

# Metal cluster chemistry: Structure and stereochemistry in the polynuclear rhodium hydrides $H_nRh_n[P(OR)_3]_{2n}$

(metal cluster-metal surface analogy/neutron and x-ray crystallographic studies)

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**ABSTRACT** Crystallographic analyses of x-ray and neutron diffraction data have provided a definitive structural representation of  $\{HRh[P(O-i-C_3H_7)_3]_2\}_2$  and  $\{HRh[P(OCH_3)_3]_2\}_3$ . These polynuclear hydrides are generated from square planar  $H_2Rh[P(OR)_3]_2$  units by edge (hydrogen atom) sharing and by vertex (hydrogen atom) sharing to form the dimeric and trimeric structures, respectively. The square-planar units are held together through four-center and three-center two-electron Rh—H—Rh bonds in the dimer and trimer, respectively. The dimer and trimer molecules each add one molecule of hydrogen to form  $H[(i-C_3H_7O)_3P]_2RhH_3Rh[P(O-i-C_3H_7)_3]_2$  and  $H_5Rh_3[P(OCH_3)_3]_6$ , respectively. NMR spectral information has served to define the stereochemical features of these polyhydrides. The significance of this chemistry in the metal cluster-metal surface analogy is described.

Discrete molecular metal clusters can be considered as simple models of metal surface coordination chemistry (1-8). This modeling approach can yield information about structure, ligand migration, chemistry, and catalytic chemistry that may be of substantive value in the analysis of metal surface chemistry (7, 8). One limitation in this formal analogy is the tendency of some molecular clusters to fragment into mononuclear metal complexes in chemical and catalytic reactions. By using coordinately unsaturated metal clusters, the probability of cluster fragmentation in reactions can be substantially decreased. We describe here the structural features of a set of coordinately unsaturated polynuclear rhodium hydrides that exhibit high catalytic activity (9, 10) in olefin hydrogenation reactions and that do not significantly fragment in these catalytic reactions.

## EXPERIMENTAL

**Procedures.** All manipulations were performed under argon by using modified Schlenk techniques, a Vacuum Atmospheres HE-43 DRI-LAB, or in vacuum. All solvents were dried by distillation from calcium hydride, sodium/benzophenone, or lithium aluminum hydride. NMR spectra were recorded on a Bruker HX 90 spectrometer.

$\{HRh[P(O-i-C_3H_7)_3]_2\}_2$ . This complex was prepared by hydrogenolysis of  $\eta^3-C_3H_5Rh[P(O-i-C_3H_7)_3]_2$  at 20°C and with hydrogen at 1 atm (101.3 kilopascals) (9-11). Single crystals of the dimer were obtained by slow cooling, to -30°C, of pentane solutions of the hydride. The crystals were black-green in color and were indefinitely stable in inert atmospheres at 20°C.

$\{HRh[P(OCH_3)_3]_2\}_3$ . This complex was prepared by hydrogenolysis of  $\eta^3-C_3H_5Rh[P(OCH_3)_3]_2$  at 20°C and 1 atm. The hydride complex was purified by repeated recrystallizations

from pentane/toluene. Black-brown single crystals were obtained by cooling such solutions of the hydride.

$H[(i-C_3H_7O)_3P]_2RhH_3Rh[P(O-i-C_3H_7)_3]_2$  and  $H_5Rh_3[P(OCH_3)_3]_6$ . These complexes were prepared in pentane/toluene and in toluene- $d_8$  solutions from  $\{HRh[P(O-i-C_3H_7)_3]_2\}_2$  and  $\{HRh[P(OCH_3)_3]_2\}_3$  and hydrogen at 0-20°C. Stoichiometry was established by vacuum line tensimetric measurements. Full reversibility of the hydrogen addition was established by evacuation at 20°C through a liquid nitrogen trap and Toepler pump analysis of the noncondensable hydrogen gas (10, 11).

**X-Ray and Neutron Crystallographic Analysis of  $\{HRh[P(O-i-C_3H_7)_3]_2\}_2$ .** Single crystals of this dinuclear rhodium hydride were triclinic, space group  $P\bar{1} - C_1^1$  (no. 2) with room temperature lattice constants (x-ray) of  $a = 12.271(2)$  Å,  $b = 13.483(2)$  Å,  $c = 9.869(2)$  Å,  $\alpha = 97.13(1)^\circ$ ,  $\beta = 105.38(1)^\circ$ ,  $\gamma = 115.90(1)^\circ$ , and  $Z = 1$  (dimeric complex). Diffraction intensities were collected for 7463 independent reflections out to  $(\sin \theta)/\lambda \leq 0.69$  Å<sup>-1</sup> on a computer-controlled four-circle Syntex P1 autodiffractometer using graphite-monochromated Mo K $\alpha$ -radiation and full (1° wide)  $\omega$  scans. The structure was solved by using the "heavy-atom" technique, and all nonhydrogen atom structural parameters have been refined to convergence [ $R = 0.042$  for 2974 independent reflections having  $Mo K\alpha 2\theta < 43^\circ$  and  $I > 3\sigma(I)$ ] by using unit-weighted full-matrix least-squares refinement techniques and anisotropic thermal parameters.

Neutron diffraction data were collected at 110 K at the Argonne CP-5 reactor, with a small crystal (6.30 mm<sup>3</sup>). Intensities were measured with neutrons of wavelength 1.142(1) Å for a total of 1142 independent reflections that had  $(\sin \theta)/\lambda \leq 0.37$  Å<sup>-1</sup>; however, only 690 had  $F_0^2 > \sigma(F_0^2)$ . The low yield of neutron diffraction data prevented a least-squares refinement and only Fourier mapping techniques were used.

**Neutron Crystallographic Study of  $\{HRh[P(OCH_3)_3]_2\}_3$ .** A large single crystal of  $\{HRh[P(OCH_3)_3]_2\}_3$ , weighing 55 mg, was sealed under dry N<sub>2</sub> in a Pb glass capillary for protection. A total of 3186 independent three-dimensional data, of which 2698 had  $F_0^2 > \sigma(F_0^2)$ , were again collected on the Chemistry Division neutron diffractometer. All data were collected at 110 K, by using a device based on the Strouse (12) design, out to  $(\sin \theta)/\lambda = 0.577$  Å<sup>-1</sup> [ $\lambda = 1.142(1)$  Å]. A least-squares fit of 21 automatically centered reflections ( $40^\circ < 2\theta < 50^\circ$ ) confirmed the monoclinic unit cell ( $P2_1$ ) [ $C_2^2$ , no. 4] with  $a = 10.792(6)$  Å,  $b = 13.438(8)$  Å,  $c = 13.438(8)$  Å,  $\beta = 91.64(4)^\circ$ ,  $V_c = 1948.02$  Å<sup>3</sup>, and  $d_{\text{calcd.}} = 1.801$  g/cm<sup>3</sup> for  $Z = 2$ . All integrated intensities were corrected for absorption ( $\mu_c = 2.38$  cm<sup>-1</sup>) and the range of transmission coefficients was 0.354-0.505. By using initial nonhydrogen atom coordinates from the room-temperature x-ray investigation (9), all atoms were located by Fourier techniques. Final anisotropic full-matrix least-squares refinement of all 102 atoms (919 parameters) on the Argonne

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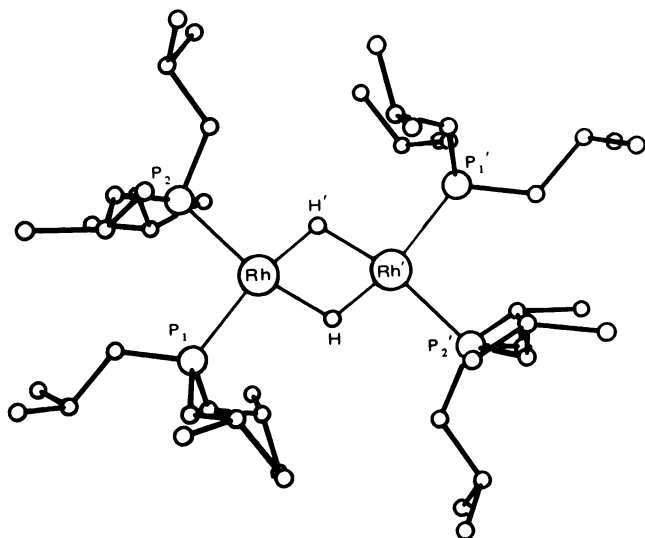


FIG. 1. Perspective drawing (adapted from an ORTEP plot) of nonhydrogen atoms and hydrido ligands for  $[\text{HRh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2]_2$ , **1**. Rhodium and phosphorus atoms are represented by large- and medium-sized open circles, respectively; oxygen, carbon, and hydride hydrogen atoms are represented by small open circles. Atomic positions for the nonhydrogen atoms represent least-squares refined values based on x-ray diffraction data; those for the two hydride hydrogens were determined by difference Fourier analyses using neutron diffraction data. Atoms of a given type labeled with and without a prime (') are related to each other by the crystallographic inversion center midway between the two Rh atoms.

IBM 370/195 computer gave  $R(F_0^2) = 0.117$  and  $R(F_0) = 0.101$  with a "goodness of fit" of 1.42 for all data and  $R(F_0^2) = 0.106$  and  $R(F_0) = 0.072$  for 2698 data with  $F_0^2 > \sigma(F_0^2)$ .

## RESULTS AND DISCUSSION

The nonhydrogen skeleton of  $\{\text{HRh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2\}_2$ , **1** (Fig. 1) had a dimeric, ethylene-like structure in which the two Rh atoms and the four coordinated P atoms were coplanar to within 0.01 Å. Although reliable positions for the hydride ligands could not be determined from difference Fourier syntheses based on the x-ray data, their locations at sites in the  $\text{Rh}_2\text{P}_4$  plane that symmetrically bridged the two Rh atoms could be inferred from the nonhydrogen atomic arrangement if square-planar geometry were assumed for each Rh atom. The results of the preliminary neutron diffraction study at 110 K for a relatively small crystal of **1** clearly indicated the presence of only two hydride ligands at these bridging sites. Although difference Fourier syntheses utilizing phases derived from the nonhydrogen positions of the x-ray study clearly revealed the hydride and a majority of the isopropyl hydrogen atoms, the low yield of neutron diffraction data prevented a least-squares structural refinement.

Basically,  $\{\text{HRh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2\}_2$  is a dimer based on two square-planar  $\text{P}_2\text{RhH}_2$  units that share an edge although the two hydrogen atoms may lie slightly to each side of the  $\text{Rh}_2\text{P}_4$  plane. Average bond lengths and angles for chemically equivalent groupings (the first number in the parentheses is the root mean square-estimated SD of an individual datum; the second and third numbers, when given, are the average and maximal deviations from the averaged value, respectively; and the fourth number is the number of individual measurements included in the average value) include: Rh—Rh, 2.650(1) Å; Rh—P, 2.167(4,15,15,2) Å; P—O, 1.59(1,1,1,6) Å; O—C, 1.43(2,3,6,6) Å; Rh—H, 1.66(–,23,23,2) Å;  $\text{P}_1\text{—Rh—P}_2$ , 96.0(2)°; P—

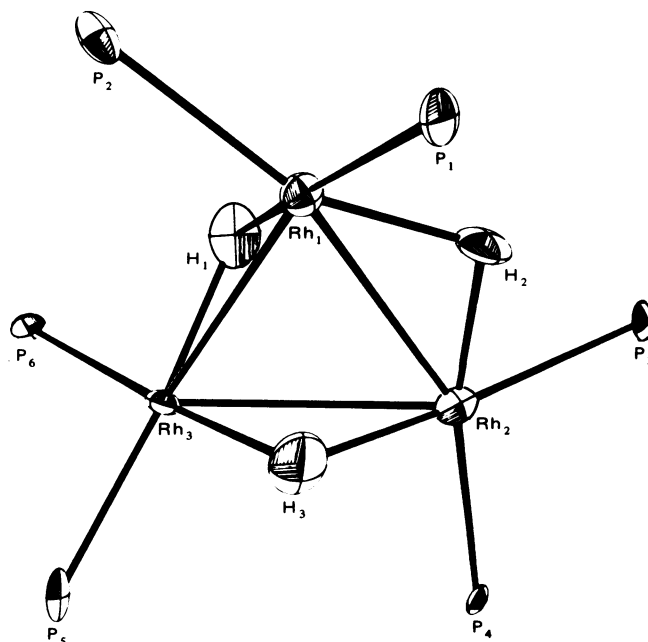
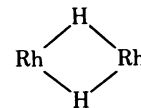


FIG. 2. The inner core ( $\text{Rh}_3\text{H}_3\text{P}_6$ ) of the  $\{\text{HRh}[\text{P}(\text{OCH}_3)_3]_2\}_3$  molecular structure. Atoms denoted as above the  $\text{Rh}_3$  plane (in text) are viewed as below the plane of the paper. Note the pseudo (non-crystallographic) 2-fold axis about a vector through  $\text{Rh}_3\text{H}_2$ . The thermal ellipsoids of nuclear motion for all atoms are scaled to enclose 50% probability.

Rh—Rh', 132.0(2,19,19,2)°; Rh—H—Rh', 105°; H—Rh—H', 75°; and P—Rh—H, 95(–,8,8,2)°.

Crystals of  $\{\text{HRh}[\text{P}(\text{OCH}_3)_3]_2\}_3$  are comprised of discrete neutral trimeric molecules with no unusually short intermolecular contacts. In Fig. 2, the inner core of the molecular structure is presented; in Fig. 3, a stereopair is displayed for clarity. A triangular Rh atom array is the basis of the cluster framework with each Rh atom bonded in an approximately square-planar fashion to two terminal  $\text{P}(\text{OCH}_3)_3$  groups and two bridging hydrides. There is an approximate (noncrystallographic) two-fold axis passing through  $\text{Rh}_3$  and  $\text{H}_2$ .  $\text{H}_2$  is only 0.20(2) Å above the plane of the three Rh atoms whereas  $\text{H}_1$  is 1.13(2) Å above the plane and  $\text{H}_3$  is 1.03(2) Å below the plane. The Rh—Rh separations of 2.803(7), 2.780(6), and 2.856(7) Å arise from formation of three Rh—H—Rh two-electron three-center bonds. These Rh—Rh separations are significantly longer than the 2.650(2) Å found for  $\{\text{HRh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2\}_2$ , which can be considered to arise from two



two-electron four-center bonding interactions (see below). Examination of the bond distances and angles (Table 1) clearly demonstrates the square-planar nature of each of the three  $\text{RhP}_2\text{H}_2$  moieties. Square-planar groups centered at  $\text{Rh}_1$  and  $\text{Rh}_2$  are tilted approximately equally, by 35.1° and 37.7°, respectively, but in opposite directions relative to the  $\text{Rh}_3$  plane. The unique (relative to the pseudo 2-fold axis)  $\text{RhP}_2\text{H}_2$  group centered at  $\text{Rh}_3$  makes a dihedral angle of 64.3° with the  $\text{Rh}_3$  plane. This tilting of the  $\text{H}_2\text{RhP}_2$  coordination planes probably represents the best geometric compromise satisfying electronic constraints in generating a trimer composed of vertex-shared square-planar  $\text{H}_2\text{RhP}_2$  units. The Rh—H distances, which

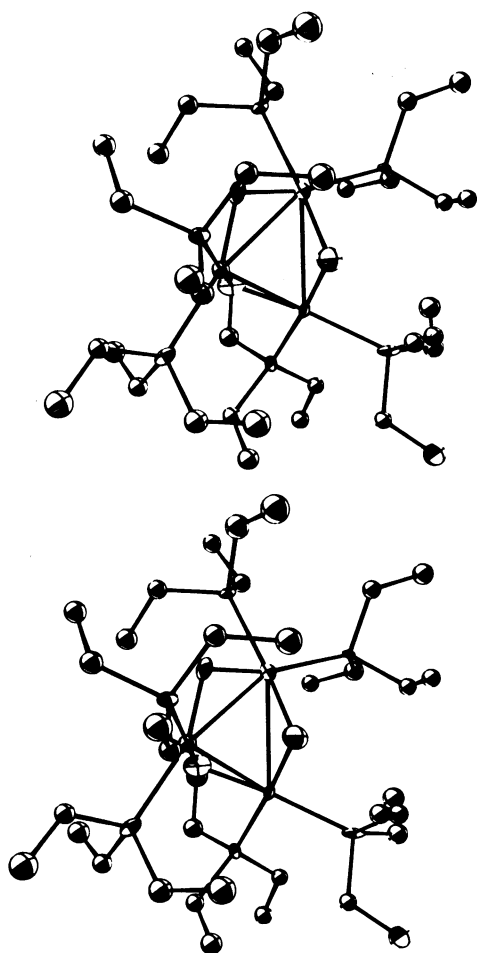
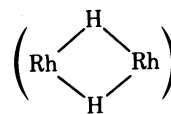


FIG. 3. Stereoscopic drawing of  $\{HRh[P(OCH_3)_3]_2\}_3$  as derived from neutron diffraction data with methoxy hydrogen atoms eliminated for clarity. Thermal ellipsoids are scaled to enclose 50% probability.

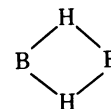
range from 1.73 to 1.84 Å, may be compared with an *approximate* covalent radii sum (Rh = 1.35 Å; H = 0.37 Å) of 1.72 Å. The lack of other precisely established Rh—H<sub>t</sub> and Rh—H<sub>b</sub> distances precludes further comparison.

Structural details of these polynuclear hydrides as derived from the crystallographic studies incisively establish the intrinsic square-planar character of the Rh coordination geometry. Edge- and vertex-sharing generate the dimeric and trimeric structures, respectively. The disjoint Rh—Rh separations in the dimer and trimer warrant comment regarding the electronic structure of these complexes. The short separation in the dimeric complex is the result of the two Rh—H—Rh bonding interactions versus only one per Rh—Rh edge in the trimer. In molecular orbital terms, there is no net *direct* Rh—Rh bonding interaction in the dimer; two four-center (2 Rh and 2 H atoms) two-electron interactions yield the relatively short Rh—Rh separation of 2.650 Å; the Rh—Rh separation in Rh metal is 2.69 Å. For the near  $D_{2h}$  symmetry of  $\{HRh[P(O-i-C_3H_7)_3]_2\}_2$ , there are six low-lying, bonding molecular orbitals (largely ligand in character) of  $a_g$  and  $b_{2u}$  (hydrogen) and of  $a_g$ ,  $b_{1g}$ ,  $b_{2u}$ , and  $b_{3u}$  (phosphorus) symmetries. Intermediate are 10 molecular orbitals (largely Rh 4d in character) of 2  $a_g$ ,  $a_u$ ,  $b_{1g}$ ,  $b_{1u}$ ,  $b_{2g}$ ,  $b_{2u}$ ,  $b_{3g}$ , and 2  $b_{3u}$  symmetries of which an  $a_g$  and  $b_{2u}$  set, antibonding in character, is probably the lowest set of unoccupied molecular orbitals. The lowest-lying bonding levels,  $a_g$  and  $b_{2u}$ ,

represent the two four-center two-electron



molecular orbitals in a full formal analogy to the diborane

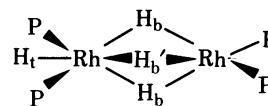


bridge bond. In a qualitative molecular orbital scheme, the net direct Rh—Rh interaction appears to be nonbonding or even slightly antibonding. Similarly for  $\{HRh[P(OCH_3)_3]_2\}_3$ , the primary internuclear bonding interactions are single Rh—H—Rh three-center two-electron bonds with no significant net Rh—Rh direct bonding interactions.

The dimer and trimer Rh hydrides constitute the smallest oligomers for a potentially large set of hydrides based on an  $L_2RhH$  unit. Possibly, a tetrameric hydride could be obtained in the phosphite series by using the less bulky  $CH_3C(CH_2O)_3P$  ligand. Even larger clusters or aggregates should be more readily derived with more compact ligands, such as isocyanides, rather than phosphites. If the quasi-square-planar coordination geometry is always preserved in  $\{L_2RhH\}_n$  aggregates derived from hydrogenolysis of  $\eta^3-C_3H_5RhL_2$  complexes, then ring rather than polyhedral structures may be formed.

Both the dimer and trimer structures constitute coordinately unsaturated complexes. Consistent with this representation, both are exquisitely reactive in a chemical context. They are destroyed by oxygen and are quantitatively converted to a mononuclear complex,  $HRh[P(OCH_3)_3]_4$ , by excess trimethyl phosphite. More significantly from the purview of the cluster-surface analogy (1–9), both dimer and trimer reversibly and rapidly add hydrogen in an oxidative-addition reaction and both are extremely active catalyst precursors for olefin hydrogenation reactions. The hydrogen addition products instantly react with olefins to produce alkanes and the original dimer or trimer complex.

Somewhat surprisingly, the hydrogen oxidative addition reactions to the dimer and the trimer did not yield mononuclear  $H_3Rh[P(OR)_3]_2$  complexes, at least detectably. Dimer and trimer molecules each added precisely one molecule of hydrogen to form  $H_4Rh_2[P(O-i-C_3H_7)_3]_4$  and  $H_5Rh_3[P(OCH_3)_3]_6$ , respectively. On the basis of the  $^1H$  and  $^{31}P$  NMR spectra, the former is proposed to have a triple hydrogen bridged structure of the form



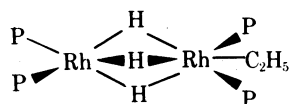
wherein the bonding interaction is solely based on Rh—H—Rh three-center bonds; there is no net, direct Rh—Rh bonding (10). Effectively, the hydrogen addition to the dimer occurs over one Rh center although one Rh—H—Rh bridge bond is formed. In the reaction of this hydrogen adduct with ethylene, the critical ethylene interaction initially must be with the other Rh atom. Thus, this putative cluster model of ethylene hydrogenation at a metal surface comprises hydrogen addition largely at one metal center and initial olefin complexation at an adjacent metal center. On a metal surface, the high mobility of

Table 1. Selected bond distances (Å) and angles (deg) for {HRh[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>]<sub>3</sub>

Distances		
Rh <sub>1</sub> —Rh <sub>2</sub> = 1.838(10)	Rh <sub>1</sub> —Rh <sub>2</sub> = 2.803(7)	Rh <sub>1</sub> —P <sub>1</sub> = 2.155(7)
Rh <sub>1</sub> —H <sub>2</sub> = 1.734(11)	Rh <sub>1</sub> —Rh <sub>3</sub> = 2.780(6)	Rh <sub>1</sub> —P <sub>2</sub> = 2.197(8)
Rh <sub>2</sub> —H <sub>2</sub> = 1.732(11)	Rh <sub>2</sub> —Rh <sub>3</sub> = 2.856(7)	Rh <sub>2</sub> —P <sub>3</sub> = 2.164(9)
Rh <sub>2</sub> —H <sub>3</sub> = 1.753(13)		Rh <sub>2</sub> —P <sub>4</sub> = 2.202(8)
Rh <sub>3</sub> —H <sub>1</sub> = 1.750(12)		Rh <sub>3</sub> —P <sub>5</sub> = 2.178(9)
Rh <sub>3</sub> —H <sub>3</sub> = 1.785(12)		Rh <sub>3</sub> —P <sub>6</sub> = 2.180(8)
Angles		
Rh <sub>1</sub> —Rh <sub>2</sub> —Rh <sub>3</sub> = 58.8(2)	H <sub>2</sub> —Rh <sub>1</sub> —P <sub>2</sub> = 160.1(4)	
Rh <sub>2</sub> —Rh <sub>3</sub> —Rh <sub>1</sub> = 59.6(2)	H <sub>2</sub> —Rh <sub>2</sub> —P <sub>3</sub> = 79.8(4)	
Rh <sub>3</sub> —Rh <sub>1</sub> —Rh <sub>2</sub> = 61.5(2)	H <sub>2</sub> —Rh <sub>2</sub> —P <sub>4</sub> = 166.3(5)	
H <sub>1</sub> —Rh <sub>1</sub> —H <sub>2</sub> = 91.9(5)	H <sub>3</sub> —Rh <sub>2</sub> —P <sub>3</sub> = 172.3(6)	
H <sub>2</sub> —Rh <sub>2</sub> —H <sub>3</sub> = 92.5(6)	H <sub>3</sub> —Rh <sub>2</sub> —P <sub>4</sub> = 93.6(5)	
H <sub>1</sub> —Rh <sub>3</sub> —H <sub>3</sub> = 90.8(6)	H <sub>3</sub> —Rh <sub>3</sub> —P <sub>5</sub> = 89.1(5)	
P <sub>1</sub> —Rh <sub>1</sub> —P <sub>2</sub> = 91.3(3)	H <sub>3</sub> —Rh <sub>3</sub> —P <sub>6</sub> = 175.5(5)	
P <sub>3</sub> —Rh <sub>2</sub> —P <sub>4</sub> = 93.9(3)	H <sub>1</sub> —Rh <sub>3</sub> —P <sub>5</sub> = 171.7(5)	
P <sub>5</sub> —Rh <sub>3</sub> —P <sub>6</sub> = 94.9(3)	H <sub>1</sub> —Rh <sub>3</sub> —P <sub>6</sub> = 85.4(4)	
H <sub>1</sub> —Rh <sub>1</sub> —P <sub>1</sub> = 171.7(4)	Rh <sub>1</sub> —H <sub>1</sub> —Rh <sub>3</sub> = 101.5(5)	
H <sub>1</sub> —Rh <sub>1</sub> —P <sub>2</sub> = 94.2(4)	Rh <sub>1</sub> —H <sub>2</sub> —Rh <sub>2</sub> = 107.9(6)	
H <sub>2</sub> —Rh <sub>1</sub> —P <sub>1</sub> = 80.9(4)	Rh <sub>2</sub> —H <sub>3</sub> —Rh <sub>3</sub> = 107.6(6)	

Estimated SD in parentheses.

hydrogen atoms does not require initial chemisorption of the hydrogen and the olefin at adjacent sites. After the first hydrogen atom transfer to the metal-bonded olefin, the ethyl—Rh intermediate is presumed to have the structure



by analogy to the initial hydrogen adduct (10). Low-temperature NMR studies failed to detect the ethyl—Rh intermediate although there was evidence of the olefin intermediate complex. A similar chemistry seems to prevail for {HRh[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>]<sub>3</sub> but lack of detail in the NMR spectra of the hydrogen adduct precluded definitive structural characterization (10).

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