It is well-known that bonds between a central atom and electronegative ligands tend to shorten as the remaining ligands are substituted by more electronegative ones. For example, the P=S distance is PSF_3[18] is less than in $PSCl_3$[19] and the P—Cl distance in $POCl_3$[19] is less than that in $PSCl_3$, reflecting the relative electronegativities F > Cl and O > S. Operation of the principle in the molecules of Table I is seen in the fact that the W=O bond in WOF_4 is shorter than in $WOCl_4$ and the W—Cl bonds in $WOCl_4$ are shorter than in $WSCl_4$. In view of the successes, it is surprising to find the principle violated by the length found for the W=S bonds in WSF_4 and $WSCl_4$. The reason for this bond length inversion is obscure, but it seems more likely that it reflects abnormality in the structure of WSF_4 rather than in the structure of $WSCl_4$. In WSF_4 the W=S distance, for example, is about equal to that in solid $WSCl_4$,[20] where there is a weak W··Cl interaction trans to the sulfur atom; moreover it is about equal to W=S distances in a number of other six-coordinate adducts of $WSCl_4$.[21] There remains, of course, the possibility that our results have been significantly affected by the presence of sample impurity. We do not believe this likely because the amount of impurity was not excessive and its effect on the scattered intensity could be easily taken account of.

The relative bond orders of the bonds W=S and W=O in, respectively, WSF_4 and WOF_4 are of some interest. We believe that the latter is greater than the former. There are two pieces of evidence that support this view. The first concerns the stretching wavenumbers of these bonds, ν(W=S) = 577 cm^{-1} [23] and ν(W=O) = 1055 cm^{-1}.[24] A rough comparison of the corresponding force constants is obtained from $k_{W=O}/k_{W=S} = (\nu^2\mu)_{W=O}/(\nu^2\mu)_{W=S} = 1.77$, a value similar to the value 1.86 obtained for these bonds in $WSCl_4$ and $WOCl_4$. The second piece of evidence involves a consideration of the sums of the covalent radii. For both W=O and W=S the observed bond lengths are less than the nominal double-bond values (1.834 and 2.134 Å) obtained by subtracting 0.21 Å from the sums of the covalent single bond radii. However, the difference for W=O (0.17 Å) is much greater than that for W=S (0.03 Å), suggesting much higher bond multiplicity. We note in passing that these differences themselves differ by about the same amount as do the lengths of a triple bond and double bond and that the ratio of the force constants for such bonds is very close to the ratio 1.77 we calculate for k(W=O)/k(W=S).

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Registry No. WSF_4, 41831-80-5.

Supplementary Material Available: Total scattered intensities $s^4I_t(s)$ from each plate (Table III), calculated backgrounds for each plate (Table IV), and average molecular intensities $sI_m(s)$ from each camera distance (Table V) (6 pages). Ordering information is given on any current masthead page.

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Low-Temperature Neutron Diffraction Analysis of $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4][BF_4]_2$[1]

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A low-temperature (12 K) neutron diffraction study of $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4][BF_4]_2$ has been undertaken in order to determine whether the hydride ligands bridge the edges or faces of the tetranuclear rhodium cluster. Both anions and cations lie on sites of $\bar{4}$-S_4 symmetry. The cation is a stable, 58-electron, diamagnetic complex consisting of a tetrarhodium cluster with a C_5Me_5 ligand attached to each metal. The Rh_4 core shows substantial distortion from a regular tetrahedron, resulting in four long and two short Rh–Rh distances. The hydrides were found to bridge the faces of the tetrarhodium cluster at a distance of 0.96 Å above the planes formed by three Rh atoms. The Rh–Rh distances are 2.610 (5) and 2.829 (5) Å, and the Rh atoms are 1.84 Å from the C_5-ring planes. A detailed ^1H and ^{13}C NMR analysis establishes that the hydride ligands also are face bridging in solution. Calculations based on idealized tetrahedral geometry for the molecular framework show no abnormally short nonbonded contacts, and thus distortion from T_d symmetry appears to be electronic rather than steric in origin. Crystallographic data for $[C_{40}H_{64}Rh_4][BF_4]_2$: tetragonal, space group $I\bar{4}$, $Z = 2$, $a = 11.459$ (3) Å, $c = 15.481$ (8) Å, $R(F^2) = 0.069$ for 1371 reflections with $(\sin\theta)/\lambda < 0.83$ Å^{-1}.

Introduction

The X-ray crystal structure of the polynuclear transition-metal hydride $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4][BF_4]_2$ was reported recently.[6] The cation contains four rhodium atoms clustered in a distorted tetrahedral array with four long and two short Rh–Rh bonds. Each rhodium atom is symmetrically η^5 bonded to a C_5Me_5 ligand. Attempts to locate the hydride ligands were unsuccessful, and it was predicted on the basis of earlier structural work on metal hydride clusters that the four hydrogens would bridge the longer Rh–Rh bonds. ^1H NMR measurements showed that the four hydrides were chemically equivalent as were the rhodium nuclei but that the hydride ligands were not free to move over the molecular framework.[6]

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Table I. Experimental Details and Refinement Parameters

cryst wt, mg	1.55
cryst vol, mm^3	0.86
cryst boundary faces	{010}, {101}, {011}, {111}
calcd transmission range	0.657–0.804
no. of reflcns measd	1607
no. of independent reflcns (n)	1371
agreement factor for averaging: $R_c = \Sigma\Sigma_{i=1}^{n}\lvert\langle F_o^2\rangle - F_{oi}^2\rvert/\Sigma n'\langle F_o^2\rangle$	0.060
$R(F^2) = \Sigma\lvert F_o^2 - k^2F_c^2\rvert/\Sigma\lvert F_o^2\rvert$	0.069
$R_w(F^2) = [\Sigma w(F_o^2 - k^2F_c^2)^2/\Sigma wF_o^4]^{1/2}$	0.075
$S = [\Sigma w(F_o^2 - k^2F_c^2)^2/(n-m)]^{1/2}$	1.60
no. of variable parameters (m)	267

A theoretical analysis of bonding in tetranuclear hydride clusters by Hoffmann et al.[7] suggests that a cluster of the type $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4]^{2+}$ would be paramagnetic with two unpaired electrons and face-bridging hydrides, if the Rh_4H_4 core had $\bar{4}3m\text{-}T_d$ symmetry. In fact, the 58-electron tetrarhodium cluster is low-spin diamagnetic with distortion away from T_d symmetry.

The present neutron diffraction study was carried out in order to locate the hydrogen atoms and to assess the origin of the distortion of the tetranuclear framework.

Experimental Section

Black single crystals of the title compound suitable for neutron diffraction work were obtained by methods previously reported.[6] The largest was a tetrahedral specimen with a volume of 0.86 mm^3. This crystal was mounted on an aluminum pin oriented along the crystallographic (011) direction. The sample was sealed in an aluminum can under a helium atmosphere and placed in a closed-cycle helium refrigerator[8] mounted on a four-circle diffractometer[9,10] at the Brookhaven High Flux Beam Reactor. A beryllium (002) single-crystal monochromator was employed to produce a neutron beam of wavelength 1.0468 (2) Å based on KBr (a = 6.6000 Å at T = 298 K).[11] A sample temperature of 12.0 (5) K[12] was maintained during the experiment, and unit-cell dimensions at this temperature were determined by a least-squares fit of the observed $\sin^2\theta$ values of 30 reflections ($50° < 2\theta < 60°$). Crystal data for $[C_{40}H_{64}Rh_4][BF_4]_2$: M_r 1130.2; tetragonal, a = 11.459 (3) Å, c = 15.481 (8) Å, V = 2033 (1) Å^3, Z = 2, space group $I\bar{4}$, ρ_{calcd} = 1.847 g cm^{-3}. Further experimental details are given in Table I.

Three-dimensional intensity data were obtained over one octant of reciprocal space with $2\theta \leq 121°$ ($(\sin\theta)/\lambda \leq 0.83$ Å^{-1}) by using $\theta/2\theta$ step scans. The scan range was varied according to $\Delta(2\theta) = (2.09 + 0.78\tan\theta)°$ for the high-angle data ($55 \leq 2\theta \leq 121°$) and $\Delta(2\theta) = 3.0°$ for low-angle data. The step size was adjusted to give between 55 and 75 steps per scan, and counts were accumulated for approximately 12 s at each step, the exact time interval being determined by monitoring the incident-beam intensity. The intensities of two monitor reflections were measured every 100 reflections and showed no significant variation during the course of data collection.

Integrated intensities were obtained with the first and the last tenth of each scan taken as background. Absorption corrections (μ = 3.786 cm^{-1}) were applied to the observed intensities by means of numerical integration over a Gaussian grid of points[13] and converted to squared structure factors, $F_o^2 = I\sin 2\theta$. Multiple observations of the same and symmetry-related reflections were averaged to give 1371 independent values of F_o^2.

Table II. Positional Parameters

atom	x	y	z
Rh	0.0410 (2)	0.1062 (2)	0.0692 (2)
Me(O1)	0.1710 (2)	0.0844 (2)	0.2630 (2)
Me(O2)	−0.0833 (2)	0.2060 (2)	0.2519 (2)
Me(O3)	−0.0860 (2)	0.3704 (2)	0.0947 (2)
Me(O4)	0.1645 (2)	0.3525 (2)	−0.0040 (2)
Me(O5)	0.3191 (2)	0.1773 (2)	0.1082 (2)
C(O1)	0.1246 (2)	0.1579 (2)	0.1922 (2)
C(O2)	0.0131 (2)	0.2119 (2)	0.1871 (2)
C(O3)	0.0113 (2)	0.2866 (2)	0.1119 (2)
C(O4)	0.1231 (2)	0.2825 (2)	0.0715 (2)
C(O5)	0.1922 (2)	0.2007 (2)	0.1196 (2)
B(A)	0.5000 (0)	0.0000 (0)	0.2500 (0)
B(B)	0.0000 (0)	0.0000 (0)	0.5000 (0)
F(A)	0.4414 (3)	0.0808 (3)	0.3023 (2)
F(B)	0.0179 (4)	0.0977 (4)	0.4480 (3)
H	0.1048 (5)	−0.0399 (5)	0.0518 (4)
H(O11)	0.2273 (7)	0.1367 (7)	0.3055 (5)
H(O12)	0.2256 (6)	0.0146 (6)	0.2382 (5)
H(O13)	0.1021 (6)	0.0479 (6)	0.3038 (5)
H(O21)	−0.0662 (6)	0.1448 (7)	0.3038 (5)
H(O22)	−0.1661 (5)	0.1826 (8)	0.2224 (5)
H(O23)	−0.0931 (7)	0.2920 (6)	0.2811 (5)
H(O31)	−0.1711 (5)	0.3273 (6)	0.0951 (5)
H(O32)	−0.0748 (6)	0.4158 (6)	0.0339 (5)
H(O33)	−0.0879 (7)	0.4354 (6)	0.1466 (5)
H(O41)	0.0932 (6)	0.3893 (6)	−0.0403 (5)
H(O42)	0.2211 (7)	0.4233 (6)	0.0170 (5)
H(O43)	0.2157 (7)	0.2998 (6)	−0.0482 (5)
H(O51)	0.3360 (6)	0.0847 (6)	0.0998 (5)
H(O52)	0.3547 (6)	0.2267 (6)	0.0542 (4)
H(O53)	0.3652 (6)	0.2025 (8)	0.1660 (4)

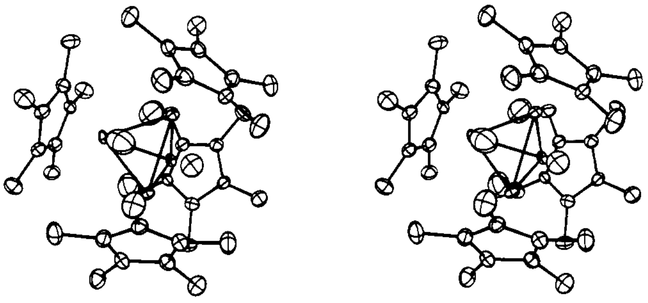

Figure 1. Stereoscopic view of the $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4]^{2+}$ cation at 12 K with thermal ellipsoids drawn to enclose 97% probability density. Methyl hydrogens are omitted for clarity.

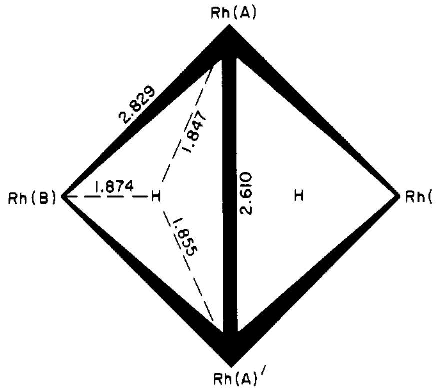

Figure 2. Projection drawing of the tetranuclear core giving the rhodium-cluster-numbering scheme and some relevant bond distances.

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

Rh(A)-Rh(A)'	2.610 (5)	C(O1)-C(O2)	1.422 (3)
Rh(A)-Rh(B)	2.829 (5)	C(O2)-C(O3)	1.444 (4)
Rh(A)-H	1.847 (6)	C(O3)-C(O4)	1.426 (4)
Rh(A)'-H	1.855 (6)	C(O4)-C(O5)	1.435 (4)
Rh(B)-H	1.874 (6)	C(O5)-C(O1)	1.452 (4)
Rh-C(O1)	2.212 (4)	C-C$_{av}$	1.436 (6)[b]
Rh-C(O2)	2.212 (4)	C(O1)-Me(O1)	1.480 (4)
Rh-C(O3)	2.196 (4)	C(O2)-Me(O2)	1.494 (4)
Rh-C(O4)	2.228 (4)	C(O3)-Me(O3)	1.496 (4)
Rh-C(O5)	2.187 (4)	C(O4)-Me(O4)	1.494 (4)
Rh-C$_{av}$	2.207 (7)[b]	C(O5)-Me(O5)	1.488 (4)
Rh-C$_5$(ring)	1.838	C-Me$_{av}$	1.490 (4)[b]
B(A)-F(A)	1.402 (3)	C-H$_{av}$	1.088 (8)[b]
B(B)-F(B)	1.394 (4)		
Rh(B)-Rh(A)-Rh(B)'	54.93 (11)	C(O1)-C(O2)-C(O3)	108.4 (2)
Rh(B)-Rh(A)-Rh(A)'	62.53 (5)	C(O2)-C(O3)-C(O4)	108.8 (2)
F(A)-B(A)-F(A)'	109.5 (1)	C(O3)-C(O4)-C(O5)	106.8 (2)
F(B)-B(B)-F(B)'	109.4 (4)	C(O4)-C(O5)-C(O1)	109.1 (2)
		C(O5)-C(O1)-C(O2)	106.8 (2)

[a] Esd's in parentheses. Ring carbons are designated C(O1)-C(O5) and methyl carbons Me(O1)-Me(O5). Atoms related by the twofold axis are primed. [b] Standard deviations of mean values are given as the larger of the individual esd's or $\sigma(\bar{x}) = [\Sigma_{i=1}{}^{n}(x_i - \bar{x})^2/n(n-1)]^{1/2}$, where $\bar{x}$ is the average value and x_i's are individual values.

Initial atomic coordinates for the non-hydrogen atoms were taken from the X-ray results,[6] and after a few cycles of differential synthesis refinement[14] a difference-scattering-density synthesis revealed the positions of all hydrogen atoms. A total of 267 variable parameters, which included positional and anisotropic thermal factors for all 31 atoms, a scale factor (k), and a type I isotropic-extinction parameter (g),[15] were varied by a full-matrix least-squares procedure minimizing $\sum w(F_o^2 - k^2F_c^2)^2$.[16] Weights were taken as $w = 1/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2_{count}(F_o^2) + (0.01F_o^2)^2]$. The most significant extinction correction factor was 0.80, dividing F_o^2 for reflection 121. Neutron scattering lengths were taken to be $b_{Rh} = 0.588 \times 10^{-12}$ cm, $b_F = 0.566 \times 10^{-12}$ cm, $b_C = 0.665 \times 10^{-12}$ cm, $b_B = 0.535 \times 10^{-12}$ cm, and $b_H = -0.374 \times 10^{-12}$ cm.[17] The refinement was terminated when the maximum shift/esd for any parameter was less than 0.1. A difference synthesis computed at this stage was essentially featureless. Final agreement factors are included in Table I, while positional parameters for all atoms are given in Table II.

NMR spectra of a solution of the title compound in $(CD_3)_2CO$ at ca. 293 K were obtained with a JEOL FX90Q spectrometer. Broad-band ^1H irradiation was employed for the ^{13}C measurement.

Results and Discussion

The molecular structure of $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4]^{2+}$ at 12 K and the rhodium-cluster-numbering scheme are illustrated in Figures 1 and 2 ,[18] respectively. The cation and both BF_4^- anions lie on sites of $\bar{4}$–S_4 symmetry. The four hydride ligands bridge the faces of the tetrarhodium cluster at a distance of 0.957 Å above the plane formed by the three Rh atoms. The remainder of the molecular geometry is in general agreement with that found by X-ray diffraction at room temperature[6] except that both BF_4^- ions were well-behaved in the refinement of the low-temperature model, whereas at room temperature one BF_4^- was found to be disordered. Selected interatomic bond distances and angles are given in Table III.

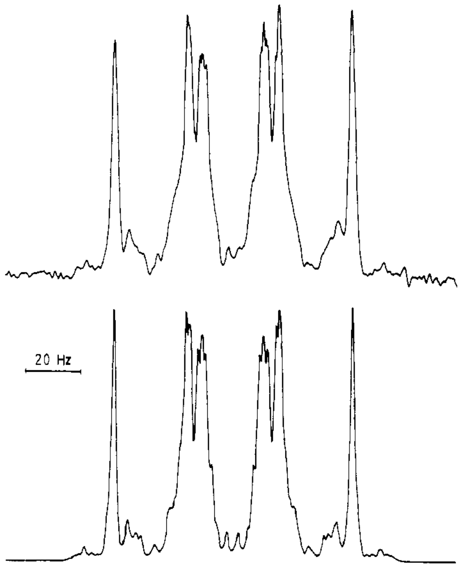

Figure 3. High-field region of the ^1H NMR spectrum of $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4]^{2+}$ processed for resolution enhancement (top) with simulation using the parameters given in the text (bottom).

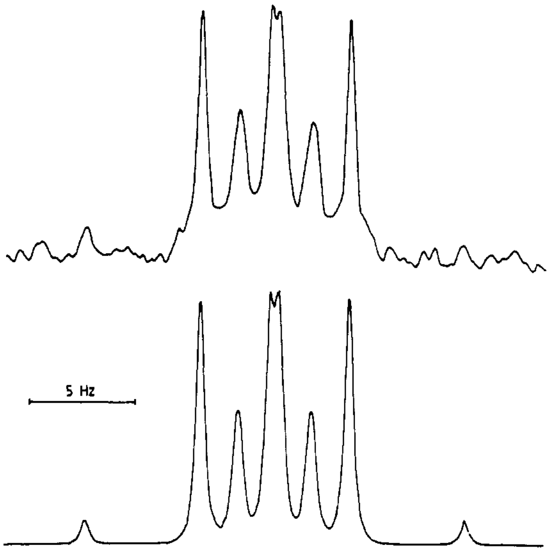

Figure 4. $^{13}C\{^1H\}$ NMR spectrum of $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4]^{2+}$ in the C_5Me_5 region (top) with simulation using the parameters given in the text (bottom).

The five ring carbons of the C_5Me_5 ligand are essentially coplanar, with the maximum displacement of an individual carbon from the best least-squares plane being 0.016 Å. The C_5 plane is 1.838 Å from the rhodium to which it is bonded and the methyl groups are bent away from the rhodium at an average distance from C_5 plane of 0.160 Å (an effect of the molecular crowding of the C_5Me_5 rings around the tetranuclear core[6]).

The ^1H NMR spectrum of $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4]^{2+}$ is complex (Figure 3), due to the magnetic inequivalence in this $[AX]_4$ spin system. The value of $^1J_{Rh-Rh}$ was established by analysis and simultation[19] of the ^{13}C spectrum of the cyclopentadienyl ring carbons (see Figure 4). The splitting of the central feature can only be reproduced if a chemical shift difference for rhodium bound to ^{13}C is introduced. This $^{12}C/^{13}C$ isotope effect (ca. 0.2 ppm) may be compared with 0.4 and <0.15 ppm reported by Salzer et al. for ^{103}Rh bound

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(19) Simulations were performed with the computer program NUMARIT written by J. S. Martin and A. R. Quirt, University of Alberta.

Table IV. Nonbonding Contact Distances (Å)[a]

	obsd	idealized (T_d)
Intramolecular H···H Contacts (<2.3 Å)[b]		
H(A31)···H(B43)	2.082 (10)	2.118
H(A13)···H(A21)	2.226 (10)	2.226
H(A13)···H(A21)′	2.247 (11)	2.390
H(A32)···H(A41)	2.262 (10)	2.262
H(A32)···H(B51)	2.265 (11)	2.114
H(A31)···H(B52)	2.418 (11)	2.255
Shortest Intermolecular Contacts		
H(A22)···H(A53)[c]	2.356 (10)	2.501
H(A33)···H(A33)[d]	2.501 (10)	2.379
H···F Contacts (<2.5 Å)[b]		
F(A)···H(A51)[e]	2.430 (7)	2.529
F(A)···H(A12)[e]	2.453 (7)	2.432
F(A)···H(A41)[f]	2.492 (8)	2.393
F(B)···H(A42)[c]	2.404 (8)	2.370
F(B)···H(A21)	2.491 (9)	2.590
F(B)···H(A13)	2.497 (9)	2.587

[a] Methyl hydrogens are denoted H(A11)–H(A53) for atoms on the ring bonded to Rh(A), and so forth. Atoms related by the twofold axis are primed. [b] The values in parentheses are the nominal sum of the Pauling–van der Waals radii. [c] $-\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$. [d] $x, 1-y, z$. [e] $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$. [f] $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$.

to C_5H_5 in two dimeric complexes.[20] The two markedly different sets of Rh–Rh distances found in the X-ray diffraction study might suggest that two values of $^1J_{Rh-Rh}$ were involved. However, simulations on such a basis clearly demonstrated that this was not so and that the Rh_4 skeleton is a symmetrical tetrahedron on the NMR time scale.

With the value of $^1J_{Rh-Rh}$ derived from the ^{13}C spectrum, we were then able to reproduce the ^1H NMR spectrum of the hydrides on the basis of a symmetrical face-bridged structure, i.e. three equal one-bond Rh–H couplings and one two-bond Rh–H coupling. The correspondence of the finer details (which are sensitive to the magnitude and relative signs of $^2J_{Rh-H}$ and J_{H-H}) was checked against spectra processed to give resolution enhancement.[21] The parameters determined by this analysis were $^1J_{Rh-Rh} = 8.2$ Hz, $^1J_{Rh-C} = 7.0$ Hz, $^2J_{Rh-C} = \sim 0$ Hz, $^1J_{Rh-H} = 28.4$ Hz, $^2J_{Rh-H} = 0.5$ Hz, (sign opposite to $^1J_{Rh-H}$), and $J_{H-H} = 2.0$ Hz (sign opposite to $^1J_{Rh-Rh}$) with estimated errors of ±0.1 Hz.

In contrast to the agreement of the observed spectra with simulations based on a symmetrical face-bridged structure, there is little correspondence with simulations based on the edge-bridged structure that had been surmised following the X-ray diffraction study.[6] Thus detailed NMR analysis establishes that the hydride ligands are face bridging in solution.

In order to investigate whether the distortion of the Rh_4H_4 core from T_d symmetry might be steric as opposed to electronic in origin, the nonbonding contacts between methyl hydrogens were calculated for an idealized tetrahedral geometry with a Rh–Rh distance of 2.756 Å. These values are given in Table IV. The shortest of the intramolecular idealized T_d contacts is 2.114 Å, or very slightly longer than the minimum value of 2.082 (10) Å in the observed structure. For intermolecular contacts, the shortest distance in the idealized model is 2.379 Å, compared to the value of 2.356 (10) Å in the observed structure. (The sum of the H···H van der Waals covalent radii[22] is 2.3 Å.) Similar calculations for the methyl hydrogen–fluorine contacts gave 2.370 Å for the shortest idealized contact as compared with an observed value of 2.404 Å (Table IV). The sum of the H and F Pauling–van der Waals radii[22] is 2.5 Å. From the above values we conclude that the departure of the Rh_4H_4 core from T_d symmetry is not likely to be steric in origin, but rather may result from a Jahn–Teller type distortion involving a pair of electrons, so that the predicted[7] near degeneracy of the cluster highest occupied molecular orbitals is split.

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Registry No. $[Rh_4(\eta^5\text{-}C_5Me_5)_4H_4][BF_4]_2$, 71250-46-9; Rh, 7440-16-6.

Supplementary Material Available: A stereoscopic drawing of the packing in the unit cell and listings of atomic thermal parameters, complete bond distances and angles, and observed and calculated squared structure factors (13 pages). Ordering information is given on any current masthead page.

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