.65 (1) Å.

Introduction

Oxomolybdenum(V) complexes are the dominant type for that oxidation state and an enormous number of both mono- and binuclear ones are known.[1] Among the mononuclear ones the $[MoOCl_4]^-$, $[MoOCl_5]^{2-}$, and $[MoOCl_4(H_2O)]^-$ ions have been extensively studied chemically and structurally. The bromo analogues to these have long been known but have not been studied nearly so thoroughly. In fact, there has not previously been an accurate structural study reported for a bromo ion. The one reported X-ray crystallographic investigation,[2] of $(Ph_4As)[MoOBr_4(H_2O)]$, gave an Mo=O distance of 1.78 (7) Å, clearly inaccurate and likely to be much too high. So far as we can determine, no type of oxoiodomolybdenum(V) compound has ever appeared in the literature.

Our previous studies[3] of the reaction of $Mo_2(O_2CCH_3)_4$ with aqueous HCl lead to the isolation of a compound containing, inter alia, the $[MoOCl_4(H_2O)]^-$ ion. We have now found that the reaction of $Mo_2(O_2CCH_3)_4$ with aqueous HBr and HI (the latter contaminated with considerable I_2) affords crystalline products containing the $[MoOBr_4(H_2O)]^-$ and $[MoOI_4(H_2O)]^-$ ions. We report here the preparations and the crystal structure determinations of three of these compounds.

Experimental Section

Preparations. $(C_5NH_6)_5[MoOBr_4(H_2O)]_3Br_2$ (1). $Mo_2(O_2CCH_3)_4$ (0.1 g), prepared by a literature method,[4] was dissolved in 25 mL of 8 M HBr. The solution was stirred and heated to ca. 80 °C. Pyridine hydrochloride, $(C_5NH_6)Cl$ (0.1 g), was added and the solution was left to stand in an open beaker. After 8 days the yellow crystals that had formed were collected; yield 85 mg. These crystals appear to be stable in the normal laboratory atmosphere indefinitely.

$(C_2H_5)_4N[MoOBr_4(H_2O)]$ (2). This compound was prepared in a way analogous to **1**. $(C_2H_5)_4NCl$ (0.1 g) was added and the yield was 70 mg.

$(C_2H_5)_4N[MoOI_4(H_2O)]$ (3). This compound was prepared in a way analogous to that used for **2**. $Mo_2(O_2CCH_3)_4$ was dissolved in aqueous HI (45%), taken directly from the shelf and doubtless contaminated with iodine.

X-ray Crystallography. Collection of Data. Data were collected for all compounds on a Syntex $P\bar{1}$ automated four-circle diffractometer using Mo (λ 0.71073 Å) radiation with a graphite crystal monochromator in the incident beam. Rotation photographs and ω scans

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