A Spiked-Butterfly Borido Cluster: Synthesis and Molecular Structure of $H_2Ru_5(CO)_{13}Cp^*BH_2$

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The reaction of [PPN][$Ru_3(CO)_9BH_4$] with [Cp^*RuCl_2]$_n$ (Cp^* = η^5-C_5Me_5) is solvent-dependent. In CH_2Cl_2, the reaction leads to the 62-electron butterfly cluster $Ru_4(CO)_{10}Cp^*BH_2$ (1), in addition to the novel cluster $H_2Ru_5(CO)_{13}Cp^*BH_2$ (2), a 78-valence-electron cluster. When the reaction is carried out in THF, compound 1 is not formed, but higher yields of 2 are observed. The molecular structure of 2 has been determined: monoclinic, $P2_1/c$, a = 15.589(3) Å, b = 11.247(3) Å, c = 17.695(4) Å, β = 90.64(2)°, V = 3102.3(12) Å^3, Z = 4; $R(F)$ = 3.42%. The structure of 2 is related to that of $HRu_4(CO)_{12}BH_2$ with one wingtip terminal carbonyl ligand replaced by a hydride ligand and a terminal $RuCp^*(CO)_2$ fragment. Thus, 2 is viewed as possessing a spiked-butterfly framework, which is unprecedented in the sense that the "metal spike" is unsupported. Selected reactions of 2 have been carried out in order to compare its reactivity with that of the butterfly boride $HRu_4(CO)_{12}BH_2$; it is found that the {Cp^*Ru}-based spike is readily lost.

We have recently reported the use of the ruthenaborane cluster $Ru_3(CO)_9BH_5$ and its conjugate base [$Ru_3(CO)_9$-BH_4]$^-$ as precursors to higher nuclearity homo- and heterometallic boron-containing clusters.[1,2] As part of our continued studies in this area, we have investigated the reaction of [$Ru_3(CO)_9BH_4$]$^-$ with [CP^*RuCl_2]$_n$ (Cp^* = η^5-C_5Me_5) and report here the isolation of tetra- and pentaruthenium boron-containing products.

Experimental Section

General Data. FT-^{1}H and ^{11}B NMR spectra were recorded at 298 K on 250- and 400-MHz instruments, respectively. ^{1}H NMR shifts are reported with respect to δ 0 for Me_4Si and ^{11}B NMR with respect to δ 0 for $F_3B{\cdot}OEt_2$. All downfield chemical shifts are positive. Infrared spectra were recorded on a Perkin-Elmer FT 1710 spectrophotometer. FAB mass spectra were recorded on Kratos instruments.

Reactions were carried out under argon by using standard Schlenk techniques. Solvents were dried over suitable reagents and freshly distilled under N_2 before use. Separations were carried out by thin-layer plate chromatography with Kieselgel 60-PF-254 (Merck). Photolysis reactions used a mercury high-pressure lamp. [PPN][$Ru_3(CO)_9BH_4$] was prepared as previously reported by us[2] ([PPN]$^+$ = bis(triphenylphosphine)nitrogen-(1+)). [Cp^*RuCl_2]$_n$ was used as received from Aldrich. Yields are based on the starting ruthenium cluster; the yield of [$Ru_6(CO)_{17}B$]$^-$ assumes that 2 mol of [$Ru_3(CO)_9BH_4$]$^-$ is required per mole of product.

Reaction of [PPN][$Ru_3(CO)_9BH_4$] with [Cp^*RuCl_2]$_n$ in CH_2Cl_2. [PPN][$Ru_3(CO)_9BH_4$] (0.25 g, 0.23 mmol) was dissolved in CH_2Cl_2 (5 mL) to give a red-orange solution. [Cp^*RuCl_2]$_n$ (0.068 g, 0.22 mmol for n = 1) was dissolved in CH_2Cl_2 (10 mL), and this red-brown solution was added to [PPN][$Ru_3(CO)_9BH_4$]. After the brown reaction mixture was stirred at room temperature for 1 h, solvent was removed *in vacuo*. The product was dissolved in CH_2Cl_2 and this solution filtered through a fine-grade sinter. Separation by TLC with hexane as eluent yielded the following fractions. The first to third fractions (all yellow) were $Ru_3(CO)_9$-BH_5,[1] $HRu_3(CO)_9B_2H_5$,[1] and $HRu_4(CO)_{12}BH_2$[3,4] and were identified by their IR spectroscopic properties. The fourth fraction was red-orange and was identified as $Ru_4(CO)_{10}Cp^*BH_2$ (1; 5 mg, 3%). The fifth fraction was $H_2Ru_5(CO)_{13}Cp^*BH_2$ (2; 24 mg, 10%). Three weak fractions were eluted next and were discarded. [PPN]-[$Ru_6(CO)_{17}B$][5,6] (30 mg, 11%) and [PPN][$HRu_5(CO)_{15}$][7] (15 mg, 4.5%) were isolated from the base line by elution with CH_2Cl_2–hexane (2:1). Compound 1: 400-MHz ^{1}H NMR ($CDCl_3$) δ 1.96 (s, 15H, *Me*), −6.4 (br, 1H, Ru–*H*–B), −20.06 (s, 1H, Ru–*H*–Ru); 128-MHz ^{11}B NMR ($CDCl_3$) δ +151.0 (d, J_{BH} = 75 Hz); IR (CH_2-Cl_2, cm^{-1}) 2083 m, 2046 vs, 2014 m, 1997 m, 1937 w; FAB-MS in 3-NBA matrix, m/z 833 (P$^+$) with 7 CO losses (calcd for $^{12}C_{20}{}^1H_{17}{}^{11}B^{16}O_{10}{}^{101}Ru_4$ 832). Compound 2: 400-MHz ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 15H, *Me*), −8.3 (br, 2H, Ru–*H*–B), −16.62 (s, 1H, Ru–*H*–Ru), −20.95 (s, 1H, Ru–*H*–Ru); 128-MHz ^{11}B NMR ($CDCl_3$) δ +106.6 (poorly resolved t, $w_{1/2}$ = 180 Hz); IR (CH_2Cl_2, cm^{-1}) 2087 w, 2050 vs, 2014 m, 2008 sh, 2000 sh, 1985 w, 1951 w; FAB-MS in 3-NBA matrix m/z 1019 (P$^+$) with 8 CO losses (calcd for $^{12}C_{23}{}^1H_{19}{}^{11}B^{16}O_{13}{}^{101}Ru_5$ 1019).

Reaction of [PPN][$Ru_3(CO)_9BH_4$] with [Cp^*RuCl_2]$_n$ in THF. The scale and procedure of the reaction were as detailed above, except that the solvent was THF (15 mL). After separation by TLC and elution with hexane, compound 2 was isolated as the third fraction (60 mg, 25%). No 1 was obtained.

Attempted Deprotonation of 2. Compound 2 (51 mg, 0.05 mmol) was dissolved in CH_2Cl_2 (5 mL), and the solution was added to a methanolic solution containing [PPN]Cl (57 mg, 0.1 mmol) and K_2CO_3 (~0.05 mmol). After the mixture was stirred for 10 min, the color of the solution had changed from orange to deep purple. Attempts to isolate the purple material led only to product decomposition.

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(7) We have isolated [PPN][$HRu_5(CO)_{15}$] from several reactions, including that of [PPN][$Ru_3(CO)_9BH_4$] with [$Ru(\eta^6$-MeC_6H_4-4-$CHMe_2)$-Cl_2]$_2$; the molecular structure of [$HRu_5(CO)_{15}$]$^-$ is based on a square pyramid despite possessing 72 valence electrons and will be reported separately: Galsworthy, J. R.; Housecroft, C. E.; Rheingold, A. L. *J. Organomet. Chem.*, to be submitted for publication.

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Table I. Crystallographic Data for 2

(a) Crystal Parameters			
formula	$C_{23}H_{19}BO_{13}Ru_5$	β/deg	90.64(2)
M_r	1019.5	V/Å^3	3102.3(12)
cryst syst	monoclinic	Z	4
space group	$P2_1/c$	D_c/g cm^{-3}	2.83
a/Å	15.589(3)	cryst dimens/mm	0.35 × 0.40 × 0.40
b/Å	11.247(5)	cryst color and habit	orange block
c/Å	17.695(4)	μ(Mo Kα)/cm^{-1}	23.94
(b) Data Collection			
diffractometer	Siemens P4	no. of rflns collected	9106
radiation	Mo Kα (λ = 0.710 73 Å)	no. indep rflns	8850
T/K	298	no. of indep obsd rflns, $F_o \geq 5\sigma(F_o)$	6187
2θ scan range/deg	4.0–55.0	max, min transmission	0.5119/0.4376
data collected (hkl)	$-21 \leq h \leq 20, 0 \leq k \leq 15, 0 \leq l \leq 24$		
(c) Refinement			
R_F/%	3.42	$\Delta(\rho)$/e Å^{-3}	0.73
R_{wF}/%	4.41	N_o/N_v	15.8
Δ/σ (max)	0.487	GOF	1.02

Photolysis of 2. Compound 2 (51 mg, 0.05 mmol) was dissolved in CH_2Cl_2 (1 mL) and photolyzed for 16 h in a quartz tube. $HRu_4(CO)_{12}BH_2$[3,4] was recovered.

Reaction of 2 with Triphenylphosphine. Compound 2 (50 mg, 0.05 mmol) and PPh_3 (78 mg, 0.30 mmol) were dissolved in CH_2Cl_2, and the solution was stirred for 45 h. The only boron-containing product after this time was $HRu_4(CO)_{11}(PPh_3)BH_2$.[8,9]

Reaction of 2 with Diphenylacetylene. Compound 2 (50 mg, 0.05 mmol) and PhC≡CPh (35.6 mg, 0.20 mmol) were dissolved in CH_2Cl_2 (1 mL) and photolyzed for 16 h in a quartz tube. $HRu_4(CO)_{12}B(H)C(Ph)CHPh$[10] was the only boron-containing product.

Crystal Structure Determinations. Crystallographic data for 2 are collected in Table I, and atomic coordinates are listed in Table II. A nearly equidimensional orange block was selected for data collection and mounted on a glass fiber. Photographic evidence revealed 2/*m* Laue symmetry, and systematic absences in the reflection data allowed a unique space group assignment. An empirical absorption correction (XEMP, 216 ψ-scan data, ellipsoidal model) was applied to the data. The five Ru atoms were obtained from an autointerpreted Patterson map. All non-hydrogen atoms were refined with anisotropic thermal parameters, and the methyl-group hydrogen atoms were treated as idealized contributions. The four bridging hydrides were located and isotropically refined with a fixed thermal parameter (U = 0.08 Å^2).

All computations used the SHELXTL (PC version 4.2) program system (G. Sheldrick, Siemens, Madison, WI).

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 2

	x	y	z	U(eq)[a]
Ru(1)	5952.5(3)	6935.2(4)	233.1(2)	32.6(1)
Ru(2)	6642.2(2)	7511.7(3)	1683.3(2)	27.4(1)
Ru(3)	7763.7(2)	6890.4(3)	465.7(2)	26.4(1)
Ru(4)	7616.1(2)	5399.5(3)	1786.0(2)	26.9(1)
Ru(5)	8547.8(2)	2960.4(3)	1647.9(2)	26.0(1)
B	6719(3)	5911(5)	971(3)	28(1)
O(1)	6033(4)	9516(4)	−309(3)	77(2)
O(2)	4101(3)	7035(6)	764(3)	80(2)
O(3)	5668(3)	5939(5)	−1354(2)	69(2)
O(4)	5678(3)	9839(4)	1446(3)	74(2)
O(5)	5152(3)	6439(5)	2520(3)	77(2)
O(6)	7562(3)	8245(4)	3136(2)	57(2)
O(7)	8030(3)	8869(4)	−702(3)	67(2)
O(8)	7995(3)	4839(4)	−616(2)	55(2)
O(9)	9651(3)	6867(5)	926(3)	73(2)
O(10)	6829(3)	4410(4)	3207(2)	67(2)
O(11)	9059(3)	6613(4)	2653(3)	58(2)
O(12)	9122(3)	3662(4)	3231(2)	61(2)
O(13)	10198(3)	3772(5)	947(3)	82(2)
C(1)	6015(4)	8561(6)	−110(3)	49(2)
C(2)	4775(4)	7013(6)	551(3)	51(2)
C(3)	5779(4)	6335(6)	−774(3)	45(2)
C(4)	6064(4)	8986(5)	1514(3)	45(2)
C(5)	5713(4)	6853(6)	2211(3)	45(2)
C(6)	7242(3)	7956(5)	2593(3)	38(2)
C(7)	7900(4)	8140(5)	−266(3)	41(2)
C(8)	7915(3)	5628(5)	−211(3)	36(2)
C(9)	8942(4)	6871(5)	785(3)	43(2)
C(10)	7156(4)	4757(5)	2674(3)	42(2)
C(11)	8522(3)	6145(5)	2318(3)	38(2)
C(12)	8910(3)	3449(5)	2628(3)	37(2)
C(13)	9580(4)	3498(5)	1227(3)	47(2)
C(21)	7329(3)	1973(4)	1293(3)	37(2)
C(22)	7979(4)	1777(5)	755(3)	38(2)
C(23)	8664(3)	1151(5)	1144(3)	37(2)
C(24)	8450(3)	1027(4)	1918(3)	34(1)
C(25)	7610(3)	1555(5)	2018(3)	31(1)
C(26)	6450(3)	2462(5)	1116(4)	48(2)
C(27)	7904(5)	1973(6)	−74(3)	57(2)
C(28)	9457(4)	662(5)	767(4)	52(2)
C(29)	8954(4)	362(6)	2501(3)	51(2)
C(30)	7108(4)	1497(6)	2722(3)	48(2)

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

The cluster anion $[Ru_3(CO)_9BH_4]^-$ is a suitable precursor to high-nuclearity boron-containing clusters such as $HRu_3Fe(CO)_{12}BH_2$.[2] The conjugate acid of $[Ru_3(CO)_9BH_4]^-$ undergoes spontaneous cluster growth, giving rise to both $HRu_4(CO)_{12}BH_2$ and $HRu_6(CO)_{17}B$ when it stands in CH_2Cl_2 solution or when such a solution is photolyzed.[2] We have more recently observed that $[Ru_3(CO)_9BH_4]^-$ undergoes similar cluster expansions to give $[HRu_4(CO)_{12}BH]^-$ and $[Ru_6(CO)_{17}B]^-$. The aim of investigating the reaction of $[Ru_3(CO)_9BH_4]^-$ with $[Cp^*RuCl_2]_n$ (Cp* = η^5-C_5Me_5) was to explore cluster growth using an {RuCp*} rather than an {$Ru(CO)_3$} fragment; compared to {$Ru(CO)_3$}, [RuCp*} provides one less electron for cluster bonding. As one possibility, this difference might be expected to lead to one or more butterfly products in which the presence of {RuCp*} rather than {$Ru(CO)_3$} causes an alteration in the number of H and/or CO ligands so as to retain a 62-electron cluster framework.

The reaction of $[Ru_3(CO)_9BH_4]^-$ with $[Cp^*RuCl_2]_n$ leads to several higher nuclearity clusters, including $HRu_4(CO)_{12}$-

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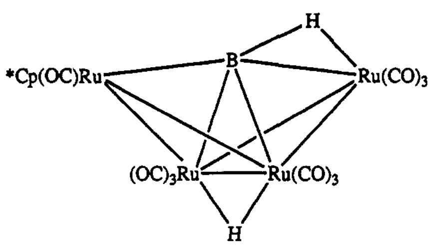
Chart I



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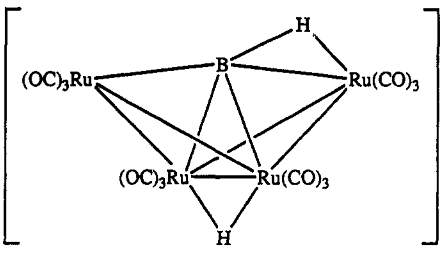

$[HRu_4(CO)_{12}BH]^-$

BH_2,[3,4] $[Ru_6(CO)_{17}B]^-$,[5,6] (which can be formed from $[Ru_3(CO)_9BH_4]^-$ itself on standing in solution), and $[HRu_5(CO)_{15}]^-$,[7] but products incorporating the {Cp*Ru} unit are limited to 1 and 2. The formation of both 1 and 2 is observed when the solvent for the reaction is dichloromethane. In THF, 1 is not produced.

Spectroscopic Characterization of 1. The structure of 1 is proposed on the basis of spectroscopic data and by comparison with the isoelectronic anion $[HRu_4(CO)_{12}BH]^-$ [3,4] (Chart I).

The mass spectral data for 1 are consistent with a formulation of $Ru_4(CO)_{10}Cp^*BH_2$; seven carbonyl losses occur from the parent ion, and the simulated isotopic envelope of this ion matches that observed. The solution ^1H NMR spectrum of 1 includes a resonance at δ +1.96 assigned to the methyl groups of the Cp* ligand. A broad signal at δ −6.4 and a sharp resonance at δ −20.06 may be assigned to Ru–H–B and Ru–H–Ru bridging hydrogen atoms, respectively. The shift for the latter is typical of an Ru_4-butterfly hinge-bridging hydride ligand; the shift is very sensitive to changes in skeletal geometry[10] and composition of the metal framework.[1,2,11] This observation lends support to the placement of the {RuCp*} unit in a wingtip rather than hinge site. The ^{11}B NMR spectrum of 1 exhibits a resonance at δ +151.0; this is quite similar to the shift observed for the anion $[HRu_4(CO)_{12}BH]^-$ (δ +142.2 for the $[PPN]^+$ salt[4] and +140.9 for the potassium salt[3]). The data for 1 are consistent with the 62-electron borido-butterfly structure shown in Chart I, although we cannot be certain whether the Ru–H–B bridge is associated with the $\{Ru(CO)_3\}$ or {RuCp*(CO)} wingtip unit.

Spectroscopic Characterization of 2. The mass spectral data for 2 indicate that the compound has a pentaruthenium core. However, the ^{11}B NMR spectral data (a poorly resolved triplet at δ +106.6) are consistent[11] with the boron atom being in contact with only four ruthenium atoms and being in an environment similar to that in $HRu_4(CO)_{12}BH_2$,[3,4] rather than in one related to the square-based-pyramidal core, recently confirmed for $Ru_5(CO)_{15}B(AuPPh_3)$.[12] Here, the presence of five rather than four Ru–B bonding contacts causes the ^{11}B NMR resonance to move to lower field; in $Ru_5(CO)_{15}B(AuPPh_3)$, the ^{11}B NMR spectral shift is δ +172.5[12] and this changes little upon loss of the gold(I) phosphine fragment.[13] The ^1H NMR spectrum of 2 shows the presence of a broad signal at δ −8.30 and a sharp resonance at δ −20.95 consistent with a cluster core related to that of $HRu_4(CO)_{12}BH_2$[3,4] and 1. However, in addition, there is a sharp resonance at δ −16.62 indicating the presence of another ruthenium-associated hydride ligand. The structure of 2 could not be unambiguously deduced from these spectroscopic properties, and thus a crystallographic study was undertaken.

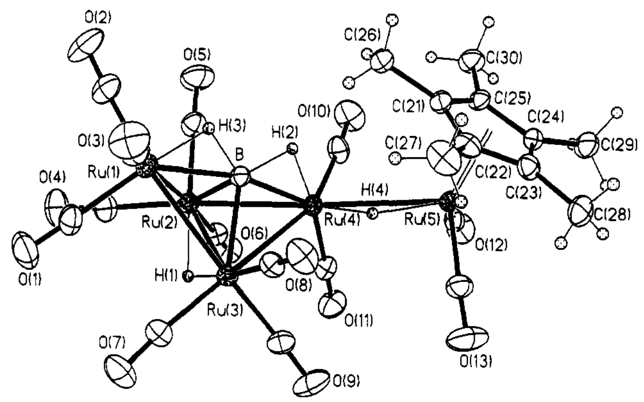

Figure 1. Molecular structure of 2.

Table III. Bond Distances and Angles for 2

(a) Bond Distances/Å			
Ru(1)–Ru(2)	2.846(1)	Ru(1)–Ru(3)	2.849(1)
Ru(2)–Ru(3)	2.876(1)	Ru(2)–Ru(4)	2.824(1)
Ru(3)–Ru(4)	2.887(1)	Ru(4)–Ru(5)	3.115(1)
Ru(1)–B	2.104(5)	Ru(2)–B	2.202(5)
Ru(3)–B	2.167(5)	Ru(4)–B	2.079(5)
Ru(2)–H(1)	1.76(7)	Ru(3)–H(1)	1.73(7)
Ru(4)–H(2)	1.62(7)	B–H(2)	1.29(7)
Ru(1)–H(3)	1.51(7)	B–H(3)	1.39(7)
Ru(4)–H(4)	1.71(7)	Ru(5)–H(4)	1.69(7)
(b) Bond Angles/deg			
Ru(2)–Ru(1)–Ru(3)	60.7(1)	Ru(2)–Ru(1)–B	50.1(1)
Ru(3)–Ru(1)–B	49.1(1)	Ru(1)–Ru(2)–Ru(3)	59.7(1)
Ru(1)–Ru(2)–Ru(4)	93.7(1)	Ru(3)–Ru(2)–Ru(4)	60.9(1)
Ru(1)–Ru(2)–B	47.2(1)	Ru(3)–Ru(2)–B	48.3(1)
Ru(4)–Ru(2)–B	46.9(1)	Ru(1)–Ru(3)–Ru(2)	59.6(1)
Ru(1)–Ru(3)–Ru(4)	92.3(1)	Ru(2)–Ru(3)–Ru(4)	58.7(1)
Ru(1)–Ru(3)–B	47.2(1)	Ru(2)–Ru(3)–B	49.4(1)
Ru(4)–Ru(3)–B	45.9(1)	Ru(2)–Ru(4)–Ru(3)	60.5(1)
Ru(2)–Ru(4)–Ru(5)	170.6(1)	Ru(3)–Ru(4)–Ru(5)	114.0(1)
Ru(2)–Ru(4)–B	50.6(1)	Ru(3)–Ru(4)–B	48.5(1)
Ru(5)–Ru(4)–B	120.0(2)	Ru(1)–B–Ru(2)	82.7(2)
Ru(1)–B–Ru(3)	83.7(2)	Ru(2)–B–Ru(3)	82.3(2)
Ru(1)–B–Ru(4)	162.8(3)	Ru(2)–B–Ru(4)	82.5(2)
Ru(3)–B–Ru(4)	85.6(2)		

Molecular Structure of $H_2Ru_5(CO)_{13}Cp^*BH_2$ (2). A crystal of 2 suitable for X-ray analysis was grown from CH_2Cl_2 layered with hexane. The molecular structure of 2 is shown in Figure 1, and selected bond distances and angles are given in Table III; the cluster core is illustrated in Figure 2. The results confirm the presence of five ruthenium atoms and also the presence of the HRu_4BH_2 butterfly core, which was anticipated from the spectroscopic data. The exceptional feature of the molecule is

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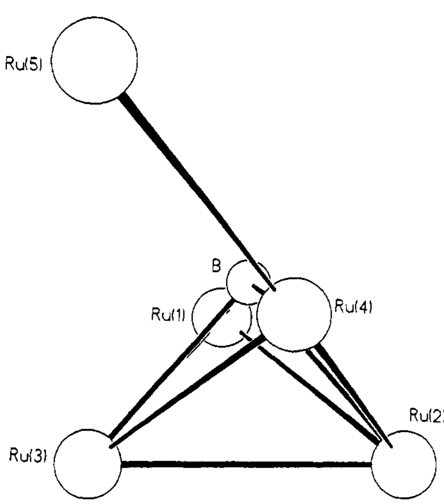

Figure 2. Molecular geometry of the Ru_5B core of 2.

the presence of a {Cp*Ru(CO)$_2$} "spike" attached to one of the butterfly wingtip atoms. Compound 2 is best regarded as a derivative of $HRu_4(CO)_{12}BH_2$ in which one wingtip terminal carbonyl ligand has been replaced by a {HRuCp*(CO)$_2$} fragment. The geometrical parameters of the HRu_4BH_2 core of 2 are similar to those of $HRu_4(CO)_{12}BH_2$;[3] in both molecules the hydride ligands have been located (see below). The internal dihedral angle of the Ru_4 butterfly is 114.2° in 2 and 118° in $HRu_4(CO)_{12}BH_2$, and the height of the boron atom above the $Ru_{wingtip}$--$Ru_{wingtip}$ axis is 0.31 Å in 2 and 0.39 Å in $HRu_4(CO)_{12}BH_2$.[3,4] The orientation of the Ru(4)–Ru(5) vector with respect to the Ru_4B butterfly core is clear from Figure 2; it effectively falls along the vector defined by one of the wingtip ruthenium–carbonyl equatorial ligands in $HRu_4(CO)_{12}BH_2$. Although as one goes from $HRu_4(CO)_{12}BH_2$ to 2 the molecular symmetry is reduced from C_{2v} (idealized) to C_1, the butterfly core suffers no significant distortion when the terminal {HRuCp*(CO)$_2$} fragment is introduced. The distance Ru(4)–Ru(5) is longer (3.115(1) Å) than those within the butterfly framework (average 2.865(1) Å).

Four hydride ligands have been located in 2. Atom H(1) bridges the hinge edge of the Ru_4 butterfly framework, and its presence is consistent with the resonance in the ^1H NMR spectrum at δ −20.95. The edges Ru(1)–B and Ru(4)–B are also bridged by hydrogen atoms, H(3) and H(2), respectively. Again, these locations are consistent with the observed broad resonance at δ −8.3 in the ^1H NMR spectrum of 2. Although H(2) and H(3) are not equivalent, their environments are not so different as to generate two distinct signals in the ^1H NMR spectrum; note that the width of the observed signal is large ($w_{1/2}$ = 280 Hz). A hydride ligand, H(4), has been located along the edge Ru(4)–Ru(5), and this is consistent with the observation in the ^1H NMR spectrum of the signal at δ −16.62. Considering the coordination sphere around atom Ru(5), a typical three-legged piano-stool complex has 90° angles between the "legs"; this criterion is met if atom H(4) occupies one of the ligand sites of atom Ru(5), and thus the Ru(5)–Ru(4) interaction appears not to be a direct one but is supported by a bridging hydrogen atom. Consider now the electronic requirements of the two portions of the molecule. The 18-electron rule is satisfied for atom Ru(5) if a localized Ru(4)–Ru(5) bond is included. The 62-electron count for the butterfly is achieved if the boron atom contributes all three of its valence electrons,[3,14] one electron is contributed by the *exo*-Ru–Ru bond, and all four cluster hydrogen atoms contribute one electron each. Hence, from an electron-counting point of view, atom H(4) would be expected to be essentially terminal with respect to the butterfly cluster. The esd's associated with the location of atom H(4) do allow for an ambiguity: Ru(4)–H(4) = 1.71(7) Å and Ru(5)–H(4) = 1.69(7) Å.

Compound 2 appears to be the first example of a spiked-butterfly cluster in which the "spike" is unsupported. Spiked-triangular clusters are known, but most usually, the interaction between the spike and the M_3 unit is supported by a bridging ligand,[10,15] as is the case in previous examples of spiked-butterfly clusters.[16,17] Several spiked-trigonal-bipyramidal clusters have also been characterized,[18-20] but only one[18] has an unsupported-spike–cluster interaction. The strategy for preparing some of these species has been the addition of a monometallic fragment to a preformed cluster core; for example, the reaction of trigonal-bipyramidal $Os_5(CO)_{15}(NCMe)$ with $H_2Os(CO)_4$ leads to $H_2Os_6(CO)_{19}$, a spiked-trigonal-bipyramidal cluster.[18]

Formation of 1 and 2. Originally, we had expected that $[Ru_3(CO)_9BH_4]^-$ would react with $[Cp^*RuCl_2]_n$ to incorporate $\{Cp^*Ru\}^+$ and generate a 62-electron butterfly product of the type "$Ru_4Cp^*(CO)_9BH_4$" or "$Ru_4Cp^*(CO)_{10}BH_2$". Thus, 1 is an anticipated product, but its formation is dependent on the reaction conditions and, even then, it is generated in low yield. On the other hand, the formation of the more dominant product, 2, is unexpected and the pathway to its formation is therefore of interest to us. Since the anion $[Ru_3(CO)_9BH_4]^-$ undergoes spontaneous cluster expansion to $[HRu_4(CO)_{12}BH]^-$, we considered the possibility that 2 does not arise directly from $[Ru_3(CO)_9BH_4]^-$ but is instead formed from the butterfly cluster. However, a test reaction of $[HRu_4(CO)_{12}BH]^-$ with $[Cp^*RuCl_2]_n$ under the same conditions as those described for the formation of 2 from $[Ru_3(CO)_9BH_4]^-$ does *not* yield 2 but instead leads only to the isolation of neutral $HRu_4(CO)_{12}BH_2$. Interestingly, as the reactivity patterns discussed below indicate, the "spike" in 2 is very readily lost, and this fact is consistent with the observation that a $\{Cp^*Ru\}^+$-based unit does not add to $[HRu_4(CO)_{12}BH]^-$. To date, we have not made further progress in understanding the mechanism of the formation of 2 from $[Ru_3(CO)_9BH_4]^-$.

Reactivity of 2. The unusual nature of the structure of 2 prompted us to embark upon a preliminary study of its reactivity. We wished in particular to compare the reactivity of 2 with that of $HRu_4(CO)_{12}BH_2$. $HRu_4(CO)_{12}BH_2$ deprotonates cleanly by the loss of one Ru–H–B bridging proton (Chart I); however, attempts to deprotonate 2 only lead to decomposition products.

Since we were not able to access the conjugate base of 2, we turned to attempts to close up the spiked-butterfly

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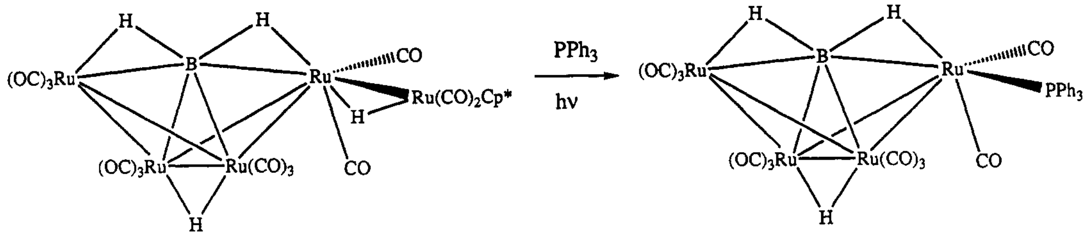
Scheme I



framework. We argued that it should be possible to transform the open 78-electron framework to, for example, a 76-electron molecule related to the carbido clusters $XRu_5Cp(CO)_{13}C$ (X = H, $AuPPh_3$)[21] and $Ru_5(CO)_{15}(MeCN)C$[22] or a 74-electron square-based-pyramidal borido cluster[12,13] via the extrusion of H_2 or CO. The method chosen for the investigation was that of photolysis. However, the photolysis of **2** in dichloromethane solution leads to the loss of the "spike" and the formation of $HRu_4(CO)_{12}BH_2$ as the only boron-containing product.

An attempt to perform a simple ligand substitution reaction on **2** was tried. Compound **2** was stirred in dichloromethane solution, first for 10 h with a 2-fold excess of PPh_3 and then for 45 h with a 6-fold excess of PPh_3. The progress of the reaction was monitored by IR spectroscopy. Once again, the loss of the "spike" is observed. The phosphine ligand substitutes for the terminal ruthenium group rather than a carbonyl ligand in **2**, and the only product is $HRu_4(CO)_{11}(PPh_3)BH_2$ (Scheme I). We have observed $HRu_4(CO)_{11}(PPh_3)BH_2$ to be a product of the direct substitution reaction of PPh_3 with $HRu_4(CO)_{12}BH_2$[8] and also as a product in the reaction of PPh_3 with $Ru_3(CO)_9BH_5$.[9]

Finally, the reaction of **2** with PhC≡CPh was examined. The photolysis of $HRu_4(CO)_{12}BH_2$ with PhC≡CPh leads to the insertion product $HRu_4(CO)_{12}B(H)C(Ph)CHPh$.[10] This reaction involves the opening up of the butterfly framework. The insertion of unsaturated ligands into clusters which already exhibit opened structures is documented,[23] and we anticipated that **2** might interact with PhC≡CPh while retaining a pentaruthenium cluster core. Although compound **2** indeed reacted with a 3-fold excess of diphenylacetylene, the only boron-containing product to be obtained was $HRu_4(CO)_{12}B(H)C(Ph)CHPh$.[10]

After the trial reactions described above, we conclude that the retention of the "spike" in **2** is not a preferred pathway during (at least in those studied) the reactions of **2**. The butterfly cluster $HRu_4(CO)_{12}BH_2$ appears to possess a particularly stable core, and during its reactions, compound **2** shows a preference to collapse to products which are derivatives of $HRu_4(CO)_{12}BH_2$.

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Supplementary Material Available: For **2**, tables giving a structure determination summary, atomic coordinates, bond distances, bond angles, thermal parameters, and H atom coordinates (10 pages). Ordering information is given on any current masthead page.

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