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New Di- and Trinuclear Complexes of Ruthenium with Octahedra Joined on Faces or Edges: $Ru_2Cl_6(PBu_3)_3$, $Ru_2Cl_6(PBu_3)_4$, and $Ru_3Cl_8(PBu_3)_4$ (Bu = $CH_3CH_2CH_2CH_2$)

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The reactions of $RuCl_3\cdot 3H_2O$ with $(CH_3CH_2CH_2CH_2)_3P$ (PBu_3) in methanol and ethanol afford one or more of the following products, depending on conditions and procedures: $Ru_2Cl_6(PBu_3)_4$ (**1**), $Ru_2Cl_5(PBu_3)_4$ (**2**), $Ru_2Cl_6(PBu_3)_3$ (**3**), $Ru_3Cl_8(PBu_3)_4$ (**4**). Compounds **1**, **3**, and **4** have been characterized structurally by X-ray crystallography, and procedures for the preparation of **1** and **4** in good yields are presented. Compound **1** forms monoclinic crystals in space group $C2/c$ with four molecules in a unit cell of the following dimensions: $a = 15.567$ (5) Å, $b = 20.17$ (1) Å, $c = 20.36$ (1) Å, $\beta = 101.49$ (3)°. The $Ru_2Cl_6(PBu_3)_4$ molecule consists of two octahedra sharing a Cl···Cl edge; the phosphine ligands are axial in one octahedron and equatorial in the other. The Ru···Ru distance, 3.733 (2) Å, indicates a nonbonded, repulsive interaction between the two metal atoms, and this is confirmed by the magnetic moment of 2.14 μ_B/metal atom. Compound **3** forms monoclinic crystals in space group $P2_1/n$ with four molecules in a unit cell of the following dimensions: $a = 12.833$ (2) Å, $b = 26.999$ (6) Å, $c = 15.488$ (3) Å, $\beta = 107.70$ (3)°. The molecule is a face-sharing bioctahedron, $(PBu_3)Cl_2Ru(\mu\text{-}Cl)_3RuCl(PBu_3)_2$, with a ligand arrangement that affords a plane of symmetry containing both metal atoms. The Ru···Ru distance is 3.176 (1) Å. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with two centrosymmetric molecules in a unit cell of the following dimensions: $a = 13.953$ (3) Å, $b = 17.615$ (5) Å, $c = 13.992$ (2) Å, $\beta = 108.33$ (1)°. The molecule is a linear sequence of three face-sharing octahedra with Ru–Ru distances of 2.854 (2) Å. Metal–metal bonding is believed to occur along the presumed Ru^{III}–Ru^{II}–Ru^{III} chain.

Introduction

Over 20 years ago Nicholson[1] reported that ruthenium(III) chloride reacts with tri-*n*-butylphosphine (PBu_3) to give the products $Ru_2Cl_6(PBu_3)_4$ (**1**) and $Ru_2Cl_5(PBu_3)_4$ (**2**). Compound **1** was postulated to have an edge-sharing bioctahedral structure, but this has not heretofore been confirmed. A face-sharing bioctahedral structure for **2** was demonstrated in 1968 by X-ray crystallography.[2] Between the studies just mentioned and the present time, there have been a number of studies by the late T. A. Stephenson and co-workers on face-sharing bioctahedral complexes of ruthenium[3] but mostly of the II,II and II,III types. These have provided little structural information apart from indirect inferential conclusions and one crystal structure[3e] of $L_3Ru(Cl_3)RuCl_2L$ (L = PEt_2Ph). There is also a considerable amount of literature, much of it due to Chatt, Shaw, and Nixon, that deals mainly with II,II complexes of Ru, Cl, and various phosphines; this work is summarized, with references, in Seddon and Seddon's tome[4] on ruthenium.

However, rather little is known about binuclear III,III complexes, and the work reported here began simply as an attempt to extend our knowledge of these by characterizing Nicholson's $Ru_2Cl_6(PBu_3)_4$ (**1**). We wished to make a comparison with the only edge-sharing bioctahedral III,III compound of Ru with Cl and phosphine ligands that had previously been structurally characterized,[5] namely, $Ru_2Cl_6(dmpm)_2$ (dmpm = $Me_2PCH_2PMe_2$). However, as will be seen, considerably more interesting results were obtained. In addition to accomplishing the original objective, we have also obtained and characterized the two new species $Ru_2Cl_6(PBu_3)_3$ (**3**) and $Ru_3Cl_8(PBu_3)_4$ (**4**). Compound **3** is the first face-sharing III,III compound of ruthenium whose structure has been determined, and compound **4**, which can be regarded as a substitution product of the $Ru_3Cl_{12}{}^{4-}$ ion that we reported previously,[6] is only the second structurally defined example, for any metal, of a linear trinuclear complex consisting of three face-sharing octahedra.

Experimental Procedures

$RuCl_3\cdot 3H_2O$ (Aldrich) was used as received. Tri-*n*-butylphosphine (PBu_3) (Strem) was placed in a Schlenk tube in an argon atmosphere prior to use. Methanol and ethanol were dried by refluxing over magnesium. All reactions were carried out in an argon atmosphere. Melting points were measured with a Thomas Hoover capillary melting point apparatus with silicone oil (flash point 315 °C) and are given uncorrected. Electronic absorption spectra in CH_2Cl_2 were recorded on a Cary 17D spectrometer. Magnetic susceptibilities were measured on a Johnson Matthey magnetic balance at ambient temperature (ca. 25 °C).

Reexamination of the Nicholson Reaction. The procedure described by Nicholson[1] was repeated and found to proceed substantially as he described it. A mixture of 1.21 g (4.66 mmol) of $RuCl_3\cdot 3H_2O$ and 2.08 g (10.3 mmol) of PBu_3 was used in 5 mL of ethanol. The first crop of crystals we obtained (corresponding to what Nicholson called $[RuCl_3(PBu_3)_2]_2$ with a melting point he reported as 132–134 °C) had a weight of 0.46 g (a 16% yield, assuming it to be **1**) and mp 140–142 °C. These crystals were isolated by filtration in air, and 1 day later another crop of crystals (0.76 g; a 27% yield) with mp 96–98 °C was collected from the filtrate. The latter was shown conclusively to be **2** by determining the unit cell and showing that it was identical with that reported previously[2] for **2**.

A small portion (ca. 0.05 g) of the first crop of crystals was dissolved in boiling methanol containing a few drops of CH_2Cl_2, and this solution was placed in a refrigerator freezing compartment (ca. −5 °C). After 24 h a small crop (ca. 9 mg) of well-formed crystals was obtained. These had mp 192–193 °C. Since this did not correspond to the melting point of either **1** or **2**, one of these crystals was used for an X-ray structure determination, which showed it to be compound **4**.

Preparation of $Ru_3Cl_8(PBu_3)_4$ (4). The best procedure for preparing pure **4** is as follows. $RuCl_3\cdot 3H_2O$ (0.30 g, 1.15 mmol) is dissolved in 1.50 mL of methanol and 0.32 g (1.58 mmol) of PBu_3 is added, dropwise. The mixture is stirred for 2 h and then left undisturbed. After 8 days a dark crystalline solid is collected by filtration in air. This solid is washed with methanol (2 × 5 mL) and then dried in a vacuum: yield 0.20 g (37%); mp 196–198 °C. The electronic absorption spectrum, measured on a blue-violet solution in CH_2Cl_2, is shown in Figure 1. The maxima are at 840, 590 (vw), 460 (vw), and 385 nm (vw).

Preparation of $Ru_2Cl_6(PBu_3)_4$ (1). The best procedure for preparing pure **1** is as follows. $RuCl_3\cdot 3H_2O$ (0.61 g, 2.33 mmol) is dissolved in 2.50 mL of ethanol and PBu_3 (1.39 g, 6.87 mmol) added dropwise. No solid

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Table I. Crystal Data

	1	3	4
formula	$Ru_2Cl_6P_4C_{48}H_{108}$	$Ru_2Cl_6P_3C_{36}H_{81}$	$Ru_3Cl_8P_4C_{48}H_{108}$
fw	1224.12	1021.83	1396.1
space group	$C2/c$	$P2_1/n$	$P2_1/c$
syst abs	hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$	$0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$
a, Å	15.567 (5)	12.833 (2)	13.953 (3)
b, Å	20.17 (1)	26.999 (6)	17.615 (5)
c, Å	20.36 (1)	15.488 (3)	13.992 (2)
α, deg	90.07 (5)	90.0	90.0
β, deg	101.49 (3)	107.70 (3)	108.33 (1)
γ, deg	90.07 (4)	90.0	90.0
V, Å^3	6264.65	5112 (3)	3264 (1)
Z	4	4	2
d_{calc}, g/cm^2	1.30	1.327	1.420
cryst size, mm	0.38 × 0.12 × 0.10	0.2 × 0.4 × 0.6	0.3 × 0.15 × 0.05
μ(Mo Kα), cm^{-1}	8.60	10.11	11.288
data collcn instrum	Enraf-Nonius CAD-4S	Syntex P3	Rigaku AFC5R
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	Mo Kα (λ_α = 0.71073 Å)	Mo Kα (λ_α = 0.71073 Å)
orientation reflcns: no; range (2θ), deg	18; $20 < 2\theta < 30$	25; $20 < 2\theta < 30$	25; $20 < 2\theta < 30$
temp °C	-80 ± 1	20	21
scan method	ω	ω	ω–2θ
data collcn range (2θ), deg	$4 < 2\theta < 45$	4–50	4, 45
no. of unique data; tot. no. with $F_o^2 > 3\sigma(F_o^2)^2$	3576; 2104	6213; 4014	2783; 1598
no. of params refined	275	244	295
rel transmissn factors: max; min	1.00; 0.96	0.999; 0.763	1.00; 0.913
R^a	0.0465	0.0606	0.0665
$R_w{}^b$	0.0490	0.0865	0.0800
quality-of-fit indicator^c	1.27	1.649	1.560
largest shift/esd, final cycle	0.323	0.08	0.11
largest peak, e/Å^3	0.709	0.628	0.96

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

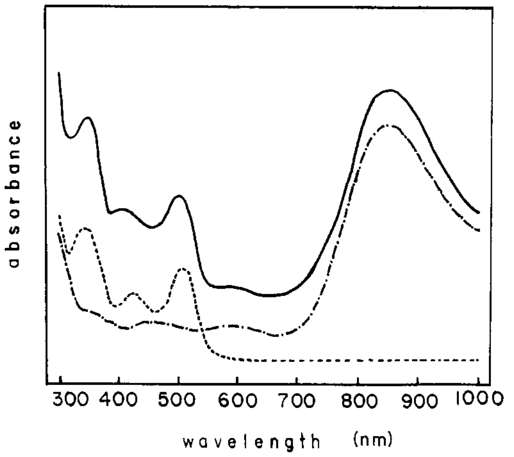

Figure 1. Electronic absorption spectra of $Ru_2Cl_6(PBu_3)_4$ (---), $Ru_3Cl_8(PBu_3)_4$ (-·-), and their mixture (—), all in CH_2Cl_2.

product separates (even after 7 days); after 3 days, the Schlenk tube is opened to the air and left undisturbed for 2 more days. A crop of brown crystals is now harvested by filtration, washed with ethanol (2 × 5 mL), and dried in a vacuum: yield 0.38 g (27%); mp 134–136 °C. The electronic absorption spectrum in CH_2Cl_2 is shown in Figure 1. The maxima are at 340, 420, and 505 nm.

Preparation of $Ru_2Cl_6(PBu_3)_3$ (3). On only one occasion when the preparation of Nicholson was repeated, the initial crop of crystals (consisting, presumably, of both **1** and **4**) was redissolved in CH_2Cl_2 and a layer of ether placed over that solution. One month later, a small amount of crystalline, brown solid had appeared. One of these crystals was used for a structure determination.

X-ray Crystallography. In each case, the structure determination was carried out in a more or less routine fashion by employing methods standard in this laboratory.[7] The usual information pertaining to data acquisition, unit cell and space group, and the refinement are summarized in Table I for compounds **1**, **3**, and **4**. We give here a few additional details for each one. The final positional and thermal parameters for each structure are available in the supplementary material.

For **1**, the heavy atoms were found by direct methods (SHELXS-86) and were consistent with space group $C2/c$. This was assumed (in preference to C/c) and allowed for satisfactory refinement. The carbon atoms were then located in an alternating series of Fourier maps and least-squares refinement cycles. Hydrogen atoms were then located and refined with the constraint that they ride on their carbon atoms. The γ and δ carbon atoms of the butyl group all had very large thermal displacement parameters and tended to give unrealistically short C–C distances until these were constrained to correspond to 1.54 Å. However, no actual disorder was seen.

For **3**, oscillation photographs were used to confirm the Laue class as $2/m$ and absorption corrections were made based on the results of ψ scans. The structure was partially solved by direct methods (SHELXS-86) and a succession of Fourier maps and least-squares refinement cycles used to locate all non-hydrogen atoms. The model finally refined treated all carbon atoms isotropically and the Ru, Cl, and P atoms anisotropically and omitted hydrogen atoms altogether.

For **4**, the ruthenium atoms were found by the Patterson interpretation provided by SHELXS-86, and all of the other non-hydrogen atoms were located by a series of Fourier maps and refinement cycles. As in the other cases, the γ and δ carbon atoms had large thermal displacement parameters and one of them, C(13), was clearly disordered over two positions, both of which were refined at half-occupancy. It is possible that other carbon atoms are also disordered, but we were unable to develop any acceptable models for these. All non-hydrogen atoms were refined anisotropically, albeit with some rather large displacement parameters. Hydrogen atoms were omitted entirely. No doubt our inability to model the probable disorder of many carbon atoms accounts for the somewhat high figures of merit for this structure.

Results and Discussion

Preparative Chemistry. We have found that the reaction of $RuCl_3 \cdot 3H_2O$ with PBu_3 is more complex than Nicholson realized. As far as compound **2** is concerned, we find that his description of how this is obtained is fully reproducible and evidently complete. With regard to his first product, which he believed to consist entirely of compound **1**, our work shows that this solid is a mixture of **1** and **4**. The solid spectrum in Figure 1 is obtained for the crude material he considered to be **1**. Therefore, the exact procedure previously reported is not a convenient way to obtain either

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(7) The calculations were done on a MicroVax II computer with an SDP package software. ψ-Scan absorption corrections were made by following: North, A. C. T.; Philips, D. C.; Mathews, *Acta Crystallogr., Sect. A.* **1968**, *A24*, 351. Structure solutions employed: Sheldrick, G. M. "SHELXS-86", Institut für Anorganische Chemie der Universität, Göttingen, F.R.G.

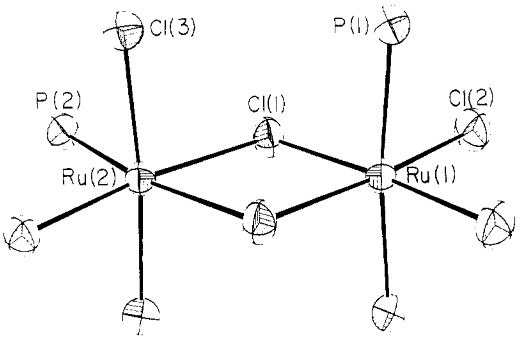

Figure 2. Structure of the central part of $Ru_2Cl_6(PBu_3)_4$ (**1**). Each atom is represented by its thermal displacement ellipsoid contoured at the 40% probability level. A 2-fold symmetry axis passing through the metal atoms relates labeled atoms to be unlabeled ones.

Table II. Selected Bond Distances (Å) and Angles (deg) for $Ru_2Cl_6(n\text{-}Bu_3P)_4$[a]

Bond Distances			
Ru(1)–Cl(1)	2.414 (3)	P(1)–C(1)	1.813 (13)
Ru(1)–Cl(2)	2.324 (3)	P(1)–C(5)	1.829 (10)
Ru(1)–P(1)	2.397 (3)	P(1)–C(9)	1.830 (10)
Ru(2)–Cl(1)	2.504 (3)	P(2)–C(13)	1.828 (9)
Ru(2)–Cl(3)	2.331 (2)	P(2)–C(17)	1.840 (11)
Ru(2)–P(2)	2.321 (3)	P(2)–C(21)	1.820 (11)
Bond Angles			
Cl(1)–Ru(1)–Cl(1)	83.05 (9)	Cl(3)–Ru(2)–P(2)	92.3 (1)
Cl(1)–Ru(1)–Cl(2)	91.21 (9)	P(2)–Ru(2)–P(2)	97.4 (1)
Cl(1)–Ru(1)–Cl(2)	174.20 (9)	Ru(1)–Cl(1)–Ru(2)	98.75 (9)
Cl(1)–Ru(1)–P(1)	93.43 (9)	Ru(1)–P(1)–C(1)	116.3 (4)
Cl(1)–Ru(1)–P(1)	91.49 (9)	Ru(1)–P(1)–C(5)	117.5 (4)
Cl(2)–Ru(1)–Cl(2)	94.5 (1)	Ru(1)–P(1)–C(9)	112.2 (3)
Cl(2)–Ru(1)–P(1)	87.9 (1)	C(1)–P(1)–C(5)	101.4 (5)
Cl(2)–Ru(1)–P(1)	87.6 (1)	C(1)–P(1)–C(9)	103.9 (5)
P(1)–Ru(1)–P(1)	173.4 (1)	C(5)–P(1)–C(9)	103.9 (5)
Cl(1)–Ru(2)–Cl(1)	79.44 (9)	Ru(2)–P(2)–C(13)	111.0 (3)
Cl(1)–Ru(2)–Cl(3)	90.84 (9)	Ru(2)–P(2)–C(17)	113.7 (4)
Cl(1)–Ru(2)–Cl(3)	93.97 (9)	Ru(2)–P(2)–C(21)	115.8 (4)
Cl(1)–Ru(2)–P(2)	91.64 (9)	C(13)–P(2)–C(17)	103.9 (5)
Cl(1)–Ru(2)–P(2)	170.74 (9)	C(13)–P(2)–C(21)	103.6 (5)
Cl(3)–Ru(2)–Cl(3)	173.7 (1)	C(17)–P(2)–C(21)	107.7 (5)
Cl(3)–Ru(2)–P(2)	83.6 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

1 or **4**, and we have worked out methods that are better suited to obtaining each one separately.

As for compound **3**, we do not yet have a real understanding of how it is formed. On the one occasion when it was isolated, it came from a CH_2Cl_2 solution of $Ru_2Cl_6(PBu_3)_4$ (which presumably also contained some $Ru_3Cl_8(PBu_3)_4$ as well) that had been layered with diethyl ether and allowed to stand for a long period of time. In view of the fact that **1** and **3** contain ruthenium in the same oxidation state and differ in composition only in the number of phosphine ligands, it is tempting to suppose that there is a simple process of extrusion of one PBu_3 ligand from **1** to give **3**. From a structural point of view this could occur very smoothly. If the phosphine ligand P(1) in Figure 2 were to leave and the chlorine ligand Cl(3) were then to lean over, with concomitant buckling along the Cl(1)···Cl(1)′ line, the transformation of **1** to **3** would be complete. It may be that over the long period of time during which **3** was formed, molecules of PBu_3 that became free reacted with adventitious oxygen to become trapped as Bu_3PO so that the return of **3** to **1** was prevented.[8]

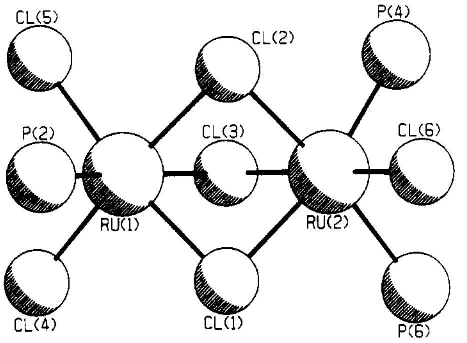

Figure 3. Ball and stick drawing of the inner portion of $Ru_2Cl_6(PBu_3)_3$ (**3**).

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $Ru_2Cl_6(n\text{-}Bu_3P)_3$[a]

Bond Distances			
Ru(1)–Ru(2)	3.176 (1)	Ru(2)–Cl(1)	2.513 (3)
Ru(1)–Cl(1)	2.385 (3)	Ru(2)–Cl(2)	2.486 (3)
Ru(1)–Cl(2)	2.406 (3)	Ru(2)–Cl(3)	2.352 (3)
Ru(1)–Cl(3)	2.597 (3)	Ru(2)–Cl(6)	2.307 (3)
Ru(1)–Cl(4)	2.308 (4)	Ru(2)–P(4)	2.328 (4)
Ru(1)–Cl(5)	2.313 (3)	Ru(2)–P(6)	2.346 (3)
Ru(1)–P(2)	2.268 (3)		
Bond Angles			
Cl(4)–Ru(1)–Cl(5)	93.5 (1)	Cl(2)–Ru(1)–Cl(3)	82.8 (1)
Cl(4)–Ru(1)–P(2)	91.4 (1)	Cl(1)–Ru(2)–Cl(2)	78.7 (1)
Cl(5)–Ru(1)–P(2)	90.8 (1)	Ru(1)–Cl(1)–Ru(2)	80.8 (1)
Cl(1)–Ru(1)–Cl(2)	82.9 (1)	Ru(1)–Cl(2)–Ru(2)	80.9 (1)
Cl(1)–Ru(1)–Cl(3)	81.77 (9)	Ru(1)–Cl(3)–Ru(2)	79.67 (8)
Cl(6)–Ru(2)–P(4)	95.8 (1)	Cl(1)–Ru(2)–Cl(3)	84.2 (1)
Cl(6)–Ru(2)–P(6)	86.5 (1)	Cl(2)–Ru(2)–Cl(3)	86.32 (9)
P(4)–Ru(2)–P(6)	97.4 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Structure and Bonding for $Ru_2Cl_6(PBu_3)_4$ (1). The structure of the central part of this compound is shown in Figure 2. A crystallographic 2-fold axis of symmetry passes through the two metal atoms, thus relating each of the unlabeled ligand atoms to one of the labeled ones. A drawing that shows all of the carbon atoms and their numbers is included with the supplementary material, along with a stereoview of the entire unit cell. Table II gives the principal bond lengths and angles in the molecule. We note also that the Ru···Ru separation is 3.733 (2) Å. This long distance, together with the indications of a repulsion between the Ru atoms, namely a Ru(1)–Cl(1)–Ru(2) angle of 98.8° and Cl(1)–Ru–Cl(1)′ angles of 79.5 and 83.1°, tell us that there is no Ru–Ru bond, even though the two d^5 configurations ought to be able to form a σ bond. We obtained confirmation of this by measuring the magnetic susceptibility at ca. 25°. The results are as follows: $\chi_g = 2.40 \times 10^{-6}$ cgsu, $\chi_{mol} = 2.95 \times 10^{-3}$ cgsu, and $\chi_{mol}^{cor} = 3.85 \times 10^{-3}$ cgsu. From this, by employing the Curie expression, $\mu_{eff} = 2.83 (\chi_{mol}^{cor}T)^{1/2}$, we obtain $\mu_{eff} = 3.03\ \mu_B$. This corresponds to 2.14 μ_B/metal atom, which is consistent with two separate, low-spin d^5 configurations.

The arrangement of the phosphine ligands is one already known in other compounds of the type $M_2X_6L_4$, e.g., $WCl_6(py)_4$, where it was first observed,[9] as well as in $Ta_2Cl_6(PMe_3)_4$[10] and in $Rh_2Cl_6(PBu_3)_4$, which is isomorphous[11] with **1**. However, this type of arrangement is not always adopted, as witness $Zr_2Cl_6(PR_3)_4$ ($PR_3 = PEt_3$, PBu_3, $PPhMe_2$)[12] where all four phosphine ligands occupy the terminal positions in the equatorial plane. It is in-

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(8) M. H. Chisholm in a private communication informs us that he has directly observed an equilibrium in solution between $W_2Cl_6(PEt_3)_4$ and $W_2Cl_6(PEt_3)_3 + PEt_3$ and that by pumping off PEt_3 he can isolate $W_2Cl_6(PEt_3)_3$ from a solution originally prepared from $W_2Cl_6(PEt_3)_4$. These results are fully consistent with our hypothesis concerning the **1** → **3** conversion. However, the two systems differ in that both W_2 compounds display strong metal–metal bonds whereas a Ru–Ru bond is absent in **1** and is probably weak in **3**.

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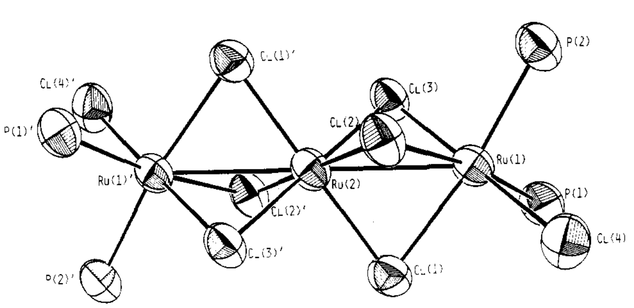

Figure 4. Structure of the central part of the $Ru_3Cl_8(PBu_3)_4$ (**4**) molecule. The inversion center at Ru(2) relates primed and unprimed atoms, which are drawn at the 50% probability level as thermal displacement ellipsoids.

teresting to note that in the Rh analogue, where the d^6 configurations make metal–metal bonding entirely impossible and dictate a net repulsive interaction, the Rh···Rh distance is 3.75 (1) Å, that is, essentially indistinguishable from that in compound **1**, where we have concluded that no metal–metal bond exists, even though the electronic structure might allow one to be formed.

Structure and Bonding for $Ru_2Cl_6(PBu_3)_3$ (3). The inner portion ($Ru_2Cl_6P_3$) of this molecule is depicted in Figure 3, and the bond distances and angles are listed in Table III. A drawing of the entire molecule giving the atom labels is included with the supplementary material. Bond distances and angles in the rest of the molecule are also available in the supplementary material. There is no crystallographically imposed symmetry, but the inner portion has approximate mirror symmetry about the plane defined by the two metal atoms and the bridging chlorine atom Cl(3).

The question of whether a Ru–Ru bond exists in this compound would be most conclusively answered if we had obtained enough of it for a magnetic measurement. Failing that, we turn to structural criteria. We cannot compare it directly with any other face-sharing bioctahedral ruthenium compound of the III,III type since this is the first such compound to be structurally characterized. For four structurally characterized II,II compounds[4] with a Ru(μ-Cl)$_3$Ru unit at the center, the Ru···Ru distances are in the range 3.35–3.44 Å; in these compounds, there is, unequivocally, no Ru–Ru bond. Thus, the remarkable contraction to 3.176 Å in **3**, even though the charges on the metal atoms have increased (a factor that usually introduces more repulsion), strongly favors the view that a Ru–Ru single bond has been formed in **3**. It may be noted here that the tremendous shortening of the Ru···Ru distance *cannot* be attributed to the occurrence of shorter Ru–Cl(br) bonds, since the latter effect is small (ca. 0.04 Å).

A comparison of the structures of **2**[2] and **3** lends further support to this conclusion. In **2** where there is also likely to be a Ru–Ru σ bond (albeit with an "extra" electron occupying a π^* orbital) the distance is 3.115 Å. A slightly shorter bond in **2** would be in keeping with the II,III pair of charges, whereby there is less metal–metal repulsion than for a III,III pair. The considerably shorter distance in the III,III compound $Ru_2Cl_6(dmpm)_2$,[5] viz., 2.933 Å, cannot be used as a benchmark because of the great structural difference, especially the buttressing effect of the dmpm ligands.

Structure and Bonding for $Ru_3Cl_8(PBu_3)_4$ (4). The inner portion ($Ru_3Cl_8P_4$) of this molecule is shown in Figure 4 and the pertinent bond distances and angles are listed in Table IV. A drawing of the entire molecule and lists of all distances and angles are included in the supplementary material. The molecule resides on a crystallographic inversion center. The structure of **4** closely resembles that of the $Ru_3Cl_{12}^{4-}$ ion[6] in all key respects. The Ru–Ru distances here, 2.854 (2) Å, are only slightly (though significantly) longer, by 0.049 (3) Å, than those in $Ru_3Cl_{12}^{4-}$. In both compounds, the octahedra about the ruthenium atoms are only slightly distorted. Therefore, in **4** as in the $Ru_3Cl_{12}^{4-}$ anion, we conclude that Ru–Ru bonding occurs. Our previous discussion[6] of this bonding, which entails the assigning of oxidation states as III,II,III and leads to the conclusion that the bond orders are nominally 0.5, applies here as well. These two species, $Ru_3Cl_{12}^{4-}$ and $Ru_3Cl_8(PBu_3)_4$ (which is, formally, its substitution product) are the only two proven cases of linear, trinuclear complexes formed by octahedra sharing faces. A similar structure has been suggested[13] but never proved for $Mo_3Cl_{12}^{3-}$.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for $Ru_3Cl_8(n\text{-}Bu_3P)_4$[a]

Bond Distances			
Ru(1)–Ru(2)	2.854 (2)	Ru(1)–P(1)	2.344 (6)
Ru(1)–Cl(1)	2.467 (6)	Ru(1)–P(2)	2.306 (6)
Ru(1)–Cl(2)	2.469 (6)	Ru(2)–Cl(1)	2.372 (6)
Ru(1)–Cl(3)	2.379 (5)	Ru(2)–Cl(2)	2.355 (4)
Ru(1)–Cl(4)	2.339 (5)	Ru(2)–Cl(3)	2.353 (5)
Bond Angles			
Cl(1)–Ru(1)–Cl(2)	82.7 (2)	Cl(3)–Ru(1)–P(2)	87.7 (2)
Cl(1)–Ru(1)–Cl(3)	87.5 (2)	Cl(4)–Ru(1)–P(1)	86.2 (2)
Cl(1)–Ru(1)–Cl(4)	91.5 (2)	Cl(4)–Ru(1)–P(2)	93.4 (2)
Cl(1)–Ru(1)–P(1)	89.7 (2)	P(1)–Ru(1)–P(2)	97.4 (2)
Cl(1)–Ru(1)–P(2)	171.7 (2)	Cl(1)–Ru(2)–Cl(2)	87.2 (2)
Cl(2)–Ru(1)–Cl(3)	88.9 (2)	Cl(1)–Ru(2)–Cl(3)	89.6 (2)
Cl(2)–Ru(1)–Cl(4)	91.9 (2)	Cl(2)–Ru(2)–Cl(3)	87.7 (2)
Cl(2)–Ru(1)–P(1)	172.1 (2)	Ru(1)–Cl(1)–Ru(2)	72.3 (2)
Cl(2)–Ru(1)–P(2)	90.4 (2)	Ru(1)–Cl(2)–Ru(2)	72.5 (1)
Cl(3)–Ru(1)–Cl(4)	178.7 (2)	Ru(1)–Cl(3)–Ru(2)	74.2 (2)
Cl(3)–Ru(1)–P(1)	92.9 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Additional Remarks Concerning 1. The absence of a metal–metal bond in $Ru_2Cl_6(PBu_3)_4$ is relevant to our general understanding of the factors favoring (and disfavoring) the formation of metal–metal bonds in edge-sharing bioctahedral molecules.[14] There is a rather comprehensive body of data on molecules of the type $M_2Cl_6(\mu\text{-dppm})_2$ and $M_2Cl_6(\mu\text{-dmpm})_2$ which shows that in every case for which we have data, from d^1–d^1 to d^5–d^5 electron configurations, M–M bonds are established.[5,15] In these compounds the two bridging diphosphinomethane ligands undoubtedly facilitate this because they lessen the tendency of repulsive forces between adjacent pairs of axial ligands to oppose the close approach of the metal atoms. Although in most cases where the pair of μ-dppm or μ-dmpm ligands are replaced by nonbridging phosphine ligands (either four PR_3 ligands or two chelating diphosphine ligands) the same or similar M–M bonding is also present, there are a few cases where it is not. The earliest[16] and most discussed[14,17] example is $Re_2Cl_6(dppe)_2$ which is paramagnetic and has an Re···Re distance of 3.809 (1) Å.

To explain the non-M–M bonded structure of $Re_2Cl_6(dppe)_2$, Shaik et al.[17] pointed out that repulsive forces (especially between adjacent axial ligands) would operate to increase the M···M distance and could lead to the loss of M–M bonding. That this factor alone is not sufficient to explain the structure of $Re_2Cl_6(dppe)_2$ is shown by the fact that there are similarly shaped $Nb_2Cl_6(LL)_2$ and $Ta_2Cl_6(LL)_2$ compounds that do have M–M bonds. In these group V molecules double bonds ($\sigma^2\pi^2$) are formed, and for the Re^{III}–Re^{III} system one would also expect double bonds ($\sigma^2\pi^2\delta^2\delta^{*2}$). What is the difference?

The fact that $Ru_2Cl_6(PBu_3)_4$ fails to form a single bond ($\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*2}$) while similar $Zr_2Cl_6(PR_3)_4$ compounds do form a single bond (σ^2) is clearly a situation comparable to that just discussed. The pattern that begins to emerge is that the elements in the latter half of each series (e.g., Re, Ru) are less able, other things being about equal, than those in the first half (e.g., Ta, Zr) to form M–M bonds. The reasons for this may be that the metal orbital overlaps for the metal atoms with higher nuclear charges (and hence more contracted d orbitals) are poorer and also that the presence of more electrons in the d shells leads to

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greater repulsive forces. In any event, it will be worthwhile to examine some additional edge-sharing bioctahedral complexes in the earliest and in the later columns to see if the pattern of M-M bonding for the former and no M-M bonding for the latter persists in a general way.

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Supplementary Material Available: Tables of positional parameters, anisotropic displacement parameters, and additional bond distances and angles and additional drawings for **1**, **3**, and **4** (25 pages); listings of calculated and observed structure factors (41 pages). Ordering information is given on any current masthead page.

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Energy Level Tailoring in Ruthenium(II) Polyazine Complexes Based on Calculated and Experimental Ligand Properties

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The effects of experimental and calculated ligand properties on the electronic structure of ruthenium(II) polyazines have been rationalized in the complexes $(L_3Ru)^{2+}$, $[(L)Ru(bpy)_2]^{2+}$, and $\{(\eta^4,\mu\text{-}L)[Ru(bpy)_2]_2\}^{4+}$, where L denotes the four isomeric bidiazines 3,3′-bipyridazine, 2,2′-bipyrazine, and 2,2′- and 4,4′-bipyrimidine and η^2-azo-2,2′-bipyridine and where η^4,μ-L denotes the symmetrically bridging ligands 2,2′-bipyrimidine, 2,5-bis(2-pyridyl)pyrazine, 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, and azo-2,2′-bipyridine. Crucial factors determining the redox potentials and metal-to-ligand charge-transfer (MLCT, d → π*) absorption energies are the ground-state basicities, the π* orbital energies, and electron densities at the coordinating atoms of the ligands. Mono- and binuclear complexes with unusually long wavelength MLCT absorptions have been obtained by applying the described strategies in the design and selection of ligands.

Introduction

The intensely colored $[Fe(bpy)_3]^{2+}$ ion (bpy = 2,2′-bipyridine), first observed more than a century ago[2] and of great analytical value,[3,4] has found its modern pendant in the homologous $[Ru(bpy)_3]^{2+}$ ion, a complex with outstanding and much investigated[5-7] photophysical and photochemical properties. Recent comprehensive reviews[5] illustrate the widespread use of this complex and of its derivatives in electron- and energy-transfer reactions. In view of the vast body of data,[5] a more selective approach toward such new compounds seems appropriate, a rational design of ligands that convey desired properties such as absorption energies and redox potentials to the complexes.

Employing two series of deliberately selected mono- and binucleating polyazine chelate ligands (Charts I and II),[8,9] we now present complete sets of electrochemical and optical absorption data for ruthenium(II) complexes (Chart III) and correlate the experimental information with recently published results from Hückel perturbation calculations for the π ligands.[8b,9b]

Chart I

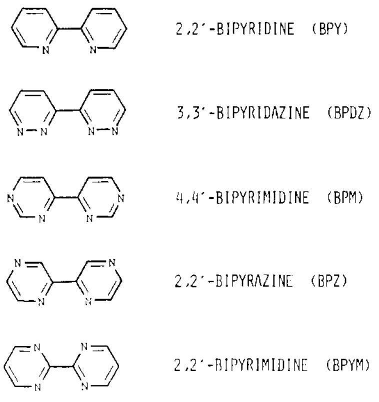

Chart II

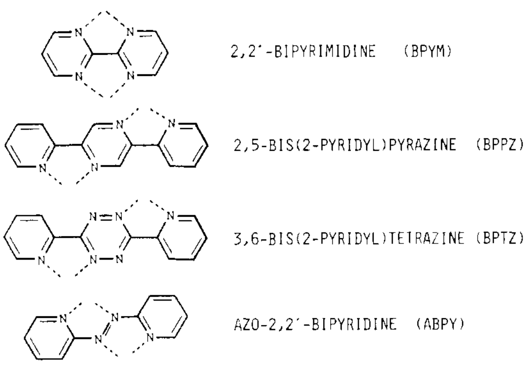

Chart III

$(L_3Ru)^{2+}$ $[(L)Ru(bpy)_2]^{2+}$

L = bpy, bpdz, bpm, bpz, bpym, abpy

$\{(\eta^4,\text{-}\mu\text{-}L)[Ru(bpy)_2]_2\}^{4+}$

η^4,μ-L = bpym, bppz, bptz, abpy

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