Inorg. Chem. **1991**, *30*, 4386-4391

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New Di- and Trinuclear Complexes of Ruthenium with Octahedra Joined on Faces or Edges. 4.[1] Compounds Containing $[(R_3P)_3RuCl_3RuCl_3Ru(PR_3)_3]^+$ Ions: Structures, EPR Spectroscopy, and Electrochemistry

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Received April 23, 1991

The preparation and properties of four new compounds are reported. These are $[Ru_3Cl_6(PEt_3)_6][RuCl_4(PEt_3)_2]$ (**1**), $[Ru_3Cl_6(PBu_3)_6][RuCl_4(PBu_3)_2]$ (**2**), $[Ru_3Cl_6(PBu_3)_6][BPh_4]$ (**3**), and $[Ru_3Cl_6(PEt_3)_6][BPh_4]$ (**4**). All of these contain a new type of derivative of the $[Ru_3Cl_{12}]^{4-}$ ion in which all six terminal chloride ligands are replaced by phosphines and a one-electron reduction has occurred. The first three of these new compounds have been characterized by X-ray crystallography, with the following results: **1**, triclinic, space group $P\bar{1}$, $a = 10.669$ (4) Å, $b = 17.682$ (6) Å, $c = 10.495$ (3) Å, $\alpha = 90.33$ (2)°, $\beta = 109.11$ (2)°, $\gamma = 99.14$ (3)°, $V = 1844$ (2) Å^3, $Z = 1$, Ru-Ru = 3.085 (1) Å; **2**, monoclinic, space group $P2_1/n$, $a = 13.490$ (2) Å, $b = 21.331$ (6) Å, $c = 23.055$ (6) Å, $\beta = 99.53$ (2)°, $V = 6542$ (3) Å^3, $Z = 2$, Ru-Ru = 3.083 (1) Å; **3**, triclinic, space group $P\bar{1}$, $a = 19.694$ (4) Å, $b = 23.193$ (4) Å, $c = 13.224$ (2) Å, $\alpha = 91.96$ (1)°, $\beta = 106.34$ (2)°, $\gamma = 100.78$ (3)°, $V = 5670$ (4) Å^3, $Z = 2$, Ru-Ru = 3.078 (1) Å.

Introduction

The first trinuclear cluster consisting of a linear array of face-sharing octahedra, $[Ru_3Cl_{12}]^{4-}$, was reported in 1980[2] and its electronic structure discussed in detail in 1983.[3] In 1989, it was shown[4] that the related neutral species $(PBu_3)_2ClRuCl_3RuCl_3RuCl(PBu_3)_2$ exists, and quite recently we have described a number of other such molecules with different phosphines.[1] In addition, the oxidation products of these, $[Ru_3Cl_8(PR_3)_4]^+$, have been isolated as the $[SbF_6]^-$ salts, and evidence of both the chemical and electrochemical nature has been presented that other redox processes should be possible for these trinuclear species with retention of their structural integrity.

We can now report that a differently substituted type of derivative can be prepared, namely $[(PR_3)_3RuCl_3RuCl_3Ru(PR_3)_3]^+$, which is also in a different oxidation state, formally "Ru_3^{7+}". In this paper, we report the preparation and properties, including several X-ray crystal structures, of four such compounds.

Experimental Section

All chemical reactions and operations, unless otherwise indicated, were done under an argon atmosphere by employing standard vacuum-line and Schlenk techniques.[5] All solvents were predried over 8-12-mesh molecular sieves and freshly distilled under nitrogen prior to use. CH_2Cl_2 was distilled from phosphorus pentoxide; benzene, *n*-hexane, and toluene were distilled from Na-K/benzophenone; ethanol and methanol were distilled from Mg. $RuCl_3{\cdot}3H_2O$ was purchased from Aldrich Chemical Co. and was either used as received or heated under vacuum for 1 h before mixing it with other chemicals. PBu_3 and PEt_3 (Strem Chemicals) were transferred into Schlenk tubes and kept under argon. These were stored in the refrigerator when not in use. $(C_4H_9)_4NPF_6$ (Aldrich) was recrystallized before use. $NaBPh_4$, purchased from Sigma Chemical Co., was used as received. Mg turnings (Fisher) were used as received.

The electronic absorption spectra in CH_2Cl_2 were recorded on a Cary 17D spectrophotometer. Cyclic voltammetric studies were carried out using a BAS 100 electrochemical analyzer. All CV studies were done in CH_2Cl_2 solutions with $(C_4H_9)_4NPF_6$ as supporting electrolyte and Ag/AgCl as reference electrode. The scan rate used for all reported

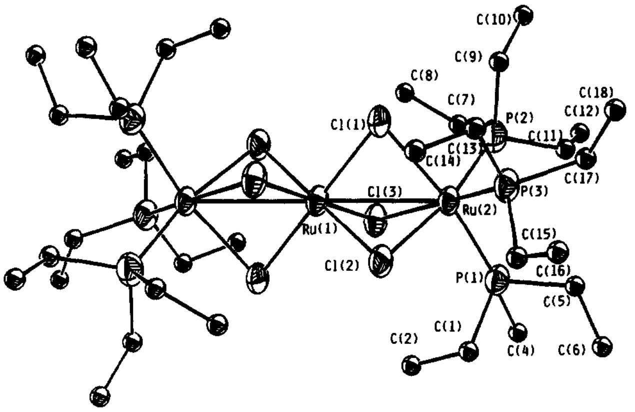

Figure 1. ORTEP drawing of the $[Ru_3Cl_6(PEt_3)_6]^+$ ion in **1**. The central Ru atom lies on a crystallographic center of inversion and relates each unlabeled atom to a labeled one. Carbon atoms were given arbitrary radii.

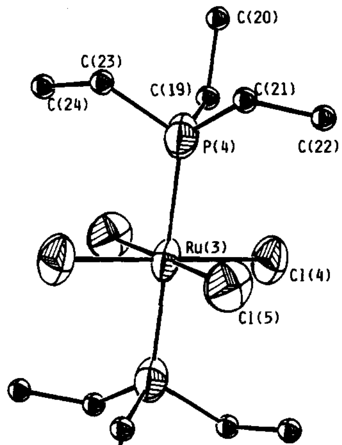

Figure 2. ORTEP drawing of the $[RuCl_4(PEt_3)_2]^-$ ion in **1**. The Ru atom lies on a crystallographic center of inversion and relates each unlabeled atom to a labeled one. Carbon atoms were given arbitrary radii.

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(1) Part 3: Cotton, F. A.; Torralba, R. C. *Inorg. Chem.* **1991**, *30*, 3293.
(2) Bino, A.; Cotton, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 608.
(3) Bursten, B. E.; Cotton, F. A.; Fang, A. *Inorg. Chem.* **1983**, *22*, 2127.
(4) Cotton, F. A.; Matusz, M.; Torralba, R. C. *Inorg. Chem.* **1989**, *28*, 1516.
(5) Shriver, D. F.; Drezden, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

0020-1669/91/1330-4386$02.50/0

Table I. Crystal Data for Compounds **1–3**

compd	**1**	**2**	**3**
formula	$Ru_4Cl_{10}P_8C_{48}H_{120}$	$Ru_4Cl_{10}P_8C_{96}H_{216}$	$Ru_3Cl_6P_6C_{96}BH_{182}$
fw	1704.09	2376.6	2049.10
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
systematic absences	none	$h0l$, $h + l - 2n + 1$ $0k0$, $k = 2n + 1$	none
a, Å	10.669 (4)	13.490 (2)	19.694 (4)
b, Å	17.682 (6)	21.331 (6)	23.193 (4)
c, Å	10.495 (3)	23.055 (6)	13.224 (2)
α, deg	90.33 (2)	90	91.96 (1)
β, deg	109.11 (2)	99.53 (2)	106.34 (2)
γ, deg	99.14 (3)	90	100.78 (2)
V, Å	1844 (2)	6542 (3)	5670 (4)
Z	1	2	2
d_{calc}, g/cm	1.535	1.207	1.20
cryst size, mm	0.20 × 0.12 × 0.40	0.38 × 0.13 × 0.20	0.35 × 0.30 × 0.38
μ(Mo Kα), cm^{-1}	13.562	7.818	6.50
data collcn instrument	Syntex P3	Syntex P3	Syntex P3
radiation (monochromated in incident beam) (λ_α, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
orientation reflcns: no.; range (2θ), deg	23; $20 < 2\theta < 28$	25; $20 < 2\theta < 25$	25; $20 < 2\theta < 30$
temp, °C	21 ± 1	21 ± 1	21 [illegible] 1
scan method	$2\theta-\omega$	$2\theta-\omega$	ω
data collcn range (2θ), deg	$4 < 2\theta < 50$	$4 < 2\theta < 50$	$4 < 2\theta < 50$
no. of unique data, tot. with $F_o > 3\sigma(F_o)$	5072, 3579	3991, 2160	12792, 8943
no. of params refined	325	535	967
transm factors, %: max, min	0.997, 0.570	0.999, 0.904	1.00, 0.954
R^a	0.0685	0.0606	0.0755
$R_w{}^b$	0.0850	0.0727	0.0956
quality-of-fit indicator^c	1.533	1.403	1.802
largest shift/esd, final cycle	0.00	0.22	0.608
largest peak, e/Å	1.875	0.416	0.875

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

Table II. Positional and Isotropic Equivalent Thermal Displacement Parameters (Å^2) for $[Ru_3Cl_6(PEt_3)_6][RuCl_4(PEt_3)_2]$ (**1**)^a

atom	x	y	z	B_{iso}
Ru(1)	0.000	0.000	0.000	2.97 (3)
Ru(2)	−0.1166 (1)	0.13684 (5)	−0.14659 (9)	2.83 (2)
Ru(3)	−0.500	0.500	−0.500	3.98 (4)
Cl(1)	−0.1382 (3)	0.0742 (2)	0.0598 (3)	3.40 (7)
Cl(2)	0.1202 (3)	0.1152 (2)	−0.0424 (3)	3.41 (7)
Cl(3)	−0.1454 (3)	−0.0016 (2)	−0.2253 (3)	3.52 (7)
Cl(4)	−0.6536 (4)	0.5713 (3)	−0.6432 (4)	6.4 (1)
Cl(5)	−0.3401 (4)	0.6132 (2)	−0.4210 (4)	6.3 (1)
P(1)	−0.0858 (3)	0.1726 (2)	−0.3465 (3)	3.33 (7)
P(2)	−0.3463 (4)	0.1375 (2)	−0.2178 (3)	3.85 (8)
P(3)	−0.0484 (3)	0.2577 (2)	−0.0388 (3)	3.41 (8)
P(4)	−0.5986 (4)	0.5177 (2)	−0.3317 (4)	4.8 (1)
C(1)	0.084 (1)	0.1662 (7)	−0.356 (1)	4.1 (3)
C(2)	0.110 (1)	0.0833 (8)	−0.367 (1)	4.6 (3)
C(3)	−0.204 (1)	0.1101 (8)	−0.494 (1)	4.5 (4)
C(4)	−0.185 (2)	0.1240 (9)	−0.631 (1)	5.3 (4)
C(5)	−0.110 (1)	0.2706 (7)	−0.401 (1)	4.4 (3)
C(6)	−0.026 (2)	0.3114 (9)	−0.481 (2)	6.6 (4)
C(7)	−0.453 (2)	0.0434 (8)	−0.287 (2)	5.7 (4)
C(8)	−0.449 (1)	−0.0178 (9)	−0.180 (1)	5.6 (4)
C(9)	−0.401 (1)	0.163 (1)	−0.072 (1)	6.1 (4)
C(10)	−0.554 (2)	0.159 (1)	−0.102 (2)	6.9 (5)
C(11)	−0.421 (1)	0.2023 (9)	−0.349 (1)	5.3 (4)
C(12)	−0.559 (2)	0.177 (1)	−0.449 (2)	9.3 (6)
C(13)	−0.017 (1)	0.2601 (8)	0.147 (1)	4.1 (3)
C(14)	0.106 (1)	0.2246 (8)	0.228 (1)	4.6 (4)
C(15)	0.118 (1)	0.3057 (7)	−0.046 (1)	4.4 (3)
C(16)	0.174 (2)	0.3858 (9)	0.026 (1)	5.7 (4)
C(17)	−0.159 (1)	0.3316 (7)	−0.100 (1)	4.8 (3)
C(18)	−0.176 (2)	0.385 (1)	0.001 (2)	9.4 (6)
C(19)	−0.781 (2)	0.5007 (9)	−0.400 (2)	6.0 (4)
C(20)	−0.859 (2)	0.509 (1)	−0.300 (2)	7.1 (5)
C(21)	−0.549 (2)	0.611 (1)	−0.232 (2)	6.8 (5)
C(22)	−0.600 (2)	0.677 (1)	−0.316 (2)	8.5 (6)
C(23)	−0.559 (2)	0.456 (1)	−0.185 (1)	6.8 (5)
C(24)	−0.607 (2)	0.371 (1)	−0.221 (2)	7.9 (6)

[a] B values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. The numbers in parentheses are the estimated standard deviations in the least significant digit.

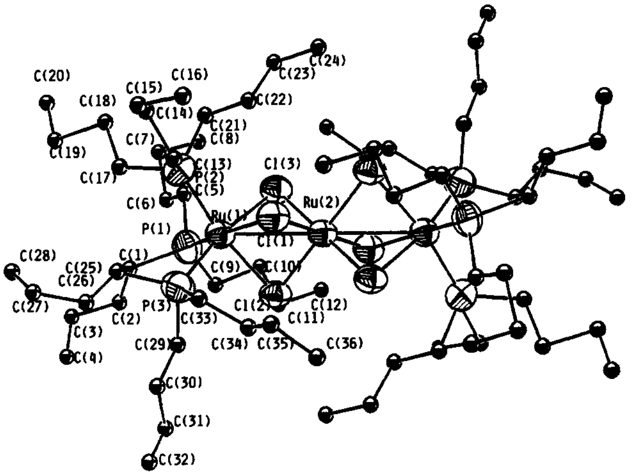

Figure 3. ORTEP drawing of the $[Ru_3Cl_6(PBu_3)_6]^+$ ion in **2**. The central Ru atom lies on a crystallographic center of inversion and relates each unlabeled atom to a labeled one. Carbon atoms were given arbitrary radii.

results was 100 mV/s unless indicated otherwise. Under these conditions Cp_2Fe had $E_{1/2}$ at 0.42–0.47 V.

The bulk magnetic susceptibility of compound **3** was measured by the Gouy method using a Johnson-Matthey magnetic balance. For CH_2Cl_2 solutions of compounds **1** and **4**, the Evans method[6] was used employing the EM390 NMR spectrometer at 90 MHz. ESR spectra of frozen CH_2Cl_2–toluene solutions were recorded at 77 K by an IBM Instruments, Inc., ER200D-SRC spectrometer equipped with Bruker ER082(155/45) magnet.

Preparation of $[Ru_3Cl_6(PBu_6)_6][RuCl_4(PBu_3)_2]$ (2) and $[Ru_3Cl_6(PBu_6)_6][BPh_4]$ (3). For compound **2**, $RuCl_3{\cdot}3H_2O$ (0.61 g, 2.33 mmol) was dissolved in 2.5 mL of ethanol and PBu_3 (1.39 g, 6.87 mmol) was added slowly. The mixture was stirred for 2 h and then left undisturbed. No solid product separated (even when the mixture was left in argon for 7 days). After 3 days the Schlenk tube was exposed to air and left undisturbed. The reaction mixture deposited large, green, red, and brown

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(6) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

Table III. Positional and Isotropic Equivalent Thermal Displacement Parameters (Å^2) for $[Ru_3Cl_6(PBu_3)_6][RuCl_4(PBu_3)_2]$ (**2**)[a]

atom	x	y	z	B_{iso}
Ru(1)	0.0334 (1)	0.08283 (9)	0.11108 (9)	5.67 (5)
Ru(2)	0.000	0.000	0.000	5.40 (7)
Ru(3)	0.000	0.500	0.000	7.59 (9)
Cl(1)	0.0346 (4)	−0.0346 (3)	0.0999 (3)	6.4 (2)
Cl(2)	0.1274 (4)	0.0766 (3)	0.0257 (3)	6.2 (2)
Cl(3)	−0.1150 (4)	0.0725 (3)	0.0294 (3)	6.2 (2)
Cl(4)	−0.0595 (5)	0.3947 (3)	−0.0048 (3)	9.6 (2)
Cl(5)	0.0963 (5)	0.4811 (4)	0.0946 (3)	10.0 (2)
P(1)	0.0152 (5)	0.1919 (3)	0.1009 (3)	7.1 (2)
P(2)	−0.0663 (5)	0.0692 (3)	0.1836 (3)	6.6 (2)
P(3)	0.1886 (5)	0.0828 (4)	0.1734 (3)	7.4 (2)
P(4)	−0.1429 (5)	0.5344 (4)	0.0413 (4)	8.6 (2)
C(1)	0.081 (2)	0.244 (1)	0.1626 (9)	7.5 (7)
C(2)	0.136 (2)	0.300 (1)	0.149 (1)	12 (1)
C(3)	0.187 (3)	0.336 (2)	0.204 (1)	17 (1)
C(4)	0.273 (3)	0.358 (2)	0.199 (2)	19 (2)
C(5)	−0.124 (2)	0.213 (1)	0.097 (1)	7.9 (7)
C(6)	−0.144 (2)	0.282 (1)	0.089 (2)	15 (1)
C(7)	−0.264 (3)	0.295 (2)	0.097 (1)	16 (1)
C(8)	−0.311 (3)	0.268 (2)	0.045 (2)	21 (2)
C(9)	0.056 (2)	0.226 (1)	0.034 (1)	7.8 (7)
C(10)	−0.015 (2)	0.207 (1)	−0.0271 (9)	6.3 (6)
C(11)	0.045 (2)	0.230 (1)	−0.074 (1)	10.1 (9)
C(12)	−0.018 (3)	0.212 (1)	−0.136 (1)	13 (1)
C(13)	−0.029 (2)	−0.002 (1)	0.2309 (9)	6.8 (6)
C(14)	−0.102 (2)	−0.012 (1)	0.278 (1)	9.9 (9)
C(15)	−0.058 (3)	−0.071 (1)	0.320 (2)	15 (1)
C(16)	−0.076 (3)	−0.122 (2)	0.285 (1)	17 (1)
C(17)	−0.068 (2)	0.135 (1)	0.239 (1)	8.0 (7)
C(18)	−0.173 (2)	0.155 (1)	0.253 (1)	10.1 (9)
C(19)	−0.132 (2)	0.217 (2)	0.298 (1)	20 (1)
C(20)	−0.223 (4)	0.233 (2)	0.305 (2)	25 (2)
C(21)	−0.205 (1)	0.055 (1)	0.1539 (9)	7.1 (7)
C(22)	−0.224 (2)	−0.012 (1)	0.1259 (9)	7.5 (7)
C(23)	−0.337 (2)	−0.015 (1)	0.088 (1)	11 (1)
C(24)	−0.356 (2)	−0.082 (2)	0.060 (1)	14 (1)
C(25)	0.187 (2)	0.110 (1)	0.249 (1)	8.9 (8)
C(26)	0.272 (3)	0.120 (2)	0.288 (1)	16 (1)
C(27)	0.278 (3)	0.143 (2)	0.353 (1)	17 (1)
C(28)	0.214 (3)	0.200 (2)	0.360 (2)	19 (2)
C(29)	0.286 (2)	0.132 (1)	0.144 (1)	8.2 (7)
C(30)	0.396 (2)	0.129 (2)	0.176 (1)	13 (1)
C(31)	0.459 (2)	0.170 (2)	0.140 (2)	20 (1)
C(32)	0.544 (3)	0.168 (2)	0.164 (2)	27 (2)
C(33)	0.250 (2)	0.002 (1)	0.187 (1)	7.9 (7)
C(34)	0.289 (2)	−0.024 (1)	0.128 (1)	7.5 (7)
C(35)	0.311 (2)	−0.095 (1)	0.138 (1)	11 (1)
C(36)	0.361 (2)	−0.121 (1)	0.086 (1)	12 (1)
C(37)	−0.255 (2)	0.483 (1)	0.034 (1)	9.1 (8)
C(38)	−0.312 (2)	0.479 (1)	−0.029 (1)	9.0 (8)
C(39)	−0.406 (2)	0.432 (1)	−0.028 (1)	13 (1)
C(40)	−0.470 (2)	0.435 (1)	−0.088 (2)	14 (1)
C(41)	−0.191 (2)	0.612 (1)	0.012 (2)	13 (1)
C(42)	−0.278 (2)	0.640 (1)	0.036 (1)	12 (1)
C(43)	−0.332 (2)	0.695 (1)	−0.009 (1)	15 (1)
C(44)	−0.406 (3)	0.727 (2)	0.020 (2)	22 (2)
C(45)	−0.114 (2)	0.549 (1)	0.121 (1)	12 (1)
C(46)	−0.122 (2)	0.487 (2)	0.154 (1)	12 (1)
C(47)	−0.078 (2)	0.489 (2)	0.219 (2)	16 (1)
C(48)	−0.080 (2)	0.435 (2)	0.254 (1)	17 (1)

[a] B values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. The numbers in parentheses are the estimated standard deviations in the least significant digit.

crystals after 3 days. These were recovered after 2 more days, separated manually, and later identified by X-ray crystallography as $[Ru_3Cl_6(PBu_3)_6][RuCl_4(PBu_3)_2]$ (**2**; yield = 14%), $[Ru_2Cl_3(PBu_3)_6][RuCl_4(PBu_3)_2]$[7] (yield = 7%), and $Ru_2Cl_6(PBu_3)_4$ (yield = 20%), respectively. The electronic absorption spectrum of **2** had maxima at 370 nm (ϵ = 12.7 × 10^3 cm^{-1} M^{-1}), 380 nm (ϵ = 12.8 × 10^3 cm^{-1} M^{-1}), 500 nm (3.73 × 10^3 cm^{-1} M^{-1}), and 850 nm (7.57 × 10^3 cm^{-1} M^{-1}). The mother liquor left after isolating the initial solid products deposited green crystals of $Ru_2Cl_5(PBu_3)_4$[7] within 2 days (yield = 13%).

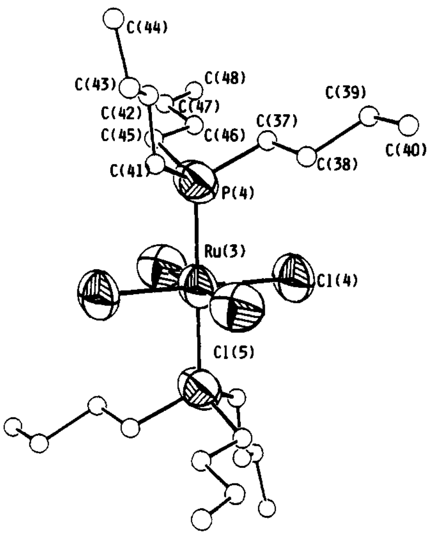

Figure 4. ORTEP drawing of the $[RuCl_4(PBu_3)_2]^-$ ion in **2**. The Ru atom lies on a crystallographic center of inversion and relates each unlabeled atom to a labeled one. Carbon atoms were given arbitrary radii.

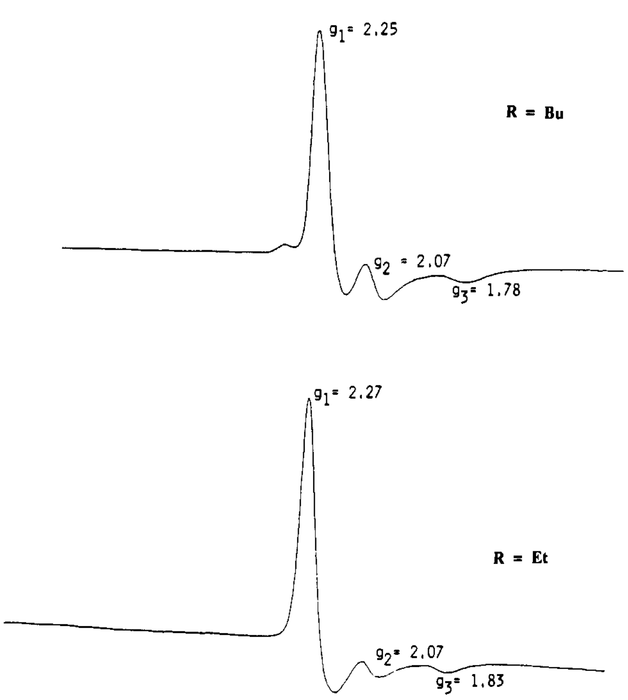

Figure 5. EPR spectra of frozen CH_2Cl_2–toluene solutions of $[Ru_3Cl_6(PR_3)_6][BPh_4]$, R = Et (**1**) and Bu (**2**), at 77 K.

For compound **3**, 0.02 g (0.008 mmol) of $[Ru_3Cl_6(PBu_3)_6][RuCl_4(PBu_3)_2]$ was dissolved in methanol. The green $[Ru_3Cl_6(PBu_3)_6][BPh_4]$ (**3**) precipitated immediately upon addition of excess $NaBPh_4$. This was filtered out, washed with methanol (2 × 3 mL), and dried in air. The yield was 0.014 g (96%). A greater amount of this product was obtained by adding $NaBPh_4$ earlier in the preparation of $[Ru_3Cl_6(PBu_3)_6][RuCl_4(PBu_3)_2]$, i.e., by adding $NaBPh_4$ 2 days after exposing the reaction mixture to air and after isolating any $Ru_2Cl_6(PBu_3)_4$ crystals that may have formed. The resulting precipitate formed was a mixture of $[Ru_2Cl_3(PBu_3)_6][BPh_4]$[7] and $[Ru_3Cl_6(PBu_3)_6][BPh_4]$. The solid mixture was filtered out, washed with methanol (2 × 3 mL), and dried in air. This was recrystallized by layering its benzene solution with *n*-hexane. Yellow and green crystals of the resulting $[BPh_4]^-$ salts of the diruthenium and triruthenium ions, respectively, were obtained within 2 days. Separation was done manually. Compound **3** was present as 65%–75% of the mixture based on several trials. The electronic ab-

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[7] Part 2: Cotton, F. A.; Torralba, R. C. *Inorg. Chem.* **1991**, *30*, 2196.

Table IV. Positional and Isotropic Equivalent Thermal Displacement Parameters (Å^2) for $[Ru_3Cl_6(PBu_3)_6][BPh_4]$ (3)[a]

atom	x	y	z	B_{iso}	atom	x	y	z	B_{iso}
Ru(1)	0.65285 (5)	0.00378 (4)	0.64814 (7)	3.91 (3)	C(42)	0.722 (1)	0.3358 (8)	0.282 (1)	10.3 (7)
Ru(2)	0.500	0.000	0.500	3.74 (4)	C(43)	0.708 (1)	0.320 (1)	0.389 (2)	14 (1)
Ru(3)	0.66367 (6)	0.50585 (4)	0.08654 (8)	5.20 (3)	C(44)	0.633 (1)	0.307 (1)	0.384 (2)	18 (1)
Ru(4)	0.500	0.500	0.000	5.22 (4)	C(45)	0.8091 (8)	0.4280 (7)	0.144 (1)	8.8 (6)
Cl(1)	0.5733 (2)	0.0778 (1)	0.6234 (2)	4.68 (8)	C(46)	0.837 (1)	0.3787 (8)	0.108 (2)	10.7 (8)
Cl(2)	0.5350 (2)	−0.0646 (1)	0.6298 (2)	4.66 (8)	C(47)	0.916 (1)	0.386 (1)	0.133 (2)	14 (1)
Cl(3)	0.6040 (1)	−0.0076 (1)	0.4516 (2)	4.39 (8)	C(48)	0.958 (1)	0.441 (1)	0.124 (3)	17 (1)
Cl(4)	0.5920 (2)	0.5851 (1)	0.0472 (3)	6.1 (1)	C(49)	0.7148 (8)	0.6074 (6)	−0.085 (1)	6.6 (5)
Cl(5)	0.5613 (2)	0.4630 (2)	0.1556 (3)	6.0 (1)	C(50)	0.6437 (8)	0.5911 (7)	−0.181 (1)	7.7 (5)
Cl(6)	0.5733 (2)	0.4589 (1)	−0.0826 (3)	5.9 (1)	C(51)	0.624 (1)	0.6526 (9)	−0.217 (2)	12.9 (8)
P(1)	0.7113 (2)	−0.0726 (1)	0.6300 (2)	4.72 (9)	C(52)	0.563 (1)	0.643 (1)	−0.309 (2)	15 (1)
P(2)	0.7481 (2)	0.0792 (1)	0.6499 (2)	4.75 (9)	C(53)	0.7359 (8)	0.4864 (6)	−0.120 (1)	7.4 (5)
P(3)	0.6708 (2)	0.0092 (2)	0.8295 (3)	5.8 (1)	C(54)	0.784 (1)	0.5089 (8)	−0.191 (1)	10.8 (7)
P(4)	0.7090 (2)	0.4219 (2)	0.1251 (3)	6.1 (1)	C(55)	0.796 (2)	0.454 (2)	−0.263 (3)	20 (2)
P(5)	0.7384 (2)	0.5429 (2)	−0.0126 (3)	5.9 (1)	C(56)	0.731 (2)	0.448 (2)	−0.331 (3)	26 (3)
P(6)	0.7287 (2)	0.5607 (2)	0.2447 (3)	6.9 (1)	C(57)	0.8380 (7)	0.5675 (6)	0.053 (1)	7.3 (5)
C(1)	0.7532 (7)	−0.0637 (5)	0.523 (1)	5.3 (4)	C(58)	0.8776 (9)	0.6238 (7)	0.021 (1)	8.2 (5)
C(2)	0.7868 (7)	−0.1161 (6)	0.494 (1)	6.0 (4)	C(59)	0.9598 (9)	0.6335 (7)	0.090 (1)	9.3 (6)
C(3)	0.8285 (8)	−0.1001 (7)	0.412 (1)	7.4 (5)	C(60)	1.000 (1)	0.6919 (8)	0.069 (1)	10.7 (7)
C(4)	0.782 (1)	−0.0853 (8)	0.310 (1)	10.4 (7)	C(61)	0.8177 (8)	0.5437 (7)	0.320 (1)	8.2 (5)
C(5)	0.6503 (6)	−0.1472 (5)	0.590 (1)	5.4 (4)	C(62)	0.855 (1)	0.578 (1)	0.426 (2)	14 (1)
C(6)	0.5962 (7)	−0.1546 (6)	0.479 (1)	6.6 (4)	C(63)	0.922 (1)	0.554 (1)	0.479 (2)	14 (1)
C(7)	0.554 (1)	−0.222 (1)	0.468 (2)	13.3 (8)	C(64)	0.916 (2)	0.522 (2)	0.557 (3)	23 (2)
C(8)	0.495 (2)	−0.232 (1)	0.407 (5)	33 (3)	C(65)	0.6802 (8)	0.5511 (9)	0.354 (1)	10.8 (7)
C(9)	0.7876 (7)	−0.0849 (6)	0.744 (1)	6.1 (4)	C(66)	0.619 (1)	0.581 (1)	0.332 (2)	13.8 (9)
C(10)	0.7915 (7)	−0.1503 (6)	0.767 (1)	6.1 (4)	C(67)	0.576 (2)	0.554 (1)	0.417 (2)	18 (1)
C(11)	0.8515 (8)	−0.1497 (6)	0.871 (1)	7.4 (5)	C(68)	0.511 (2)	0.586 (2)	0.395 (2)	25 (2)
C(12)	0.857 (1)	−0.2150 (7)	0.894 (1)	9.9 (7)	C(69)	0.750 (1)	0.641 (1)	0.224 (2)	15 (1)
C(13)	0.7554 (7)	0.0958 (6)	0.515 (1)	6.7 (4)	C(70)	0.790 (2)	0.678 (1)	0.274 (3)	23 (2)
C(14)	0.6954 (8)	0.1275 (6)	0.454 (1)	7.6 (5)	C(71)	0.795 (2)	0.743 (1)	0.259 (3)	19 (2)
C(15)	0.697 (1)	0.117 (1)	0.333 (2)	16 (1)	C(72)	0.773 (3)	0.762 (2)	0.167 (3)	28 (3)
C(16)	0.638 (1)	0.135 (1)	0.262 (2)	20 (1)	C(73)	0.9633 (5)	0.2625 (4)	0.4457 (6)	5.2 (4)
C(17)	0.7421 (7)	0.1496 (5)	0.714 (1)	6.0 (4)	C(74)	0.9259 (5)	0.3083 (4)	0.4250 (6)	7.3 (5)
C(18)	0.7931 (9)	0.2071 (7)	0.702 (1)	9.5 (6)	C(75)	0.9132 (5)	0.3393 (4)	0.5078 (6)	9.2 (6)
C(19)	0.772 (2)	0.261 (1)	0.730 (3)	17 (1)	C(76)	0.9379 (5)	0.3245 (4)	0.6113 (6)	8.7 (6)
C(20)	0.723 (2)	0.272 (1)	0.759 (3)	21 (2)	C(77)	0.9754 (5)	0.2787 (4)	0.6319 (6)	8.9 (6)
C(21)	0.8422 (7)	0.0682 (6)	0.720 (1)	7.6 (5)	C(78)	0.9881 (5)	0.2477 (4)	0.5491 (6)	7.6 (5)
C(22)	0.9057 (7)	0.1131 (8)	0.712 (1)	9.4 (6)	C(79)	0.9805 (4)	0.1566 (4)	0.3678 (6)	5.0 (4)
C(23)	0.9746 (7)	0.0976 (9)	0.783 (2)	12.2 (8)	C(80)	0.9318 (4)	0.1248 (4)	0.4145 (6)	6.4 (5)
C(24)	1.030 (2)	0.134 (1)	0.780 (3)	22 (2)	C(81)	0.9276 (4)	0.0644 (4)	0.4210 (6)	7.3 (5)
C(25)	0.7619 (7)	0.0344 (6)	0.9202 (9)	6.6 (4)	C(82)	0.9721 (4)	0.0358 (4)	0.3807 (6)	6.5 (4)
C(26)	0.770 (1)	0.0277 (7)	1.040 (1)	9.7 (6)	C(83)	1.0208 (4)	0.0676 (4)	0.3340 (6)	6.0 (4)
C(27)	0.854 (1)	0.0500 (9)	1.104 (1)	11.6 (8)	C(84)	1.0250 (4)	0.1280 (4)	0.3275 (6)	5.7 (4)
C(28)	0.899 (1)	0.013 (1)	1.073 (2)	19 (1)	C(85)	0.9185 (6)	0.2234 (4)	0.2349 (7)	5.8 (4)
C(29)	0.6245 (9)	0.0660 (9)	0.879 (1)	9.1 (6)	C(86)	0.8464 (6)	0.2167 (4)	0.2342 (7)	6.4 (4)
C(30)	0.544 (1)	0.0448 (9)	0.856 (1)	10.7 (7)	C(87)	0.7916 (6)	0.2077 (4)	0.1382 (7)	8.7 (6)
C(31)	0.515 (1)	0.104 (1)	0.874 (2)	14 (1)	C(88)	0.8088 (6)	0.2054 (4)	0.0430 (7)	8.4 (6)
C(32)	0.434 (2)	0.084 (1)	0.839 (2)	17 (1)	C(89)	0.8809 (6)	0.2121 (4)	0.0437 (7)	7.8 (6)
C(33)	0.629 (1)	−0.0541 (8)	0.887 (1)	9.3 (6)	C(90)	0.9357 (6)	0.2211 (4)	0.1397 (7)	6.9 (5)
C(34)	0.660 (1)	−0.1038 (9)	0.882 (1)	10.7 (8)	C(91)	1.0629 (5)	0.2643 (4)	0.3514 (6)	4.7 (4)
C(35)	0.625 (2)	−0.160 (2)	0.937 (3)	20 (2)	C(92)	1.0678 (5)	0.3121 (4)	0.2908 (6)	6.1 (4)
C(36)	0.563 (2)	−0.186 (2)	0.870 (3)	25 (3)	C(93)	1.1352 (5)	0.3464 (4)	0.2968 (6)	8.3 (6)
C(37)	0.6661 (9)	0.3570 (6)	0.023 (1)	8.3 (6)	C(94)	1.1978 (5)	0.3329 (4)	0.3634 (6)	8.9 (7)
C(38)	0.588 (1)	0.3314 (7)	0.022 (1)	8.9 (6)	C(95)	1.1930 (5)	0.2850 (4)	0.4239 (6)	7.5 (5)
C(39)	0.554 (1)	0.290 (1)	−0.089 (2)	14 (1)	C(96)	1.1255 (5)	0.2507 (4)	0.4179 (6)	6.3 (4)
C(40)	0.476 (2)	0.268 (1)	−0.104 (2)	19 (1)	B	0.9828 (8)	0.2275 (6)	0.351 (1)	4.7 (4)
C(41)	0.6957 (8)	0.3946 (6)	0.250 (1)	7.7 (5)					

[a] B values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. Starred atoms are in calculated positions and were not refined. The numbers in parentheses are the estimated standard deviations in the least significant digit.

sorption spectrum had maxima at 385 nm (4.14 × 10^3 cm^{-1} M^{-1}) and 840–850 nm (5.28 × 10^3 cm^{-1} M^{-1}).

Preparation of $[Ru_3Cl_6(PEt_3)_6][Y]$. (a) Y = $RuCl_4(PEt_3)_2^-$ (1). The synthesis and isolation of $[Ru_3Cl_6(PEt_3)_6][RuCl_4(PEt_3)_2]$ were effected in the same way as in the corresponding PBu_3 compound using 0.6 g (2.33 mmol) of $RuCl_3{\cdot}3H_2O$ and 0.83 g (7 mmol) of PEt_3. The yield, though not measured, was low after 2 days but was more substantial after 8 days. The electronic absorption spectrum had maxima at 365, 375, 500, and 830 nm.

(b) Y = BPh_4 (4). An excess of $NaBPh_4$ was added to the reaction mixture 2 days after reacting 0.6 g (2.33 mmol) of $RuCl_3{\cdot}3H_2O$ and 0.83 g (7 mmol) of PEt_3 in 3 mL of ethanol. A 0.35-g amount of green $[Ru_3Cl_6(PEt_3)_6][BPh_4]$ precipitated immediately. The electronic absorption spectrum had maxima at 385 and 840–850 nm.

X-ray Crystallography. The structure determination for each compound was carried out by employing procedures routine in this laboratory.[8] Pertinent crystallographic data and refinement results are listed in Table I. The final positional and thermal parameters, together with full tables of bond distances and angles, are available in the supplementary material.

For **1**, preliminary tests revealed that the crystal system was triclinic and the Laue group was $\bar{1}$. The heavy atoms were found by direct methods and were consistent with the assumed space group, $P\bar{1}$. The

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(8) The calculations were done on a MicroVax II computer with an SDP package software. ψ-Scan absorption corrections were made following: North, A. C. T.; Phillips, D. C.; Matthews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351. Structure solutions employed: Sheldrick, G. M. SHELXS-86. Institut fur Anorganische Chemie der Universitat, Götingen, FRG, 1986. Sheldrick, G. M. SHELX-76, Program for Crystal Structure Determination. University of Cambridge, Cambridge, England, 1976.

Table V. Selected Bond Distances (Å) and Angles (deg) for $[Ru_3Cl_6(PEt_3)_6][RuCl_4(PEt_3)_2]$ (**1**)[a]

Bond Distances			
Ru(1)–Cl(1)	2.346 (3)	Ru(2)–P(1)	2.303 (4)
Ru(1)–Cl(2)	2.355 (3)	Ru(2)–P(2)	2.318 (4)
Ru(1)–Cl(3)	2.362 (3)	Ru(2)–P(3)	2.306 (3)
Ru(2)–Cl(1)	2.500 (3)	Ru(3)–Cl(4)	2.367 (4)
Ru(2)–Cl(2)	2.495 (3)	Ru(3)–Cl(5)	2.361 (4)
Ru(2)–Cl(3)	2.518 (3)	Ru(3)–P(4)	2.372 (5)
Bond Angles			
Cl(1)–Ru(1)–Cl(1′)	180.00 (0)	Cl(3)–Ru(2)–P(1)	89.1 (1)
Cl(1)–Ru(1)–Cl(2)	87.6 (1)	Cl(3)–Ru(2)–P(2)	93.5 (1)
Cl(1)–Ru(1)–Cl(2′)	92.4 (1)	Cl(3)–Ru(2)–P(3)	167.4 (1)
Cl(1)–Ru(1)–Cl(3)	87.1 (1)	P(1)–Ru(2)–P(2)	96.2 (1)
Cl(1)–Ru(1)–Cl(3′)	92.9 (1)	P(1)–Ru(2)–P(3)	96.1 (1)
Cl(2)–Ru(1)–Cl(2′)	180.00 (0)	P(2)–Ru(2)–P(3)	97.3 (1)
Cl(2)–Ru(1)–Cl(3)	86.8 (1)	Cl(4)–Ru(3)–Cl(4′)	180.00 (0)
Cl(2)–Ru(1)–Cl(3′)	93.2 (1)	Cl(4)–Ru(3)–Cl(5)	90.5 (1)
Cl(3)–Ru(1)–Cl(3′)	180.00 (0)	Cl(4)–Ru(3)–Cl(5′)	89.5 (1)
Cl(1)–Ru(2)–Cl(2)	81.3 (1)	Cl(4)–Ru(3)–P(4)	88.2 (2)
Cl(1)–Ru(2)–Cl(3)	80.6 (1)	Cl(4)–Ru(3)–P(4′)	91.8 (2)
Cl(1)–Ru(2)–P(1)	169.0 (1)	Cl(5)–Ru(3)–Cl(5′)	180.00 (0)
Cl(1)–Ru(2)–P(2)	88.2 (1)	Cl(5)–Ru(3)–P(4)	91.8 (2)
Cl(1)–Ru(2)–P(3)	93.3 (1)	Cl(5)–Ru(3)–P(4′)	88.2 (2)
Cl(2)–Ru(2)–Cl(3)	80.6 (1)	P(4)–Ru(3)–P(4′)	180.00 (0)
Cl(2)–Ru(2)–P(1)	93.4 (1)	Ru(1)–Cl(1)–Ru(2)	79.0 (1)
Cl(2)–Ru(2)–P(2)	168.7 (2)	Ru(1)–Cl(2)–Ru(2)	78.94 (9)
Cl(2)–Ru(2)–P(3)	87.6 (1)	Ru(1)–Cl(3)–Ru(2)	78.33 (8)

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

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[Ru_3Cl_6(PBu_3)_6][RuCl_4(PBu_3)_2]$ (**2**)[a]

Bond Distances			
Ru(1)–Cl(1)	2.519 (6)	Ru(2)–Cl(1)	2.389 (6)
Ru(1)–Cl(2)	2.515 (6)	Ru(2)–Cl(2)	2.375 (5)
Ru(1)–Cl(3)	2.521 (5)	Ru(2)–Cl(3)	2.368 (6)
Ru(1)–P(1)	2.346 (7)	Ru(3)–Cl(4)	2.381 (7)
Ru(1)–P(2)	2.331 (7)	Ru(3)–Cl(5)	2.380 (7)
Ru(1)–P(3)	2.334 (6)	Ru(3)–P(4)	2.402 (8)
Bond Angles			
Cl(1)–Ru(1)–Cl(2)	81.6 (2)	Cl(1)–Ru(2)–Cl(3)	87.6 (2)
Cl(1)–Ru(1)–Cl(3)	81.6 (2)	Cl(1)–Ru(2)–Cl(3′)	92.4 (2)
Cl(1)–Ru(1)–P(1)	168.0 (2)	Cl(2)–Ru(2)–Cl(2′)	180.00 (0)
Cl(1)–Ru(1)–P(2)	87.9 (2)	Cl(2)–Ru(2)–Cl(3)	87.7 (2)
Cl(1)–Ru(1)–P(3)	92.5 (2)	Cl(2)–Ru(2)–Cl(3′)	92.3 (2)
Cl(2)–Ru(1)–Cl(3)	81.5 (2)	Cl(3)–Ru(2)–Cl(3′)	180.00 (0)
Cl(2)–Ru(1)–P(1)	91.9 (2)	Cl(4)–Ru(3)–Cl(4′)	180.00 (0)
Cl(2)–Ru(1)–P(2)	168.6 (2)	Cl(4)–Ru(3)–Cl(5)	90.7 (3)
Cl(2)–Ru(1)–P(3)	88.0 (2)	Cl(4)–Ru(3)–Cl(5′)	89.3 (3)
Cl(3)–Ru(1)–P(1)	87.4 (2)	Cl(4)–Ru(3)–P(4)	91.1 (3)
Cl(3)–Ru(1)–P(2)	92.5 (2)	Cl(4)–Ru(3)–P(4′)	88.9 (3)
Cl(3)–Ru(1)–P(3)	180.00 (0)	Cl(5)–Ru(3)–Cl(5′)	180.00 (0)
P(1)–Ru(1)–P(2)	97.6 (3)	Cl(5)–Ru(3)–P(4)	92.3 (3)
P(1)–Ru(1)–P(3)	97.5 (3)	Cl(5)–Ru(3)–P(4′)	87.7 (3)
P(2)–Ru(1)–P(3)	97.1 (2)	P(4)–Ru(3)–P(4′)	180.00 (0)
Cl(1)–Ru(2)–Cl(1′)	180.00 (0)	Ru(1)–Cl(1)–Ru(2)	77.8 (2)
Cl(1)–Ru(2)–Cl(2)	87.4 (2)	Ru(1)–Cl(2)–Ru(2)	78.1 (2)
Cl(1)–Ru(2)–Cl(2′)	92.6 (2)	Ru(1)–Cl(3)–Ru(2)	78.1 (2)

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

Table VII. Selected Bond Distances (Å) and Angles (deg) for $[Ru_3Cl_6(PBu_3)_6][BPh_4]$ (**3**)[a]

Bond Distances			
Ru(1)–Cl(1)	2.502 (3)	Ru(3)–Cl(6)	2.495 (3)
Ru(1)–Cl(2)	2.498 (3)	Ru(3)–P(4)	2.305 (4)
Ru(1)–Cl(3)	2.490 (3)	Ru(3)–P(5)	2.304 (4)
Ru(1)–P(1)	2.326 (4)	Ru(3)–P(6)	2.310 (4)
Ru(1)–P(2)	2.308 (3)	Ru(4)–Cl(4)	2.347 (3)
Ru(1)–P(3)	2.319 (3)	Ru(4)–Cl(5)	2.353 (3)
Ru(2)–Cl(1)	2.345 (2)	Ru(4)–Cl(6)	2.349 (3)
Ru(2)–Cl(2)	2.358 (3)	B–C(73)	1.65 (2)
Ru(2)–Cl(3)	2.345 (3)	B–C(79)	1.66 (2)
Ru(3)–Cl(4)	2.504 (4)	B–C(85)	1.68 (1)
Ru(3)–Cl(5)	2.498 (4)	B–C(91)	1.64 (2)
Bond Angles			
Cl(1)–Ru(1)–Cl(2)	81.3 (1)	Cl(5)–Ru(3)–P(4)	88.3 (1)
Cl(1)–Ru(1)–Cl(3)	80.3 (1)	Cl(5)–Ru(3)–P(5)	167.3 (1)
Cl(1)–Ru(1)–P(1)	166.5 (1)	Cl(5)–Ru(3)–P(6)	93.3 (1)
Cl(1)–Ru(1)–P(2)	88.3 (1)	Cl(6)–Ru(3)–P(4)	93.9 (1)
Cl(1)–Ru(1)–P(3)	92.4 (1)	Cl(6)–Ru(3)–P(5)	87.5 (1)
Cl(2)–Ru(1)–Cl(3)	80.97 (9)	Cl(6)–Ru(3)–P(6)	167.7 (2)
Cl(2)–Ru(1)–P(1)	93.3 (1)	P(4)–Ru(3)–P(5)	96.7 (2)
Cl(2)–Ru(1)–P(2)	169.0 (1)	P(4)–Ru(3)–P(6)	96.7 (2)
Cl(2)–Ru(1)–P(3)	87.2 (1)	P(5)–Ru(3)–P(6)	96.6 (1)
Cl(3)–Ru(1)–P(1)	86.6 (1)	Cl(4)–Ru(4)–Cl(4)	180.00 (0)
Cl(3)–Ru(1)–P(2)	93.9 (1)	Cl(4)–Ru(4)–Cl(5)	87.5 (1)
Cl(3)–Ru(1)–P(3)	166.9 (1)	Cl(4)–Ru(4)–Cl(5)	92.5 (1)
P(1)–Ru(1)–P(2)	96.1 (1)	Cl(4)–Ru(4)–Cl(6)	87.5 (1)
P(1)–Ru(1)–P(3)	99.7 (1)	Cl(4)–Ru(4)–Cl(6)	92.5 (1)
P(2)–Ru(1)–P(3)	96.8 (1)	Cl(5)–Ru(4)–Cl(5)	180.00 (0)
Cl(1)–Ru(2)–Cl(1)	180.00 (0)	Cl(5)–Ru(4)–Cl(6)	86.6 (1)
Cl(1)–Ru(2)–Cl(2)	87.62 (9)	Cl(5)–Ru(4)–Cl(6)	93.4 (1)
Cl(1)–Ru(2)–Cl(2)	92.38 (9)	Cl(6)–Ru(4)–Cl(6)	180.00 (0)
Cl(1)–Ru(2)–Cl(3)	86.7 (1)	Ru(1)–Cl(1)–Ru(2)	78.78 (9)
Cl(1)–Ru(2)–Cl(3)	93.3 (1)	Ru(1)–Cl(2)–Ru(2)	78.63 (9)
Cl(2)–Ru(2)–Cl(2)	180.00 (0)	Ru(1)–Cl(3)–Ru(2)	79.02 (9)
Cl(2)–Ru(2)–Cl(3)	87.0 (1)	Ru(3)–Cl(4)–Ru(4)	78.7 (1)
Cl(2)–Ru(2)–Cl(3)	93.0 (1)	Ru(3)–Cl(5)–Ru(4)	78.7 (1)
Cl(3)–Ru(2)–Cl(3)	180.00 (0)	Ru(3)–Cl(6)–Ru(4)	78.8 (1)
Cl(4)–Ru(3)–Cl(5)	81.1 (1)	C(73)–B–C(79)	112.2 (9)
Cl(4)–Ru(3)–Cl(6)	81.1 (1)	C(73)–B–C(85)	111 (1)
Cl(4)–Ru(3)–P(4)	168.8 (1)	C(73)–B–C(91)	104.4 (8)
Cl(4)–Ru(3)–P(5)	93.0 (1)	C(79)–B–C(85)	101.4 (7)
Cl(4)–Ru(3)–P(6)	87.5 (1)	C(79)–B–C(91)	113 (1)
Cl(5)–Ru(3)–Cl(6)	80.5 (1)	C(85)–B–C(91)	114.5 (9)

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

Table VIII. Selected Structural Parameters for Linear Trinuclear Ru Complexes with Octahedra Joined on Faces

	Ru–Ru, Å	α_1,[a] deg	α_2,[b] deg	β,[c] deg
$[Ru_3Cl_6(PR_3)_6][Y]$				
R = Bu				
Y = $[RuCl_4(PR_3)_2]^-$	3.08	81.6	87.6	78.0
Y = $[BPh_4]^-$	3.08	80.1	87.1	78.8
R = Et				
Y = $[RuCl_4(PR_3)_2]^-$	3.08	80.8	87.2	78.8
$Ru_3Cl_8(PR_3)_4$				
R = Bu	2.85	86.4	88.2	73.0
R = Et	2.86	86.3	90.0	73.0
R = Me	2.83	87.0	88.2	72.1
$Ru_3Cl_8(PMe_3)_4 \cdot C_6H_6$	2.84	86.7	91.6	72.4
$[Ru_3Cl_{12}]^{4-}$	2.81	88.5	88.9	72.4
$[Ru_3Cl_8(PEt_3)_4][SbF_6]$	2.91	84.9	89.3	74.5

[a] $\alpha_1 = \angle Cl_b{-}Ru_t{-}Cl_b$. [b] $\alpha_2 = \angle Cl_b{-}Ru_c{-}Cl_b$. [c] $\beta = \angle Ru{-}Cl_b{-}Ru$.

remaining non-hydrogen atoms were located by an alternating series of Fourier maps and least-squares refinement cycles. Hydrogen atoms were excluded in the model. Table II lists the final positional and isotropic equivalent thermal displacement parameters.

For **2**, oscillation photographs confirmed the Laue group to be $2/m$ and the results of the preliminary tests which had revealed that the crystal system was monoclinic with a primitive lattice. The data set had systematic conditions uniquely corresponding to space group $P2_1/n$. The heavy atoms were found by the Patterson heavy-atom method and were consistent with the determined space group. The rest of the non-hydrogen atoms were located in an alternating series of Fourier maps and least-squares refinement cycles. The structure was finally refined with all the atoms having anisotropic thermal parameters. Thermal displacement parameters for the carbon atoms in the *n*-butyl groups were typically large, but disorder was not directly observed. Hydrogen atoms were not included in the model. Table III lists the final positional and isotropic equivalent thermal displacement parameters.

For **3**, the heavy atoms were found by direct methods and were consistent with space group $P\bar{1}$. This was assumed in preference over $P1$ and allowed for satisfactory refinement. The rest of the non-hydrogen atoms were located by an alternating series of Fourier maps and least-squares refinement cycles. After satisfactory refinement with all the atoms anisotropic, phenyl hydrogen atoms were added in calculated positions but

Table IX. Properties of the $[Ru_3Cl_6(PR_3)_6]^+$ Ions in Their $[BPh_4]^-$ Salts

	R = Et	R = Bu
(a) Magnetic and EPR		
μ_{eff}, μ_B/Ru_3	1.92	1.79
g_1	2.27	2.25
g_2	2.07	2.07
g_3	1.83	1.78
(b) Cyclic Voltammetry (V)		
oxidation σ_n^2/σ_n	+0.96	+1.06
oxidation $\sigma_n^2\sigma_a/\sigma_n^2$	+0.74	+0.88
reduction $\sigma_n^2\sigma_a^2/\sigma_n^2\sigma_a$	−0.38	−0.47

were not refined. The C–C distances in the *n*-butyl groups, however, were unrealistically long until they were constrained to correspond to 1.5 Å. The phenyl carbon atoms were also constrained to form a regular hexagon and were refined as a rigid group. Methyl and methylenic hydrogen atoms were not included in the model. Table IV lists the final positional and isotropic equivalent thermal displacement parameters.

Results and Discussion

Preparative Chemistry. The preparative methods for Ru/Cl/PR_3 compounds in general, as already discussed in parts 2[7] and 3,[1] tend to be complicated because of the everpresent possibility of obtaining two or even three products from the same pot. This is particularly true for **1** and **2**. These compounds were formed as coproducts in efforts to synthesize $Ru_2Cl_6(PEt_3)_4$ and $Ru_2Cl_6(PBu_3)_4$ in pure form, that is, without the $Ru_3Cl_8(PR_3)_4$ compounds as impurities. No really clean, efficient procedure has yet been found. When a $PR_3/RuCl_3\cdot3H_2O$ molar ratio of 2.9 is employed, the dimers are formed and can be isolated in the early stages but compounds **1** and **2** are then also formed, along with $[Ru_2Cl_3(PBu_3)_6][RuCl_4(PBu_3)_2]$ in the case of **2**. The formation of products with ruthenium in lower mean oxidation states is obviously attributable to the larger quantity of phosphine present, which is, of course, a reducing agent. On the other hand, when a lower molar ratio is used mixtures of $Ru_2Cl_6(PBu_3)_4$ and $Ru_3Cl_8(PR_3)_4$ are invariably obtained. Whether the labile nature of these systems or the dual nature of the PR_3 as both ligand and reducing agent will allow further improvement of the preparative procedures for **1** and **2** is at present an open question.

Once **1** and **2** are obtained, however, **3** and **4** can be obtained from them straightforwardly by anion exchange in the presence of excess $NaBPh_4$. These transformations are important because they show unambiguously that the cations and anions in **1** and **2** are +1 and −1 species.

X-ray Crystal Structures. The cation and anion in **1** are shown in Figures 1 and 2; those in **2** are shown in Figures 3 and 4. The cation in **3** is essentially identical to that in **2**. Tables V–VII present the principal bond distances and angles in **1–3**. The $[RuCl_4(PR_3)_2]^-$ ions are very similar to each other and to the previously described $[RuCl_4(PBu_3)_2]^-$ anion[7] and require no further comment.

The three $[Ru_3Cl_6(PR_3)_6]^+$ ions are virtually identical to each other in terms of their core dimensions, as shown in Table VIII. Clearly, in comparison with the $Ru_3Cl_8(PR_3)_4$ molecules,[1] the $[Ru_3Cl_{12}]^{4-}$ ion,[2] and even the $[Ru_3Cl_8(PEt_3)_4]^+$ ion,[1] they show that there is much less bonding interaction between the Ru atoms. This is exactly what would be expected from the previous MO calculations[1,3] for these trinuclear species. The $[Ru_3Cl_6(PR_3)_6]^+$ ions have one more core electron than the $Ru_3Cl_8(PR_3)_4$ or $[Ru_3Cl_{12}]^{4-}$ species, and this is predicted to occupy a σ-antibonding orbital, thus lowering the formal Ru–Ru bond order from $^1/_2$ to $^1/_4$. Thus, an increase of Ru–Ru distances from the range 2.81–2.86 Å to 3.08 Å is consistent with this prediction.

Magnetic, EPR, and Electrochemical Properties. These are summarized in Table IX for **3** and **4**. The EPR spectra for **3** and **4** are displayed in Figure 5. One unpaired electron with a rhombic *g* tensor is clearly consistent with the presence of one electron in the antibonding σ orbital, σ_a, as postulated.

The cyclic voltammetry is also very consistent with the proposed electronic structure. Removal of the antibonding electron, $\sigma_n^2\sigma_a \rightarrow \sigma_n^2$, is observed at 0.74–0.88 V, and further oxidation by removal of a nonbonding electron, $\sigma_n^2 \rightarrow \sigma_n$, is also seen at 0.96–1.06 V. One of these processes, $\sigma_n^2 \rightarrow \sigma_n$, was seen previously for the $Ru_3Cl_8(PR_3)_4$ compounds,[1] while reduction by addition of an antibonding electron, $\sigma_n^2 \rightarrow \sigma_n^2\sigma_a$, was observed (0.77–0.84 V) instead of oxidation. Of greater interest is the fact that the reduction wave corresponding to the $\sigma_n^2\sigma_a \rightarrow \sigma_n^2\sigma_a^2$ process is now in the range −0.38 to −0.47 V, that is, much more accessible than it was (ca. −0.9 V) in the $Ru_3Cl_8(PR_3)_4$ molecules. This suggests that the neutral molecules $Ru_3Cl_6(PR_3)_6$, in which Ru–Ru bonding is abolished entirely, may be isolable.

Acknowledgment. We thank the National Science Foundation for support. We also wish to thank Dr. Larry Falvello for assistance with crystallography and Dr. George Bates for the use of the EPR spectrometer.

Registry No. **1**, 136676-26-1; **2**, 133471-37-1; **3**, 136676-28-3; **4**, 136676-29-4; $[Ru_2Cl_3(PBu_3)_6][RuCl_4(PBu_3)_2]$, 133471-32-6; $Ru_2Cl_6(PBu_3)_4$, 119719-52-7; $Ru_2Cl_5(PBu_3)_4$, 133471-33-7; Ru, 7440-18-8.

Supplementary Material Available: Tables of final anisotropic displacement parameters, complete positional parameters, and bond lengths and bond angles (19 pages); listings of calculated and observed structure factors (84 pages). Ordering information is given on any current masthead page.