viz., C(P1) is further from its ring neighbors, and from iron, than are the other cyclopentadienyl carbon atoms. Thus, the C(P1)–C(P2) and C(P1)–C(P5) distances of 1.427 (5) and 1.414 (5) Å can be compared with an average value of 1.377 Å for the remaining C–C distances. The Fe–C(P1) bond length of 2.071 (4) Å is substantially larger than the average distance for the other Fe–C bonds, 2.019 (7) Å. Moreover, the C(P2)–C(P1)–C(P5) angle is only 103.1 (4)°, which is significantly smaller than all other C–C–C angles and can be compared with the average value of 108° in these planar C$_5$ rings. Since the same effect has been observed in four different metallocene-substituted boron cage species but not, in general, in organo-substituted metallocenes,[15] this perturbation of the

C$_5$H$_4$ ring can reasonably be attributed to the electron-delocalized borane framework and may involve a shift of electron density from the substituted carbon toward the cage. It will be noted that the boron atom bonded to the ferrocenyl moiety in the present structure [B(4)] is coplanar with the C$_5$H$_4$ ring (Table IV); this would permit a p orbital of suitable symmetry on B(4) to engage in a π interaction with the cyclopentadienyl system and thus facilitate ring-to-cage electron delocalization. Moreover, the B(4)–C(P1) distance of 1.516 (6) Å is relatively short for a B–C bond (sum of covalent radii is 1.59 Å), consistent with a bond-order intermediate between 1 and 2.

Registry No. (C$_5$H$_5$)Fe(C$_5$H$_4$)(CH$_3$)$_4$C$_4$B$_8$H$_7$, 74282-50-1; (C-H$_3$)$_4$C$_4$B$_8$H$_8$, 54387-54-1; FeCl$_2$, 7758-94-3; NaC$_5$H$_5$, 4984-82-1.

Supplementary Material Available: A listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, The Pennsylvania State University,
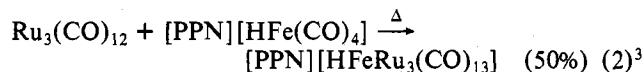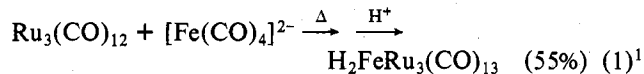University Park, Pennsylvania 16802

Synthesis and Structural Characterization of [PPN][ClRu$_4$(CO)$_{13}$]: A Butterfly Cluster with a Bridging Chloride

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The new cluster [PPN][ClRu$_4$(CO)$_{13}$] (PPN = (Ph$_3$P)$_2$N$^+$) results from the reaction of Ru$_3$(CO)$_{12}$ with [PPN]Cl in refluxing THF. It has been characterized by its spectroscopic properties and by a complete single-crystal X-ray diffraction study. It crystallizes in the space group P$\bar{1}$ with Z = 2 and unit cell dimensions a = 14.536 (2) Å, b = 16.732 (3) Å, c = 11.508 (8) Å, α = 91.35 (3)°, β = 93.88 (3)°, γ = 64.79 (2)°, and V = 2527 (2) Å. Diffraction data (0° < 2θ ≤ 50°) were collected with an Enraf-Nonius CAD4 automated diffractometer, using graphite-monochromatized Mo Kα radiation, and the structure was refined to R = 0.061 and R$_w$ = 0.087 for 5924 independent reflections with I ≥ 3.0σ(I). The molecule possesses a butterfly arrangement of the four Ru atoms with the chlorine bridging the two end metals of the open butterfly. Each Ru bears three terminal carbonyls, and one carbonyl ligand bridges the two Ru atoms which constitute the hinge of the butterfly.

The condensation of a carbonylmetalate with a closed metal carbonyl trimer is a valuable method for the synthesis of tetranuclear mixed-metal clusters,[1-5] e.g., eq 1 and 2. While

$$Ru_3(CO)_{12} + [Fe(CO)_4]^{2-} \xrightarrow{\Delta} \xrightarrow{H^+}$$
$$H_2FeRu_3(CO)_{13} \quad (55\%) \quad (1)^1$$

$$Ru_3(CO)_{12} + [PPN][HFe(CO)_4] \xrightarrow{\Delta}$$
$$[PPN][HFeRu_3(CO)_{13}] \quad (50\%) \quad (2)^3$$

attempting to extend this synthetic procedure to prepare derivatized mixed-metal clusters by bringing the desired substituent into the cluster along with the carbonylmetalate reagent, e.g., H in eq 2, we allowed [PPN][PhC(O)Fe(CO)$_4$] (PPN = (Ph$_3$P)$_2$N$^+$) to react with Ru$_3$(CO)$_{12}$ with the aim of obtaining an acyl-substituted FeRu$_3$ cluster. However, the red crystalline product obtained from these reactions in ~25%

yield proved not to be an acyl cluster but rather a new Ru$_4$ cluster, [PPN][ClRu$_4$(CO)$_{13}$]. Herein we report the characterization of this compound by a complete single-crystal X-ray diffraction study which shows it to have an unusual butterfly structure with a bridging chloride. Significantly, we have also found that the best preparative method for the cluster is the reaction of Ru$_3$(CO)$_{12}$ with [PPN]Cl in refluxing THF.

Experimental Section

Ru$_3$(CO)$_{12}$[6] and [PPN][PhC(O)Fe(CO)$_4$][7] were prepared according to the literature procedures. MeLi (Aldrich Chemical Corp.), Fe-(CO)$_5$, and [PPN]Cl (Alfa Ventron Corp.) were purchased and used as received. Tetrahydrofuran (THF), hexane, petroleum ether, and diethyl ether were dried by distillation from sodium benzophenone ketyl under N$_2$. All manipulations of compounds were accomplished by using standard Schlenk techniques.[8] IR spectra were recorded on a Perkin-Elmer 580 grating infrared spectrophotometer using 0.5-mm NaCl solution IR cells. These were sealed with Luer-lock fittings and purged with N$_2$ to record spectra of air-sensitive solutions.

Preparation of [PPN][ClRu$_4$(CO)$_{13}$]. In the most convenient preparation, a solution of Ru$_3$(CO)$_{12}$ (210 mg, 0.337 mmol) and [PPN]Cl (188 mg, 0.337 mmol) in 40 mL of dried, deoxygenated

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**Table I.** Data for the X-ray Diffraction Study of
[PPN] [ClRu$_4$(CO)$_{13}$]

Crystal Parameters

crystal system: triclinic	space group: $P\bar{1}$
$a = 14.536$ (2) Å	$V = 2527$ (2) Å^3
$b = 16.732$ (3) Å	temp = 23 °C
$c = 11.508$ (8) Å	$Z = 2$
$\alpha = 91.35$ (3)°	mol wt = 1342.47
$\beta = 93.88$ (3)°	d(calcd) = 1.764 g cm^{-3}
$\gamma = 64.79$ (2)°	

Measurement of Intensity Data

radiation: Mo Kα ($\lambda = 0.71073$ Å)
monochromator: graphite crystal
reflctns measd: $+h$, $\pm k$, $\pm l$
max $2\theta = 50.0°$
min $2\theta = 0°$
scan type = θ–2θ
scan speeds: variable (see text)
reflctns collected: 9024 unique reflctns; 5924
    observed above $3\sigma(I)$ level
std reflctns: 3 measured every 2 h (~200 reflctns);
    no significant decay over the course of the data collection

THF was refluxed for 1 h under N$_2$ during which time the color changed from yellow to dark red. Evaporation of THF gave a red solid which was extracted with deoxygenated Et$_2$O until the extract was colorless. The volume of solution was reduced to 30 mL and the compound recrystallized by slow diffusion of hexane into the Et$_2$O solution under vacuum to give a 50% yield (221 mg) of red, slightly air-sensitive microcrystalline [PPN][ClRu$_4$(CO)$_{13}$]. Anal. Calcd for [PPN][ClRu$_4$(CO)$_{13}$]: C, 43.84; H, 2.25; Ru, 30.11; Cl, 2.64. Found: C, 43.57; H, 2.68; Ru, 28.71; Cl, 2.47 (Schwarzkopf Microanalytical Laboratory). IR (THF): 2030 s, 2006 vs, 1975 m (br), 1965 m (br), 1838 w cm^{-1}.

Collection and Reduction of X-ray Data for [PPN][ClRu$_4$(CO)$_{13}$]. Dark red crystals of [PPN][ClRu$_4$(CO)$_{13}$] were grown under N$_2$ by slow diffusion of petroleum ether into a saturated Et$_2$O solution of the complex by using a double-tube recrystallizer. The irregularly shaped crystal selected for analysis had maximum dimensions of 0.4 × 0.3 × 0.1 mm. It was mounted in an arbitrary orientation on a glass fiber which was then fixed into an aluminum pin and mounted onto a eucentric goniometer. Diffraction data were collected on an Enraf-Nonius four-circle CAD4 automated diffractometer controlled by a PDP8/a computer coupled to a PDP 11/34 computer. The Enraf-Nonius program SEARCH was employed to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and to provide cell dimensions.[9] Pertinent crystal and intensity data are listed in Table I.

A graphite-crystal incident-beam monochromator was used with Mo Kα radiation, and data were collected at a takeoff angle of 2.80°. A θ–2θ scan method was employed with a variable scan rate ranging from 20°/min for the most intense reflections to 1°/min for the weak ones. The angular scan (ω) width was variable and amounted to 0.6° below 2θ(Mo Kα) and $(0.6 + 0.347 \tan\theta)°$ above 2θ(Mo Kα). High and low 2θ backgrounds were each scanned for 25% of the total scan time. A total of 9024 unique reflections were collected out to $2\theta = 50°$. Of these, 5924 had intensities with $I \geq 3.0\sigma(I)$ and were considered observed. (Here $\sigma(I) = [S^2(C + R^2B) + (\rho I)^2]^{1/2}$ and $I = S(C - RB)$, where S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, and $\rho = 0.05$.) These data were corrected for Lorentz and polarization factors and were used in the subsequent refinement of the structure.

Solution and Refinement of the Structure. Of the two possible triclinic space groups $P1$ and $P\bar{1}$, the latter was arbitrarily selected for the initial trial solution of the structure. The successful refinement of the structure using this space group indicated that this choice was correct. The Cl and four Ru atoms were located from a three-dimensional Patterson map, and the coordinates of the remaining 65 nonhydrogen atoms were located by successive least-squares refinements and difference Fourier maps. Several cycles of least-squares
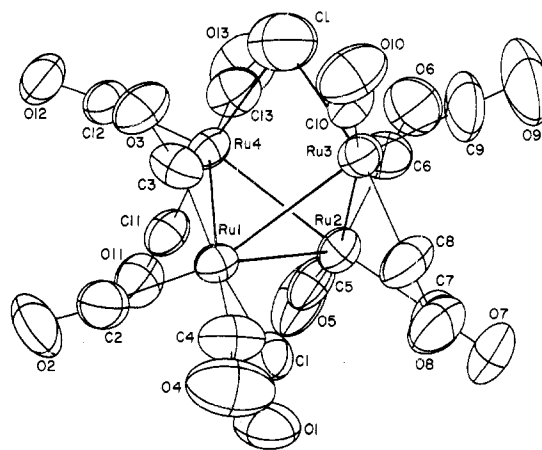
Figure 1. ORTEP drawing of [ClRu$_4$(CO)$_{13}$]$^-$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

refinement with anisotropic temperature factors for all 70 nonhydrogen atoms reduced R to 0.061 and R_w to 0.087. The residuals are defined as $R = \sum(\|F_o| - |F_c\|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

An ORTEP drawing which shows the atom numbering scheme for the [ClRu$_4$(CO)$_{13}$]$^-$ anion is shown in Figure 1, and a stereoview of the anion is given in Figure 2. Final positional and thermal parameters are listed in Table II. Relevant bond distances and bond angles are set out in Tables III and IV. A listing of the observed and calculated structure factors is given in the supplementary material.

Results and Discussion

Preparation and Characterization of [PPN][ClRu$_4$(CO)$_{13}$]. This salt was initially isolated from the reaction of [PPN]-[PhC(O)Fe(CO)$_4$][7] with Ru$_3$(CO)$_{12}$. These two reagents were allowed to react in THF solution at 60 °C over a period of 8 h during which time the color gradually changed from yellow to dark red. Recrystallization from Et$_2$O/petroleum ether gave an approximately 25% yield of [PPN][ClRu$_4$(CO)$_{13}$] as red crystals. It was subsequently shown that the chloride ligand in the product derived from excess [PPN]Cl carried into the reaction along with [PPN][PhC(O)Fe(CO)$_4$] which had been prepared by metathesis of Na[PhC(O)Fe(CO)$_4$] with [PPN]Cl.

Simultaneous to these experiments we were attempting to synthesize an acetyl- or methyl-substituted Ru$_3$ cluster by allowing Ru$_3$(CO)$_{12}$ to react with MeLi.[10] These reactions were carried out by adding MeLi to a deoxygenated THF solution of Ru$_3$(CO)$_{12}$ at 0° C in the presence of [PPN]Cl. The latter was added to facilitate workup and subsequent recrystallization of the product(s). The solution underwent an immediate change from yellow to dark red-purple upon addition of MeLi, but the only product that could be isolated was also shown to be [PPN][ClRu$_4$(CO)$_{13}$] (<5% yield).

A series of experiments was then undertaken in order to understand the chemistry occurring in these various reactions. First, it was found that [PPN][ClRu$_4$(CO)$_{13}$] results in good yield (>50%) *simply by refluxing Ru$_3$(CO)$_{12}$ together with [PPN]Cl in THF for 1–2 h.* This is clearly the preferred route to this cluster. That the PPN cation does not play a significant role in these reactions is evidenced by the preparation of [(PhCH$_2$)Et$_3$N][ClRu$_4$(CO)$_{13}$] and Li[ClRu$_4$(CO)$_{13}$] by refluxing THF solutions of Ru$_3$(CO)$_{12}$ in the presence of [(PhCH$_2$)Et$_3$N]Cl and LiCl, respectively.

We do not altogether understand the mechanism by which [ClRu$_4$(CO)$_{13}$]$^-$ forms. We believe that it may result by the reagents (Cl$^-$, MeLi, [PhC(O)Fe(CO)$_4$]$^-$) inducing partial or

(9) All programs used in this study are part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975; revised, 1977.

(10) The reaction of MeLi with Fe(CO)$_5$ gives (CO)$_3$Fe(μ-MeC(O))$_2$Fe-(CO)$_3$ as the principal product: Fischer, E. O.; Kiener, V.; Bunbury, D. St. P.; Frank, E.; Lindley, P. F.; Mills, O. S. *Chem. Commun.* **1968**, 1378.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	0.29560 (5)	0.13627 (5)	0.08023 (7)	0.0453 (3)	0.0520 (3)	0.0483 (4)	−0.0264 (2)	−0.0016 (3)	0.0000 (3)
Ru(2)	0.10892 (5)	0.22958 (5)	0.18560 (8)	0.0397 (3)	0.0653 (4)	0.0535 (5)	−0.0222 (3)	−0.0008 (3)	0.0045 (4)
Ru(3)	0.22383 (6)	0.31803 (5)	0.11809 (8)	0.0530 (4)	0.0507 (4)	0.0597 (5)	−0.0251 (3)	−0.0088 (4)	0.0056 (4)
Ru(4)	0.29054 (6)	0.15266 (5)	0.32384 (7)	0.0504 (4)	0.0609 (4)	0.0474 (4)	−0.0268 (3)	−0.0063 (3)	0.0092 (4)
Cl	0.3131 (2)	0.2906 (2)	0.3151 (3)	0.142 (2)	0.130 (2)	0.125 (2)	−0.071 (1)	−0.014 (2)	−0.009 (1)
P(1)	0.6951 (2)	0.2428 (1)	0.4906 (2)	0.0363 (9)	0.0386 (9)	0.035 (1)	−0.0177 (7)	−0.0024 (9)	−0.0008 (9)
P(2)	0.6431 (2)	0.3712 (1)	0.2898 (2)	0.0394 (9)	0.0383 (9)	0.038 (1)	−0.0191 (7)	0.0027 (9)	−0.0011 (9)
O(1)	0.1182 (6)	0.0859 (5)	0.0040 (9)	0.077 (4)	0.117 (5)	0.128 (7)	−0.060 (3)	0.012 (5)	−0.049 (5)
O(2)	0.4220 (8)	−0.0629 (5)	0.0979 (9)	0.127 (7)	0.045 (4)	0.116 (7)	−0.015 (4)	0.006 (6)	−0.013 (4)
O(3)	0.4884 (5)	0.1634 (5)	0.1308 (8)	0.045 (3)	0.089 (4)	0.099 (6)	−0.034 (3)	−0.002 (4)	−0.008 (4)
O(4)	0.3164 (7)	0.1354 (5)	−0.1810 (8)	0.162 (6)	0.125 (6)	0.064 (5)	−0.097 (3)	0.014 (5)	−0.009 (4)
O(5)	0.0187 (6)	0.1293 (6)	0.3206 (9)	0.063 (4)	0.155 (6)	0.145 (8)	−0.050 (3)	−0.003 (5)	0.070 (5)
O(6)	0.0635 (7)	0.3644 (6)	0.3797 (8)	0.094 (6)	0.112 (6)	0.096 (6)	−0.022 (5)	0.025 (5)	−0.042 (5)
O(7)	−0.0756 (6)	0.3329 (6)	0.0175 (7)	0.055 (4)	0.114 (6)	0.068 (5)	−0.016 (4)	−0.007 (4)	0.019 (5)
O(8)	0.1216 (6)	0.3205 (5)	−0.1183 (7)	0.081 (4)	0.095 (4)	0.070 (5)	−0.044 (3)	−0.025 (4)	0.023 (4)
O(9)	0.0791 (8)	0.5033 (6)	0.5033 (6)	0.088 (6)	0.064 (6)	0.25 (1)	0.005 (5)	0.034 (8)	0.004 (7)
O(10)	0.3712 (5)	0.3710 (5)	0.0021 (7)	0.069 (4)	0.109 (4)	0.083 (5)	−0.052 (3)	−0.002 (4)	0.008 (4)
O(11)	0.2473 (6)	−0.069 (5)	0.3055 (8)	0.085 (4)	0.073 (4)	0.113 (6)	−0.044 (3)	−0.012 (5)	0.029 (4)
O(12)	0.5136 (5)	−0.0391 (5)	0.3864 (7)	0.055 (3)	0.078 (4)	0.090 (5)	−0.026 (3)	−0.015 (4)	0.014 (4)
O(13)	0.2165 (8)	0.1999 (8)	0.5684 (8)	0.116 (6)	0.21 (1)	0.057 (5)	−0.057 (6)	0.024 (5)	−0.011 (6)
N	0.6515 (5)	0.3269 (4)	0.4105 (6)	0.052 (4)	0.041 (3)	0.037 (4)	−0.017 (3)	−0.001 (3)	−0.02 (3)
C(1)	0.1557 (7)	0.1235 (6)	0.0572 (10)	0.045 (4)	0.055 (5)	0.083 (7)	−0.022 (3)	0.05 (5)	−0.001 (5)
C(2)	0.3716 (8)	0.0089 (7)	0.0934 (10)	0.077 (6)	0.066 (5)	0.065 (7)	−0.034 (4)	−0.001 (5)	−0.000 (5)
C(3)	0.4105 (8)	0.1600 (6)	0.1119 (10)	0.074 (5)	0.056 (5)	0.069 (7)	−0.036 (3)	0.007 (5)	−0.010 (5)
C(4)	0.3020 (8)	0.1403 (6)	−0.0846 (9)	0.102 (5)	0.084 (5)	0.048 (6)	−0.065 (3)	0.006 (5)	0.002 (5)
C(5)	0.0539 (7)	0.1643 (8)	0.2691 (11)	0.050 (5)	0.099 (7)	0.081 (8)	−0.036 (4)	−0.008 (5)	0.024 (6)
C(6)	0.0846 (10)	0.3160 (8)	0.3067 (11)	0.086 (7)	0.081 (7)	0.062 (7)	−0.025 (6)	0.007 (6)	−0.012 (6)
C(7)	−0.0042 (7)	0.2941 (7)	0.0767 (10)	0.049 (5)	0.072 (6)	0.072 (7)	−0.025 (4)	0.005 (5)	−0.000 (5)
C(8)	0.1559 (7)	0.3182 (7)	−0.0263 (10)	0.070 (5)	0.082 (5)	0.081 (7)	−0.050 (3)	−0.031 (5)	0.032 (5)
C(9)	0.1320 (9)	0.4344 (8)	0.1587 (15)	0.050 (6)	0.064 (7)	0.15 (1)	0.006 (6)	0.009 (8)	0.002 (8)
C(10)	0.3194 (7)	0.3494 (7)	0.0509 (9)	0.052 (5)	0.060 (5)	0.058 (6)	−0.018 (4)	−0.014 (5)	0.004 (5)
C(11)	0.2619 (7)	0.0554 (6)	0.3097 (10)	0.054 (4)	0.071 (5)	0.068 (7)	−0.032 (3)	−0.002 (5)	0.014 (5)
C(12)	0.4318 (7)	0.0836 (6)	0.3650 (9)	0.062 (5)	0.055 (4)	0.062 (6)	−0.029 (3)	−0.012 (5)	0.015 (4)
C(13)	0.2432 (9)	0.1854 (8)	0.4806 (10)	0.077 (6)	0.109 (8)	0.057 (7)	−0.040 (5)	0.013 (6)	−0.009 (6)
C(14)	0.7432 (6)	0.1411 (5)	0.4122 (8)	0.037 (4)	0.045 (4)	0.046 (5)	−0.017 (3)	−0.004 (4)	−0.001 (4)
C(15)	0.8408 (8)	0.0742 (6)	0.4397 (11)	0.046 (5)	0.067 (6)	0.080 (8)	−0.010 (4)	−0.006 (5)	−0.010 (6)
C(16)	0.8763 (8)	−0.0053 (7)	0.3760 (12)	0.056 (6)	0.066 (6)	0.106 (9)	−0.010 (5)	−0.006 (6)	−0.043 (5)
C(17)	0.8152 (8)	−0.0155 (7)	0.2878 (11)	0.061 (6)	0.067 (6)	0.081 (8)	−0.019 (4)	0.002 (6)	−0.022 (6)
C(18)	0.7193 (7)	0.0491 (6)	0.2588 (9)	0.062 (5)	0.061 (5)	0.056 (6)	−0.027 (4)	0.001 (5)	−0.014 (5)
C(19)	0.6842 (7)	0.1271 (6)	0.3204 (8)	0.055 (4)	0.051 (4)	0.047 (5)	−0.028 (3)	−0.007 (4)	−0.000 (4)
C(20)	0.7981 (6)	0.2426 (5)	0.5891 (7)	0.040 (4)	0.046 (4)	0.035 (4)	−0.017 (3)	−0.002 (4)	−0.011 (4)
C(21)	0.8146 (7)	0.2054 (7)	0.6984 (9)	0.050 (4)	0.080 (6)	0.044 (5)	−0.030 (4)	−0.010 (4)	−0.004 (5)
C(22)	0.8956 (8)	0.2037 (8)	0.7726 (10)	0.070 (6)	0.104 (7)	0.059 (7)	−0.039 (5)	0.001 (5)	0.000 (6)
C(23)	0.9581 (8)	0.2385 (8)	0.7386 (11)	0.060 (6)	0.081 (6)	0.081 (8)	−0.021 (5)	−0.008 (6)	−0.028 (6)
C(24)	0.9384 (8)	0.2772 (8)	0.6227 (14)	0.064 (5)	0.089 (6)	0.13 (1)	−0.048 (4)	0.014 (6)	−0.019 (7)
C(25)	0.8593 (6)	0.2788 (6)	0.5500 (10)	0.042 (4)	0.079 (5)	0.071 (7)	−0.040 (3)	−0.005 (4)	−0.004 (5)
C(26)	0.5971 (6)	0.2432 (5)	0.5784 (7)	0.035 (3)	0.040 (4)	0.037 (4)	−0.017 (3)	−0.009 (4)	0.006 (3)
C(27)	0.5701 (7)	0.1733 (6)	0.5785 (9)	0.056 (4)	0.050 (4)	0.053 (5)	−0.028 (3)	0.011 (4)	0.000 (4)
C(28)	0.4935 (7)	0.1769 (6)	0.6447 (11)	0.071 (5)	0.059 (5)	0.087 (8)	−0.040 (4)	0.019 (5)	−0.001 (5)
C(29)	0.4406 (7)	0.2533 (6)	0.7145 (10)	0.056 (5)	0.060 (5)	0.076 (7)	−0.026 (4)	0.019 (5)	−0.009 (5)
C(30)	0.04694 (8)	0.3213 (6)	0.7137 (11)	0.74 (5)	0.054 (5)	0.095 (8)	−0.034 (3)	0.038 (5)	−0.011 (5)
C(31)	0.5453 (7)	0.3169 (6)	0.6453 (10)	0.057 (4)	0.051 (4)	0.072 (6)	−0.030 (3)	0.020 (5)	−0.012 (5)
C(32)	0.6887 (6)	0.2956 (5)	0.1733 (7)	0.043 (4)	0.037 (3)	0.038 (4)	−0.019 (3)	0.001 (4)	0.004 (3)
C(33)	0.6210 (7)	0.2811 (6)	0.0902 (8)	0.055 (4)	0.050 (4)	0.052 (5)	−0.028 (3)	−0.008 (4)	0.010 (4)
C(34)	0.6553 (8)	0.2153 (6)	0.0081 (10)	0.074 (5)	0.048 (4)	0.064 (6)	−0.032 (4)	0.004 (5)	−0.014 (4)
C(35)	0.7596 (8)	0.1601 (7)	0.0072 (10)	0.089 (6)	0.058 (5)	0.062 (6)	−0.031 (4)	0.028 (5)	−0.012 (5)
C(36)	0.8291 (8)	0.1727 (7)	0.0894 (10)	0.053 (5)	0.071 (6)	0.076 (7)	−0.021 (4)	0.015 (5)	−0.018 (6)
C(37)	0.7930 (7)	0.2395 (6)	0.1732 (9)	0.042 (4)	0.058 (5)	0.063 (6)	−0.018 (3)	0.008 (4)	−0.013 (5)
C(38)	0.524 (6)	0.4430 (5)	0.2525 (8)	0.050 (4)	0.036 (4)	0.036 (4)	−0.018 (3)	−0.006 (4)	−0.004 (3)
C(39)	0.4356 (6)	0.4376 (6)	0.3148 (8)	0.045 (4)	0.061 (4)	0.042 (5)	−0.029 (3)	0.005 (4)	0.002 (4)
C(40)	0.3340 (7)	0.4940 (6)	0.2859 (9)	0.051 (4)	0.056 (5)	0.054 (6)	−0.023 (3)	0.004 (4)	−0.011 (4)
C(41)	0.3083 (7)	0.5555 (6)	0.1954 (9)	0.050 (5)	0.051 (5)	0.064 (6)	−0.016 (4)	0.004 (5)	−0.015 (5)
C(42)	0.3837 (8)	0.5614 (6)	0.1341 (10)	0.065 (6)	0.044 (5)	0.067 (7)	−0.014 (4)	−0.011 (5)	0.010 (5)
C(43)	0.4883 (7)	0.5046 (5)	0.1602 (8)	0.068 (5)	0.043 (4)	0.041 (5)	−0.025 (3)	−0.002 (4)	0.002 (4)
C(44)	0.7123 (6)	0.4377 (5)	0.2975 (8)	0.044 (4)	0.040 (4)	0.050 (5)	−0.021 (3)	−0.001 (4)	0.005 (4)
C(45)	0.7569 (6)	0.4515 (6)	0.1992 (9)	0.045 (4)	0.052 (4)	0.064 (6)	−0.024 (3)	0.006 (4)	0.005 (4)
C(46)	0.8101 (8)	0.5065 (7)	0.2128 (11)	0.063 (5)	0.065 (5)	0.096 (8)	−0.038 (3)	0.004 (6)	0.008 (5)
C(47)	0.8157 (8)	0.5454 (8)	0.3167 (12)	0.089 (5)	0.074 (5)	0.095 (9)	−0.058 (3)	−0.001 (6)	0.002 (6)
C(48)	0.7713 (9)	0.5310 (7)	0.4091 (11)	0.107 (6)	0.077 (5)	0.077 (8)	−0.063 (4)	−0.015 (6)	−0.003 (5)
C(49)	0.7176 (8)	0.4794 (6)	0.4040 (9)	0.092 (5)	0.070 (5)	0.048 (6)	−0.051 (3)	−0.005 (5)	−0.007 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

total fragmentation of $Ru_3(CO)_{12}$ to yield monomeric and/or dimeric ruthenium carbonyl fragments which then reassemble around the Cl⁻ ligand present in solution. Note that net redox chemistry is *not* involved since removal of Cl⁻ from the [ClRu₄(CO)₁₃]⁻ anion would leave "Ru₄(CO)₁₃" in which each Ru has a formal oxidation state of zero.
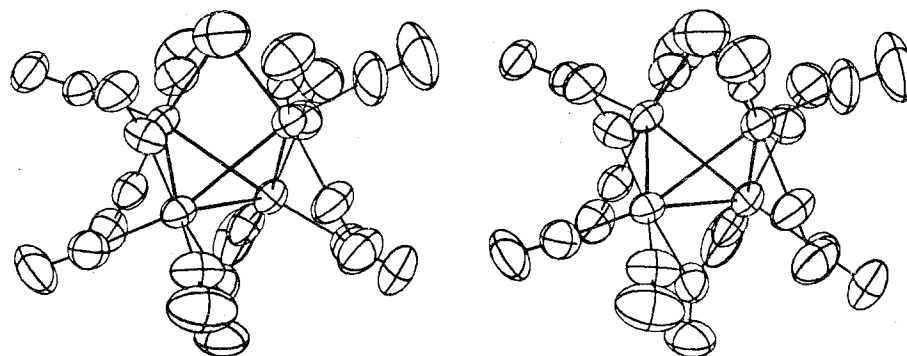
Figure 2. Stereoscopic view of $[ClRu_4(CO)_{13}]^-$.

Table III. Selected Bond Distances (Å) in [PPN][ClRu₄(CO)₁₃]

Ru(1)–Ru(2)	2.832 (1)	Ru(4)–C(11)	1.845 (8)
Ru(1)–Ru(3)	2.797 (1)	Ru(4)–C(12)	1.910 (8)
Ru(1)–Ru(4)	2.813 (1)	Ru(4)–C(13)	1.956 (4)
Ru(2)–Ru(3)	2.814 (1)	C(1)–O(1)	1.138 (8)
Ru(2)–Ru(4)	2.791 (1)	C(2)–O(2)	1.110 (9)
Ru(3)–Cl	2.486 (2)	C(3)–O(3)	1.165 (8)
Ru(4)–Cl	2.471 (2)	C(4)–O(4)	1.137 (8)
Ru(1)–C(1)	2.133 (7)	C(5)–O(5)	1.126 (9)
Ru(1)–C(2)	1.942 (9)	C(6)–O(6)	1.117 (9)
Ru(1)–C(3)	1.885 (8)	C(7)–O(7)	1.147 (8)
Ru(1)–C(4)	1.909 (8)	C(8)–O(8)	1.134 (9)
Ru(2)–C(1)	2.187 (8)	C(9)–O(9)	1.097 (9)
Ru(2)–C(5)	1.911 (8)	C(10)–O(10)	1.145 (8)
Ru(2)–C(6)	1.922 (9)	C(11)–O(11)	1.148 (8)
Ru(2)–C(7)	1.927 (8)	C(12)–O(12)	1.116 (8)
Ru(3)–C(8)	1.874 (8)	C(13)–O(13)	1.092 (9)
Ru(3)–C(9)	1.902 (9)	N–P(1)	1.567 (1)
Ru(3)–C(10)	1.895 (8)	N–P(2)	1.563 (1)

Table IV. Selected Bond Angles (Deg) in [PPN][ClRu₄(CO)₁₃]

Ru(2)–Ru(1)–Ru(3)	60.0 (1)	Ru(2)–C(1)–O(1)	136.5 (6)
Ru(2)–Ru(1)–Ru(4)	59.3 (1)	Ru(1)–C(2)–O(2)	173.9 (8)
Ru(3)–Ru(1)–Ru(4)	75.9 (1)	Ru(1)–C(3)–O(3)	171.5 (6)
Ru(1)–Ru(2)–Ru(3)	59.4 (1)	Ru(1)–C(4)–O(4)	172.4 (8)
Ru(1)–Ru(2)–Ru(4)	60.0 (1)	Ru(2)–C(5)–O(5)	176.9 (9)
Ru(3)–Ru(2)–Ru(4)	76.0 (1)	Ru(2)–C(6)–O(6)	173.8 (9)
Ru(1)–Ru(3)–Ru(2)	60.6 (1)	Ru(2)–C(7)–O(7)	175.6 (7)
Ru(1)–Ru(3)–Cl	90.7 (1)	Ru(3)–C(8)–O(8)	173.3 (7)
Ru(2)–Ru(3)–Cl	89.5 (1)	Ru(3)–C(9)–O(9)	174.6 (11)
Ru(1)–Ru(4)–Ru(2)	60.7 (1)	Ru(3)–C(10)–O(10)	174.1 (6)
Ru(1)–Ru(4)–Cl	90.6 (1)	Ru(4)–C(11)–O(11)	176.6 (6)
Ru(2)–Ru(4)–Cl	90.4 (1)	Ru(4)–C(12)–O(12)	175.8 (7)
Ru(3)–Cl–Ru(4)	88.3 (1)	Ru(4)–C(13)–O(13)	176.6 (10)
Ru(1)–C(1)–O(1)	141.4 (6)	P(1)–N–P(2)	150.1 (1)

MeLi and $[PhC(O)Fe(CO)_4]^-$ may serve to fragment $Ru_3(CO)_{12}$ through reduction. $Ru_3(CO)_{12}$ has been reported to undergo an irreversible one-electron reduction[11] in a series of electrochemical experiments, but the product(s) were not identified. Shore and co-workers[12] have also noted that treatment of $Ru_3(CO)_{12}$ with 2 equiv of sodium benzophenone ketyl gives $[Ru_4(CO)_{13}]^{2-}$ in high yield. This latter reaction clearly involves partial or total fragmentation of $Ru_3(CO)_{12}$.

The reactivity of [PPN][ClRu₄(CO)₁₃] has been briefly investigated. Acidification of THF solutions with 20% aqueous phosphoric acid gives a small amount of $Ru_3(CO)_{12}$ as the only hexane soluble product with no evidence obtained for the expected $HClRu_4(CO)_{13}$ product. No reaction of [PPN]-[ClRu₄(CO)₁₃] with PhC≡CPh occurred in refluxing THF, even though $Ru_4(CO)_{12}(PhC≡CPh)$[13] is a viable product.

Addition of $AgPF_6$ to this reaction mixture at room temperature gave an insoluble black precipitate (Ag?) and $Ru_3(CO)_{12}$ as the only detectable Ru species present in solution.

Crystal and Molecular Structure of [PPN][ClRu₄(CO)₁₃]. The crystal structure of [PPN][ClRu₄(CO)₁₃] shows that the compound exists as discrete cations and anions with the former having the usual bent configuration (P–N–P = 150.1°). The $[ClRu_4(CO)_{13}]^-$ anion possesses a butterfly arrangement of the four Ru atoms with the chlorine bridging the two "wings" (Ru3, Ru4) of the butterfly (Figure 1). Each Ru atom bears three terminal carbonyl ligands, and one carbonyl symmetrically bridges the two Ru atoms which constitute the hinge of the butterfly (Ru(1), Ru(2)). The five Ru–Ru bond distances are nearly equal (2.813, 2.791, 2.797, 2.814, 2.832 Å) as are the Ru–Cl distances (2.471, 2.486 Å).

The Ru(3)–Cl–Ru(4) bridge angle (88.3°) in [ClRu₄(C-O)₁₃]⁻ is comparable to the bridge angles found in other halogen-bridged transition-metal dimers which do not possess a metal–metal bond or another type of bridging ligand. For example, the metal–halogen–metal bond angles are 86.3 and 90.5° for $[RuBr(\mu-Br)(CO)_3]_2$[14] and 85.3 and 84.7° for $[RhCl(C_8H_{12})]_2$.[15] An angle of 90° is expected purely from electronic grounds if the Cl⁻ ligand is considered a four-electron donor with a pair of electrons in each of two mutually perpendicular 3p orbitals.

The two Ru₃ planes which constitute the butterfly are nearly perpendicular with a 91.0° angle between them. The atoms Ru(3), Ru(4), and Cl and the midpoint of the Ru(1)–Ru(2) vector nearly define a square as indicated in structure **1**.

1
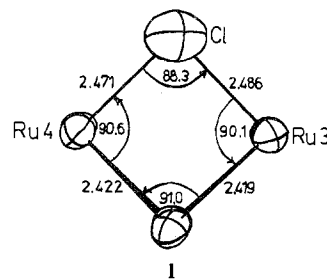
It is interesting that $[ClRu_4(CO)_{13}]^-$ does not adopt the closed tetrahedral structures of $[HFeRu_3(CO)_{13}]^-$[3] and $H_2Ru_4(CO)_{13}$[16] with which it would be isoelectronic if the chloride ligand were bound to a single Ru atom and functioned as a two-electron donor. Instead, the bridging Cl⁻ ligand must be considered a four-electron donor, donating two electrons each to Ru(3) and Ru(4), and each Ru atom has the requisite 18 valence electrons.[17] Alternately, the cluster as a whole

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has 62 valence electrons, and thus the butterfly arrangement of the metal atoms is consistent with predictions from the various skeletal electron theories.[18,19]

An isoelectronic and structurally similar $H_3Os_4(CO)_{12}I$ cluster has been reported by Johnson, Lewis, and co-workers.[20] The structure of this compound is shown in **2** and has a
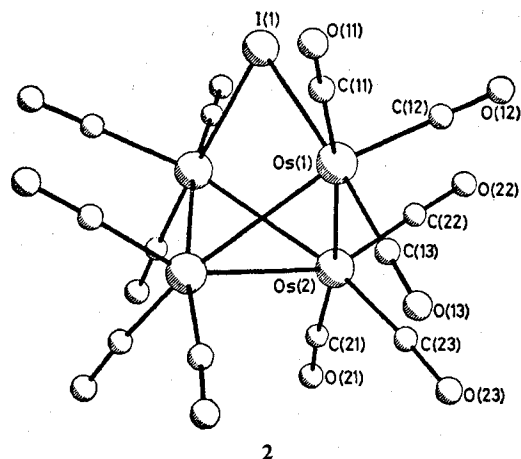
2

crystallographically imposed twofold axis passing through the iodine atom and bisecting the Os(2)–Os(2') hinge. The Os-

(1)–I–Os(1') bridge angle (87.9°) in this cluster is similar to the Ru(3)–Cl–Ru(4) angle (88.3°) in $[ClRu_4(CO)_{13}]^-$, but the hinge angle was not given. A comparison of the drawings shown in **2** and Figure 1 reveals that the arrangements of the terminal carbonyl ligands in the two structures are remarkably similar with the slight differences apparently arising as a result of the influence of the different character and location of the bridging ligands. Although the hydrides were not located in $H_3Os_4(CO)_{12}I$, one was presumed to bridge the Os–Os hinge of the butterfly with the others bridging the long Os–Os bonds of the "wings" (Os(1)–Os(2'), Os(1')–Os(2)).

The bridging chloride ligand in $[ClRu_4(CO)_{13}]^-$ would appear to offer a convenient means of functionalizing the cluster by abstracting it with Ag^+ or Tl^+ in the presence of a suitable substrate. A similar notion has been previously suggested for $Fe_2(CO)_6Cl(\mu\text{-}PPh_2)$ by Carty and co-workers.[21,22] Our preliminary experiments in this regard, summarized above, have been largely unsuccessful, but we are continuing to explore the possibility of reactions of this type.

(17) Ru(1), Ru(2): 8(Ru) + 6{(CO)₃} + 3(Ru–Ru) + 1{CO_b} = 18. Ru(3), Ru(4): 8(Ru) + 6{(CO)₃} + 2(Ru–Ru) + 2(Cl) = 18.
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Low-Temperature Crystal and Molecular Structure of μ-Bromo-hexacarbonyl[octahydrotriborato(1−)]dimanganese, (μ-Br)(CO)₆(B₃H₈)Mn₂

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The synthesis and characterization of $(\mu\text{-}X)(CO)_6(B_3H_8)Mn_2$, where X = Cl or Br, is reported. The $(\mu\text{-}Br)(CO)_6(B_3H_8)Mn_2$ forms crystals in the monoclinic space group $P2_1/c$ with $a = 10.921\ (8)$ Å, $b = 7.052\ (4)$ Å, $c = 18.982\ (12)$ Å, $\beta = 113.05\ (6)°$, $V = 1345\ (2)$ Å^3, and $Z = 4$. The low-temperature X-ray structure, solved by MULTAN and Fourier methods and refined to $R_1 = 0.056$ and $R_2 = 0.059$, consists of two octahedral manganese atoms bridged by a simultaneously bidentate $B_3H_8^-$ anion and a bromine atom. The remaining octahedral coordination sites are occupied by carbon monoxide ligands. There is no apparent metal–metal bond. The simultaneously bidentate nature of the $B_3H_8^-$ moiety presents a heretofore unknown bonding mode for octahydrotriborate complexes.

Introduction

The inclusion of metal atoms along with boron atoms in boron hydride like clusters has become the subject of much attention in recent years and is now a rapidly expanding area within the field of inorganic chemistry.[1] The bonding observed in these metalloborane complexes can be divided into several broad categories: (1) complexes containing direct metal–boron bonding, as in $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}B_4H_8)$,[2] (2) metal hydroborates containing metal–hydrogen–boron bridge bonds, as in Al(B-

H₄)₃,[3] and (3) complexes containing both metal–boron and metal–hydrogen–boron bonding.

The series of metal–hydrogen–boron bond containing species has grown from the initial characterization of doubly bridged species such as $[(C_6H_5)_3P]_2CuBH_4$[4] to reports of single[5] and triple[6] M–H–B bridge bond containing species. In each of

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