tion from the 18-electron $FeCp^*(CO)_2^-$ fragment to the vacant LUMO ($4b_1$) on the phosphenium ion.[27] The phosphorus atom lone pair is no longer considered to be significantly involved in σ donation to the iron atom unit, and consequently, the lone pair should be stereochemically active.

Hoffmann and co-workers[28] have examined in detail the bonding in $MCp(CO)_2L$ complexes. When M = Fe the conceptual approach has involved the combination of metal orbitals on the 16-electron fragment $FeCp(CO)_2^+$ with ligand MOs having only σ donation (lone pair) or both σ donation and π back-donation ability. The formation of complexes from the combination of a filled metal orbital (3a′) on the 18-electron fragment $FeCp(CO)_2^-$ with ligand MOs having only electron accepting or both σ donor and π-acceptor character was not considered.[29] Compound 4 offers an ideal example of the latter case. It is expected in 4 that electron donation from the occupied iron 3a′ orbital, which is primarily $3d_{z^2}$ in character, to an empty phosphenium ion three center MO ($4b_1$) which is antibonding with respect to the P–N bonds would result in a relatively weak Fe–P interaction and elongated P–N bonds. This is the trend observed in the structural parameters, and detailed MO calculations for 4 are in progress.

Finally, it is important to note that the structure of 4 is exactly that which would be predicted for the presently unknown complex $FeCp(CO)_2SO_2$. Other parallels between metallophosphenium ion complexes and metal–SO_2 complexes also are currently of interest.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We also acknowledge NSF Grants CHE-7802921 and MPS-06111 which facilitated the purchase of the X-ray diffractometer and the NMR data system. We also wish to recognize continuing fruitful discussions and collaborations with R. R. Ryan and D. C. Moody of Los Alamos National Laboratory over the SO_2 analogy.

Registry No. 4, 82621-27-0; $CH_3\overline{NCH_2CH_2N(CH_3)}PF$, 33672-91-2; $NaFeCp^*(CO)_2$, 82621-26-9.

Supplementary Material Available: A listing of observed and calculated structure factors, positional parameters, anisotropic thermal parameters, bond distances and angles, and least-squares planes (20 pages). Ordering information is given on any current masthead page.

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(26) The important starting planar phosphenium ion orbitals in order of increasing energy are $3b_1$, out-of-plane three-center bonding MO delocalized over the PN_2 unit (occupied), $8a_1$, in-plane MO predominantly phosphorus lone pair in character (occupied), $4a_2$ out-of-plane ligand HOMO predominantly nitrogen lone pair in character (occupied), and $4b_1$, out-of-plane ligand LUMO delocalized over the PN_2 unit (unoccupied). In 1, the P→Mo σ donation primarily involves overlap of the ligand $8a_1$ MO and the metal d_{z^2} orbital, and the Mo→P π back-donation involves the overlap of the ligand $4b_1$ LUMO and the metal d_{xz} orbital.[2]

(27) Rehybridization of the phosphenium ion will not drastically affect the frontier orbital arrangement of the ligand. It is anticipated that the lone pair will occupy one sp^3 lobe and it should possess more p character than the $8a_1$ MO in the planar ligand. The LUMO ($4b_1$) in the planar ligand will remain as the LUMO in the pyramidal ligand and to a first approximation the orbital will have more s character than in the planar case. The ligand puckering is probably a response to the nitrogen atoms distorting in an attempt to retain the delocalized three-center N–P–N character in the LUMO ($4b_1$).

(28) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

(29) $CpFe(CO)_2^-$ may be conceptually formed by electron pair addition into the 3a′ LUMO of $CpFe(CO)_2^+$. This MO is predominantly d_{z^2} in character.

A New Member of the $(HRhL_2)_x$ Cluster Class: $[(\mu\text{-}H)Rh(1,5\text{-cyclooctadiene})]_4$

Matthew Kulzick, Robert T. Price, and E. L. Muetterties*

Department of Chemistry, University of California
Berkeley, California 94720

Victor W. Day*

Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588
and The Crystalytics Company
Lincoln, Nebraska 68510

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Summary: Reaction of ethyllithium with $[(\mu\text{-}Cl)Rh(1,5\text{-cyclooctadiene})]_2$ in diethyl ether at ~−80 °C forms $[(\mu\text{-}C_2H_5)Rh(1,5\text{-cyclooctadiene})]_2$. This dinuclear species is thermally reactive and through a series of β-hydride elimination and dissociation steps yields $[(\mu\text{-}H)Rh(1,5\text{-cyclooctadiene})]_4$. This cluster is formally related to the $(HRhL_2)_x$ cluster group defined for a dimer and trimer.

Polynuclear rhodium and iridium complexes have resulted from the reaction of $[(\mu\text{-}Cl)M(1,5\text{-cyclooctadiene})]_2$ with alkyl-, aryl-, and aralkyllithium reagents.[1] One of these products, the novel $[(\mu\text{-}H)Rh(1,5\text{-cyclooctadiene})]_4$ cluster, 1, is described here in terms of structure, dynamic stereochemistry, and chemistry. Formally, this new cluster is related to the coordinately unsaturated group of $[HRh(PY_3)_2]_x$ clusters[2] initially described by us.[3–6] This structural class, rigorously established by X-ray and neutron diffraction studies[4,5,7,8] of a dimer and trimer, is characterized by a local, nearly coplanar, four-coordinate geometry (L_2RhH_2) for each rhodium atom. A projected structure[4] for the tetramer in this class was a puckered four-membered Rh_4 ring. In fact, the new $[(\mu\text{-}H)Rh(1,5\text{-cyclooctadiene})]_4$ cluster can be described in these terms (or as a conventional tetrahedral cluster).

Single crystals[9] of the toluene solvate of $H_4Rh_4(1,5\text{-}C_8H_{12})_4$, 1, were, at 20 ± 1 °C, orthorhombic of space group C_{222_1}—C_2^5 (No. 20) with $a = 10.939\ (2)$ Å, $b = 19.285\ (5)$ Å, $c = 31.548\ (8)$ Å, and $Z = 8$ $[H_4Rh_4(C_8H_{12})_4\cdot 0.5CH_3C_6H_5]$ formula units ($d_{calcd} = 1.791$ g cm^{-3}; μ_a (Mo K$\bar{\alpha}$) = 1.91 mm^{-1}). Three-dimensional X-ray diffraction data were collected for 8182 independent reflections having $2\theta_{MoK\bar{\alpha}} < 71°$ (the equivalent of 2.0 limiting Cu K$\bar{\alpha}$ spheres) on a Nicolet P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (1° wide) ω scans. The four rhodium atoms were located by using "direct methods" techniques and the remaining non-hydrogen and hydride hydrogen atoms with difference Fourier techniques; positions for cyclooctadiene hydrogen atoms were

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(1) Schmidt, G. F.; Muetterties, E. L.; Beno, M. A.; Williams, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1318.

(2) Y = OR, F, and $N(CH_3)_2$.

(3) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

(4) Brown, R. K.; Williams, J. M.; Sivak, A. J.; Muetterties, E. L. *Inorg. Chem.* **1980**, *19*, 370.

(5) Teller, R. G.; Williams, J. M.; Koetzle, T. F.; Burch, R. R.; Gavin, R. M.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1806.

(6) Meier, E. B.; Burch, R. R.; Muetterties, E. L.; *J. Am. Chem. Soc.* **1982**, *104*, 2661.

(7) Day, V. W.; Fredrich, M. F.; Reddy, G. S.; Sivak, A. J.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 8091.

(8) Brown, R. K.; Williams, J. M.; Fredrich, M. F.; Day, V. W.; Sivak, A. J.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2099.

0276-7333/82/2301-1256$01.25/0

calculated by using idealized geometry and were not least-squares refined. The structural parameters of 45[10] independent (41 anisotropic non-hydrogen and 4 isotropic hydride hydrogen) atoms were refined to convergence [R(unweighted, based on F) = 0.041 for 6082 independent absorption-corrected reflections having $I > 3\sigma(I)$] using full-matrix least-squares techniques.[11]

The crystal is composed of tetranuclear H_4Rh_4(1,5-cyclooctadiene)$_4$ molecules, **1**, and toluene molecules of crystallization; thus, the cluster does not have the composition originally proposed.[1,9b] A tetrahedron of idealized D_{2d} symmetry is defined by the four Rh atom positions. Two tetrahedral edges are long, 2.971 (1, 31, 31, 2) Å,[12] and four are short and characteristic of Rh–H–Rh (singly) bridging distances,[4,7] 2.802 (1, 5, 10, 4) Å.[12] Associated with each of the four edges is one hydride hydrogen atom that is within a bridge bonding distance of two rhodium atoms (<1.91 Å).[13] This resultant Rh_4H_4 core structure has idealized S_4 symmetry. Peripherally, each rhodium atom is bonded to the two olefinic units of a cyclooctadiene ligand. The core structure is illustrated in Figure 1 (see supplementary material for the full ORTEP presentation).

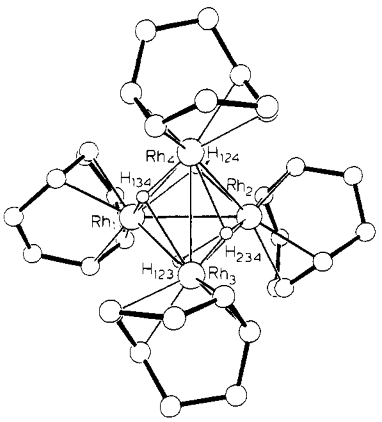

Figure 1. Perspective drawing (adapted from an ORTEP plot) of the [(μ-H)Rh(1,5-cyclooctadiene)]$_4$ molecule, **1**, as observed in the solid state with toluene molecules of crystallization. Rhodium atoms are represented by large open circles, carbon atoms by medium-sized open circles, and hydrogen atoms by small open circles. The molecule *approximates* idealized C_2 symmetry with the pseudotwofold axis passing through the midpoints of the Rh_1–Rh_2 and Rh_3–Rh_4 vectors. For clarity, the cyclooctadiene hydrogen atoms are not depicted.

In this tetranuclear rhodium complex, each rhodium atom has four close contacts, two hydride ligands and two midpoints, C_2-m, of the olefinic bonds of a cyclooctadiene ligand. Although there is a fifth atom, a hydride ligand, at a long[14] but at what could be considered to be a nominally bonding distance (≥2.07 Å), we tentatively suggest that the immediate coordination sphere of each rhodium atom can be considered to be four-coordinate, (Rh–H–)$_2$Rh–(C_2-m)$_2$; these four bonding interactions have distances that are fully consistent with this characterization.[4,5,7,8,15] In a qualitative sense, this tetranuclear cluster appears to have an electronic and geometric structure that is a logical extension[4] of the four-coordinate H_2RhP_2 units in the formally related [(μ-H)Rh[P(O-i-C_3H_7)$_3$]$_2$]$_2$ dimer, **3**, and [(μ-H)Rh[P(OCH_3)$_3$]$_2$]$_3$ trimer, **4**. Accordingly, we portray this novel tetranuclear rhodium complex as a ring structure as shown in projection as **5** in Figure 2.[13]

In both the dimer **3** and trimer **4**, the four-coordinate rhodium atoms have near coplanar form and near 90° L–M–L intraligand angles. For the tetranuclear rhodium complex, all H–Rh–H and (C_2-m)–Rh–(C_2-m) angles[15] are close to 90°, with respective ranges of 81–91° and 87.0–87.5°. However, the H–Rh–(C_2-m) angles depart more substantially from 90°, ranging from 87 to 104°; and the dihedral angles between H–Rh–H and (C_2-m)–Rh–(C_2-m) planes are not zero but 16.6, 17.3, 30.2, and 32.2°. These departures from coplanarity in the local $H_2Rh(C_2\text{-m})_2$ coordination spheres are fully explicable: were coplanarity maintained there would be impossibly

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[9] (a) For the synthesis and characterization of [(μ-C_2H_5)Rh(1,5-cyclooctadiene)]$_2$, an all-glass apparatus equipped with Teflon stopcocks was designed so that the reaction and all subsequent operations could be effected at low temperatures and that the crude product could be purified by dissolution, filtration and crystallization and then transferred by dissolution in toluene-d_8 (NMR solvent) to an NMR tube. In the synthesis of the ethyl complex, the reaction solutions and solids were never allowed to warm above ~−70 °C. The reaction chamber was charged with [(μ-Cl)Rh(1,5-cyclooctadiene)]$_2$ (50 mg, 0.1 mmol) and diethyl ether (50 mL). Two equivalents of ethyllithium in diethyl ether (0.05 M) were added. The slurry was stirred and then was cooled to −78 °C. The reaction system (dark red) was stirred for ~12 h. Two equivalents of ethyllithium in diethyl ether (0.05 M) were added. Then the ether was removed under high vacuum (<10^{-5} torr). The reaction system (dark red) was stirred for ~12 h. The residue was extracted with pentane and the pentane extract was filtered (under argon pressure through a frit of medium porosity). Then the ether was removed under high vacuum (<10^{-5} torr). Removal of pentane under high vacuum yielded dark red crystals. The residue was extracted with pentane and the pentane extract was filtered (under argon pressure through a frit of medium porosity). Toluene-d_8 (0.5 mL) was transferred onto the crystal. Removal of pentane under high vacuum yielded dark red crystals. The resultant solution was decanted into an NMR tube. Toluene-d_8 (0.5 mL) was transferred onto the crystal. The latter was then cooled to −197 °C, evacuated, and torch sealed: ^1H NMR (−70 °C) δ 4.0 (s, 2, HC═), 3.6 (s, 2, HC═), 1.6 (m, 8, CH_2), 0.6 (q, 2, ethyl CH_2), −0.6 (t, 3, ethyl CH_3, J_{HH} = 7.3 Hz); ^1H {^1H CH_3 of ethyl group} 0.6 resonance became a triplet (coupling to two ^{103}Rh atoms). The resultant solution was decanted into an NMR tube. The ^1H NMR spectra were temperature invariant to −20 °C where conversion of [(μ-C_2H_5)Rh(1,5-cyclooctadiene)]$_2$ to [(μ-H)Rh(1,5-cyclooctadiene)]$_4$ and C_2H_4 could be readily observed by NMR; conversion was complete at −20 °C in 0.5 h.

(b) For the synthesis and characterization off [(μ-H)Rh(1,5-cyclooctadiene)]$_4$, Dri-box and Schlenk techniques were employed. A Schlenk flask was charged with [(μ-Cl)Rh(1,5-cyclooctadiene)]$_2$ (100 mg, 0.2 mmol), diethyl ether (50 mL), and an argon atmosphere. The reaction flask was cooled to −78 °C, and the contents were rapidly stirred with a magnetic stir bar. Two equivalents of either K[HB(O-i-C_3H_7)$_3$] in tetrahydrofuran (~1.0 M) or C_2H_5Li in toluene (~0.1 M) was added to the reaction system via a syringe-serum cap technique. On this addition, the yellow reaction mixture turned dark red immediately. After being stirred at −78 °C for ~1 h, the reaction mixture was allowed to warm to 20 °C and stirring was continued for 3 h. Ether and other volatiles were removed by evacuation. The residue was extracted with pentane (50 mL), and then this pentane slurry was filtered. Crude **1** can be obtained directly from this pentane solution to give crude yields in the 50–60% range. Anal. Calcd for $Rh_4C_{32}H_{48}$: C, 45.52; H, 5.73. Found: C, 45.8; H, 6.0. To obtain very pure samples of **1**, the following procedure was followed. The above-mentioned pentane extract after filtration was concentrated and passed through a short (5-cm) column of activated silica gel. A short contact time on the column was essential to prevent extensive decomposition on the column. The pentane eluate was concentrated and then cooled to −30 °C to yield dark red crystals (~20 mg of crystals): ^1H NMR (toluene-d_8, +30 °C) δ 4.74 (s, 4), 2.22 (m, 4), 1.74 (d, 4, $J_{H\text{-}H}$ = 7.5 Hz), −11.8 (quint, 1, $J_{Rh\text{-}H}$ = 14 Hz). At −50 °C, the high field hydride resonance was a binomial quartet, $J_{Rh\text{-}H}$ = 19 Hz.

[10] All atoms in the cluster occupy general positions in the space group. The toluene molecule has a crystallographic twofold axis.

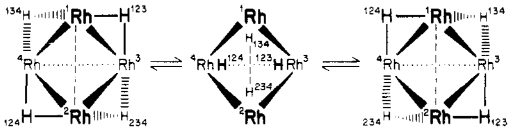
[11] All calculations were performed on a Data General Eclipse S-200 computer using locally modified versions of the Nicolet EXTL or SHELXTL interactive software system.

[12] The first number in parentheses following an average value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

[13] An alternative conceptual view of the Rh_4H_4 core is a basic idealized D_{2d} Rh_4 tetrahedron with a hydrogen atom that appears to be unsymmetrically located on each face such that the hydrogen atom is closer to two rhodium atoms than the third that comprise the face.[14] This unsymmetric placement of hydrogen atoms on each face is so arranged that the Rh_4H_4 core appears to have idealized S_4 symmetry.

[14] These long distances are Rh_1–H_{124} = 2.07 (9) Å, Rh_2–H_{123} = 2.14 (5), Rh_3–H_{134} = 2.24 (6) Å, and Rh_4–H_{234} = 2.13 (7) Å.

[15] The Rh–(C_2-m) distances and (C_2-m)–Rh–(C_2-m) angles are comparable to those in (μ-CH_3)$_2Rh_2$(1,5-cyclooctadiene)$_2$.[1]



5 6 7

Figure 2. Depicted in projection, **5**, is the ring representation of $[(\mu\text{-H})Rh(1,5\text{-cyclooctadiene})]_4$, **1**, using the labeling convention shown in Figure 1. In the projection **5** (and **7**) the hydrogen atoms have been moved away from the Rh–Rh vectors to improve the clarity of the depiction. Illustrated in the sequence from left to right of **5** → **6** → **7** is a geometric or physical process consistent with a dynamic process observed for **1** in the ^{1}H DNMR spectra. Representation **6** is of the midpoint in the proposed process. The illustrated one-step clockwise rotation of hydrogen atoms cannot continue beyond **7** without traversing a higher energy midpoint, explicitly different than **6**, in which two hydrogen atoms would be nestled between the "long" Rh_1–Rh_2 (dashed line) and Rh_3–Rh_4 (dotted line) separations.

short interligand cyclooctadiene H···H nonbonded separations. Even with the observed departures from coplanarity, the congested peripheral coordination sphere is characterized by a number of short, interligand cyclooctadiene H···H separations, <2.4 Å. Interestingly, there is not a simple torsional twist of the cyclooctadiene ligands with respect to associated RhH_2 planes but a folding of the cyclooctadiene ligand (to varying degrees for each ligand) such that one C_2-m midpoint on each rhodium atom is nearly 180° to the trans hydride ligand (the range is 170–175°), whereas the range for the other set of H–Rh–(C_2-m) angles is 146–163°. It should be noted that the representation of **1** as a ring structure **5** (Figure 2) seemingly would require that nominally nonbonded interactions[16] such as Rh_1–Rh_2 and Rh_3–Rh_4 have relatively large separations but these are not large, 3.002 and 2.940 Å, respectively. However, these small separations are a necessary consequence of forming a four-membered ring with near planar $(Rh\text{–}H)_2\text{–}Rh\text{–}(C_2\text{-m})_2$ local coordination spheres and with reasonable Rh–H–Rh bridge bond angles (see discussions in ref 4 and 8). None of the bonding or nonbonding distances, other than those specifically discussed above, is sufficiently unusual to merit separate discussion.

Nuclear magnetic resonance studies of **1** for the solution state are fully consistent with the solid-state structure. The tetranuclear rhodium cluster is stereochemically nonrigid. The observed dynamic processes are not only easily rationalized by the idealized ring representation, **5** (Figure 2), but are a natural expectation from representation **5**. At 30 °C, the ^{1}H NMR spectrum consisted of characteristic CH_2 and CH resonances for a complexed cyclooctadiene ligand and a high field ($\sim$–11.8 ppm) hydride resonance of binomial quintet form. The latter feature indicates spectroscopic equivalence of hydride hydrogen atoms and equivalent coupling of each hydride hydrogen atom to all four rhodium atoms, $I(^{103}Rh) = {}^1/_2$. As the temperature was lowered, the hydride resonance altered in form and, at –40 °C, became a binomial quartet that underwent no substantial further change down to –90 °C. The polynuclear form as established in this crystallographic study (Figure 1 or representation **5** in Figure 2) if stereochemically rigid would have a hydride resonance of dominant triplet structure. However, a *one-step* clockwise shift of hydrogen atoms as depicted for **5** → **7** (Figure 2) comprises a trivial shift of hydride hydrogen atom positions and should encounter a very small activation barrier. The net result would be a dominant and nearly equivalent spin–spin coupling of each hydride hydrogen atom to three rhodium atoms to give basically a quartet resonance as experimentally observed. However, a further clockwise rotation of hydrogen atoms in **7**, with respect to the Rh_4 ring (which is energetically equivalent to a counter clockwise shift in **5**) should encounter a much higher barrier. The midpoint in such a traverse would not be identical with the midpoint, **6**, for the process of **5** → **7**, but rather would have the hydrogen atoms near to the Rh_1–Rh_2 and Rh_3–Rh_4 vectors—a much more congested midpoint than **6**. This second step (counterclockwise rotation from **5** or clockwise rotation from **7**) may be a reasonable physical process for the NMR process that actually converts the hydride quartet to a quintet. However, there is a multitude of geometric processes that could be advanced as alternatives, including processes based on a fluxionality of the basic D_{2d} Rh_4 tetrahedron.

Chemically, the tetramer **1** is not fully analogous to the many other members of the established "square-planar" $HRhL_2$ cluster class. The others all have phosphite or phosphine ligands, and presumably, because of the relatively high electron density on the metal atoms in these derivatives, hydrogen (H_2) addition[3,6] to give $H_4Rh_2L_4$ and $H_5Rh_3L_6$ adducts is a virtually instantaneous reaction. The tetramer **1** with the more effective electron-acceptor cyclooctadiene ligands, explicably does not react rapidly with hydrogen but only *slowly* with concomitant reduction of the cyclooctadiene ligand and formation of rhodium metal. However, in the presence of a reducible substrate like ethylene the cluster is not decomposed by hydrogen, rather the cluster selectively converts the ethylene to ethane although at a low rate.

Fryzuk[17] has recently reported the isolation of the interesting $\{HRh[(CH_3O)_2PCH_2CH_2P(OCH_3)_2]\}_4$ tetramer. A crystallographic characterization of this tetramer with location of the hydride hydrogen atom positions may provide a critical test of our suggested *formal* representation of **1** as a ring structure. In addition, the Fryzuk cluster should display a hydride hydrogen atom ^{1}H DNMR behavior analogous to $[(\mu\text{-H})Rh(1,5\text{-cyclooctadiene})]_4$, **1**, if our structural representation is correct.

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Registry No. 1, 82660-97-7; $[(\mu\text{-}C_2H_5)Rh(1,5\text{-cyclooctadiene})]_2$, 82621-52-1; $[(\mu\text{-Cl})Rh(1,5\text{-cyclooctadiene})]_2$, 12092-47-6.

Supplementary Material Available: Figure 3 and caption, a full ORTEP representation, Tables I–V of atomic coordinates, anisotropic thermal parameters, idealized atomic coordinates for 1,5-cyclooctadiene hydrogen atoms, selected bond distances, and bond angles, a listing of structure factor amplitudes for crystalline $H_4Rh_4(C_8H_{12})_4\cdot 0.5CH_3C_6H_5$ (39 pages). Ordering information is given on any current masthead page.

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[16] Other notable "short", yet ostensibly nonbonded, distances are the Rh-H separations listed in ref 14.

[17] Fryzuk, M. D. *Organometallics* 1982, *1*, 408.