

equivalent *N*-alkyl groups at low temperature is inconsistent with their proposed conformation (2).

¹⁵N NMR spectra of **1c** (neat) at ambient temperature gave doublet signals at (relative to external CD₃NO₂) δ -286.0 (¹J_{PN} = 96 Hz, exocyclic) and -353.8 (¹J_{PN} = 51 Hz, two endocyclic). The latter value is close to that reported recently¹ for the endocyclic nitrogens in **1a** (¹J_{PN} = 51.8 Hz), but the exocyclic coupling in **1c** is remarkably large compared with the analogous value¹ of 24.0 Hz reported for **1a**. Thus ¹J_{PN} appears to be markedly dependent on the nitrogen substituents (as suggested by Gray and Albright¹) since **1a** and **1c** adopt a similar conformation about the P-N bond. The increased steric bulk of the *N*-alkyl groups on going from **1a** to **1c** may cause the nitrogen geometry to change from pyramidal to planar, thereby increasing ¹J_{PN} in line with theoretical predictions.¹ However, these calculated P-N couplings must be interpreted with caution owing to their failure to predict the correct PN conformation for **1a**.

The preliminary results of an ultraviolet photoelectron spectroscopy study of compound **1c** support our conformational assignment.⁶ PS data from the series and a more detailed discussion of the NMR results and work in progress will be reported in a subsequent publication.

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Metal Clusters in Catalysis. 13.¹ A New Coordinately Unsaturated Cluster Family, the Per(phosphite) Metal Clusters

Sir:

To effect a critical experimental analysis of the purported analogy¹⁻⁵ between metal clusters and metal surfaces, we have sought a synthesis of highly reactive clusters that might more closely emulate metal surfaces in difficult catalytic reactions

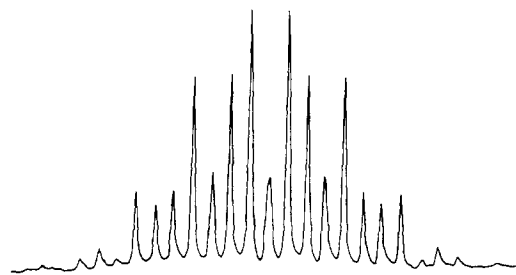
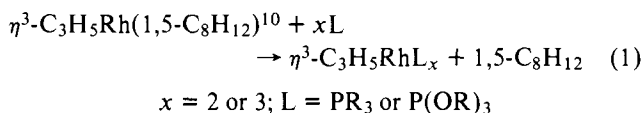


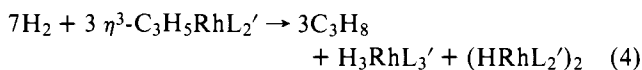
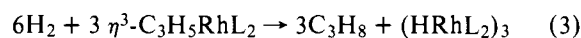
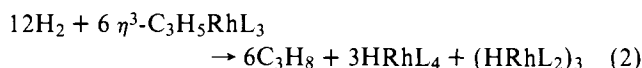
Figure 1. The hydridic (Rh-H) portion of the ¹H NMR spectrum of {HRh[P(OCH₃)₃]₂}₃ which clearly shows the septet of quartets arising from the proton spin-spin coupling with six magnetically equivalent ³¹P atoms and three magnetically equivalent ¹⁰³Rh atoms. Only 23 of the 28 lines are evident owing to near coincidences.

like the hydrogenation of molecules with triple bonds^{1,4,6-8} and of arenes⁷ and also the rearrangement and dehydrocyclizations of aliphatic hydrocarbons.^{4,7} After many unsuccessful efforts to design syntheses of per(phosphite) and per(phosphine) metal clusters, a cluster class of an anticipated high reactivity, we have accidentally discovered a rhodium-phosphite cluster family, of the general formula {HRh[P(OR)₃]₂}_x, in which there are unusual structural features and catalytic chemistry. We describe here the properties of the [HRh[P(OR)₃]₂]₂ and [HRh[P(OR)₃]₂]₃ classes and the preliminary results of an x-ray structural study of [HRh[P(OCH₃)₃]₂]₃, **1**.

Since η³-C₃H₅Co[P(OR)₃]₃ complexes proved to be homogeneous catalysts for arene hydrogenations,⁹ we developed a general synthesis of η³-C₃H₅RhL₂ and η³-C₃H₅RhL₃ complexes



to test this analogue class for catalytic properties. Of these rhodium complexes, only the η³-C₃H₅RhL₂ phosphite complexes with bulky¹² ligands were catalysts for arene hydrogenation. Lifetimes of the allylrhodium complexes were very short. Hydrogen addition was fast and propene elimination from the η³-C₃H₅RhH₂L_x intermediates was also rapid, far more rapid than for the η³-C₃H₅CoL₃ analogues.¹³ These cleavage reactions are summarized in the highly idealized equations



in which L is a compact and L' a relatively bulky phosphite ligand; the observed product distribution was sensitive to the polarity of the solvent. Propane, not propene, was the major hydrocarbon product because the reaction system was catalytically very active for olefin hydrogenation (see below). The rhodium clusters were isolated by crystallization procedures.¹⁴

The ¹H NMR spectrum of **1** consisted of a symmetric, complex O-CH₃ resonance and a symmetric 23-line Rh-H resonance (Figure 1) that was generated from a partially overlapping quartet (*J*_{Rh-H} = 16.5 Hz) of septets (*J*_{P-H} = 25 Hz); the latter reduced to a binomial quartet in an ¹H{³¹P} experiment. Since the proton spectrum was temperature independent from +40 to ~-100 °C,¹⁵ with equivalent spin-spin coupling of each Rh-H hydrogen atom to all three rhodium and all six phosphorus atoms over this temperature range, the hydridic hydrogen atoms would appear to be highly mobile in

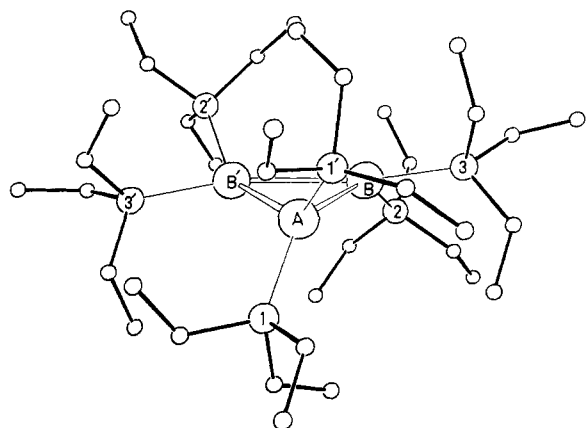


Figure 2. Perspective drawing (adapted from an ORTEP plot) of the $\{\text{HRh}[\text{P}(\text{OCH}_3)_3]_2\}_3$ molecule. **1.** Rhodium and phosphorus atoms are represented by large- and medium-sized open circles labeled with capital letters and numbers, respectively; oxygen and carbon atoms are represented by small open circles. Atoms of a given type labeled with and without a prime ($'$) are related to each other by the pseudo- C_2 axis which passes through Rh_A and the midpoint of the $\text{Rh}_B\text{-Rh}_{B'}$ bond.

this cluster. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of the cluster was complex and was temperature independent from $+50$ to -80 °C. Also isolated was the $\text{P}(\text{OC}_2\text{H}_5)_3$ analogue which exhibited similar NMR resonance features. In contrast, the isopropyl phosphite derivative,¹⁴ **2**, was a dimer, $\{\text{HRh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2\}_2$, which exhibited an overlapping triplet of quintets in the ^1H NMR spectrum, a triplet in the $^1\text{H}\{^{31}\text{P}\}$ spectrum, and an AA'XX'-A''A''' in the $^{31}\text{P}\{^1\text{H}\}$ spectrum, all of which were invariant from $+70$ to ~ -70 °C ($J_{\text{RhH}} = 34.2$ and $J_{\text{PH}} = 36.6$ Hz).¹⁵ Single-crystal x-ray and neutron diffraction studies of **1** and **2** are in progress¹⁴ and the preliminary results of the x-ray study of **1** are described below.

Single crystals¹⁴ of $\{\text{HRh}[\text{P}(\text{OCH}_3)_3]_2\}_3$, **1**, obtained as described above were monoclinic, space group $P_{21} - C_2^2$ (No. 4), with $a = 10.803$ (2) Å, $b = 13.852$ (3) Å, $c = 13.658$ (2) Å, $\beta = 92.37$ (1)°, and $Z = 2$ (trimeric species). Three-dimensional diffraction data (a total of 7361 independent reflections having $2\theta_{\text{Mo K}\alpha} < 63.7^\circ$) were collected on a computer-controlled four-circle Syntex P1 autodiffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation and full (1° wide) ω scans. The structural parameters have been refined to convergence ($R = 0.032$ for 2482 independent reflections having $2\theta_{\text{Mo K}\alpha} < 43^\circ$ and $I > 3\sigma(I)$) in cycles of unit-weighted full-matrix least-squares refinement which used anisotropic thermal parameters for all nonhydrogen atoms.¹⁶

The crystallographic results for **1** confirm the qualitative conclusions from the NMR data for the solution state. This cluster has near-equilateral triangular form with each rhodium atom directly bonded to two phosphite phosphorus atoms (Figure 2). Although the molecules possess no crystallographic symmetry there is an axis of near-twofold symmetry that passes through Rh_A and the midpoint of the $\text{Rh}_B\text{-Rh}_{B'}$ bond. At this stage, the data provide no direct evidence for the three hydridic hydrogen atom positions. There is one unexpected geometric feature: the dihedral angle between the plane of the three rhodium atoms and one of the three-atom RhP_2 coordination planes (Rh_A) is much larger than those formed with the other two RhP_2 planes (66.9 vs. 37.9 and 33.4°). At first glance, this canting of the coordination planes might appear to result from a minimization of nonbonded repulsions between the relatively bulky phosphite ligands—but there are no especially short intra- or intermolecular nonbonded distances. We suggest that this canting represents the best geometric compromise in the generation of a cyclic trimer composed of shared square-planar P_2RhH_2 units. This would require bridging hydrogen atoms and, in fact, the observed Rh–Rh distance of 2.824 (2, 14, 21,

3) Å¹⁷ is consistent with a hydrogen-bridged, two-electron Rh–Rh bond.

Actually the phosphorus and rhodium positions in the cluster molecule define a reasonable location of the hydridic hydrogen atoms. The most notable feature of the heavier atom skeleton is the near coplanarity (to within 0.09 Å) of four atoms within four different sets: $\text{P}_1, \text{Rh}_A, \text{Rh}_B$, and P_2 in set I; $\text{P}_1', \text{Rh}_A, \text{Rh}_B'$, and P_2' in set II; $\text{P}_2, \text{P}_3, \text{Rh}_B$, and Rh_B' in set III; and $\text{P}_2', \text{P}_3', \text{Rh}_B'$, and Rh_B in set IV. Furthermore, the least-squares mean planes of sets I and II intersect in a dihedral angle of 53.5° , while they individually intersect the mean plane of the three Rh atoms in angles of 88.4 and 88.7° , respectively. *Approximate*, square-planar bridging positions can therefore be derived by making vector extensions of each P–Rh bond and placing a hydrido ligand near the intersections of the following pairs of such vectors: $\text{H}_{A,B}$ at the intersection of $\text{P}_1 \rightarrow \text{Rh}_A$ and $\text{P}_2 \rightarrow \text{Rh}_B$; $\text{H}_{A,B'}$ at the intersection of $\text{P}_1' \rightarrow \text{Rh}_A$ and $\text{P}_2' \rightarrow \text{Rh}_B'$; and $\text{H}_{B,B'}$ at the intersection of $\text{P}_3 \rightarrow \text{Rh}_B$ and $\text{P}_3' \rightarrow \text{Rh}_B'$. Thus $\text{H}_{A,B}$ would be displaced vertically (relative to the horizontal plane of the Rh_3 grouping) “above” the midpoint of the $\text{Rh}_A\text{-Rh}_B$ bond and $\text{H}_{A,B'}$ would be displaced “below” the midpoint of the $\text{Rh}_A\text{-Rh}_B'$ bond; $\text{H}_{B,B'}$ would ideally lie outside the Rh_3 triangle on the pseudo- C_2 axis.

Although an unambiguous positioning of the hydrido ligands in **1** must await the results of least-squares refinement for a more sophisticated model (anisotropic nonhydrogen and isotropic hydrogen atoms) using neutron diffraction data, the following bond angles, averaged in accord with approximate C_2 symmetry, are in agreement with the proposed model: P–Rh–P, 93.4 (2, 10, 15, 3)°;¹⁷ $\text{P}_1\text{-Rh}_A\text{-Rh}_B$, 137.2 (1, 12, 12, 2)°; $\text{P}_1\text{-Rh}_A\text{-Rh}_B'$, 116.5 (1, 2, 2, 2)°; $\text{P}_2\text{-Rh}_B\text{-Rh}_A$, 145.2 (1, 6, 6, 2)°; $\text{P}_2\text{-Rh}_B\text{-Rh}_B'$, 108.9 (1, 25, 25, 2)°; $\text{P}_3\text{-Rh}_B\text{-Rh}_A$, 99.8 (1, 9, 9, 2)°; and $\text{P}_3\text{-Rh}_B\text{-Rh}_B'$, 157.6 (1, 30, 30, 2)°. Averaged lengths for the various chemically distinct bonds in **1** are Rh–P, 2.181 (4, 9, 14, 6) Å;¹⁷ P–O, 1.62 (1, 2, 4, 18) Å; and O–C, 1.43 (2, 3, 8, 18) Å. All intramolecular Rh...O and Rh...C distances are >3.19 and 3.55 Å, respectively.

These multinuclear rhodium complexes are extremely reactive, a chemical facet consistent with the unsaturated character of the complexes. Most notable, these tri- and dinuclear clusters are extraordinarily active catalysts for catalytic hydrogenation reactions. Both $\{\text{HRh}[\text{P}(\text{OCH}_3)_3]_2\}_3$ and $\{\text{HRh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2\}_2$ catalyzed the hydrogenation of 1-hexene at catalyst:substrate ratios of 1:10 000 with rates that exceeded one turnover per second at 24 °C. In fact, the rates are so high that an upper limit has been difficult to establish. By comparison, these hydrogenation rates are slightly greater by a factor of ~ 3 , than those for $\text{ClRh}[\text{P}(\text{C}_6\text{H}_5)_3]_3$, under comparable conditions.

No evidence of interaction between $\{\text{HRh}[\text{P}(\text{OCH}_3)_3]_2\}_3$ and hydrogen was detected between -30 and $+20$ °C and 1–3-atm pressure; however, olefins interacted exothermally with this cluster at 20 °C. Mechanistic details of these catalytic reactions and of those of the iridium analogues are under study. These rapid cluster catalytic reactions may arise from a facile cluster dissociation to reactive 14-electron mononuclear $\text{HRh}[\text{P}(\text{OR})_3]_2$ complexes or alternatively the cluster reactions may represent simulations of metal surface-catalyzed olefin hydrogenation reactions.⁵ Kinetic studies should yield a distinction between these two limiting possibilities.

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 (10) A literature procedure¹¹ was used for the preparation of this cyclooctadiene complex; the NMR spectrum we obtained for the complex was fully consistent with an $\eta^3\text{-C}_3\text{H}_5\text{Rh}-\eta^4\text{-C}_8\text{H}_{12}$ structure and was quite different from that reported. Observed ^1H NMR (C_6D_6 , TMS reference): δ -1.82, -2.03, -2.19 (overlapping doublet and two singlets, 10), -3.36 (doublet, 2, $J = 6.8$ Hz), -4.80 (broad singlet, 4), -5.42 (multiplet, 1, $J_{\text{H-Rh}} = 3.2$ Hz, $J = 12.8$ Hz). This pseudo-four-coordinate complex slowly decomposed (solid state) at 25 °C.
 (11) A. Kasahara and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **39**, 634 (1966).
 (12) For example, $\eta^3\text{-C}_3\text{H}_5\text{Rh}[\text{P}(\text{OCH}_3)_3]_2$ and $\eta^3\text{-C}_3\text{H}_5\text{Rh}[\text{P}(\text{OC}_2\text{H}_5)_3]_2$ were inactive, whereas $\eta^3\text{-C}_3\text{H}_5\text{Rh}[\text{P}(\text{O}-i\text{-C}_3\text{H}_7)_3]_2$ was active.
 (13) Propene elimination was also an observed, competitive reaction in the cobalt-catalyzed reactions. This elimination reaction usually produces a complex(es) catalytically inactive for arene hydrogenations.
 (14) Single crystals of **1** and **2**, respectively, were obtained by cooling pentane-toluene and pentane solutions of the complex. Satisfactory analyses were obtained for C, H, P, and Rh.
 (15) At low temperatures, there was some line broadening due to viscosity effects.
 (16) The three crystallographically independent rhodium atoms were located through direct methods and the remaining nonhydrogen atoms of the totally general position asymmetric unit were located by standard difference Fourier techniques. Further refinement is underway using the more complete ($2\theta_{\text{Mo K}\alpha} \leq 63.7^\circ$) data set; hopefully these results can be combined with those of the anticipated neutron-diffraction study to give a highly definitive characterization of the bonding in these clusters.
 (17) The first number in parentheses following an averaged 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.
 (18) Camille and Henry Dreyfus Teacher-Scholar.

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Deuterium Isotope Effects in the Solvolysis of Benzal Halides. 3. $\beta\text{-D}_3$ Isotope Effects and the Mechanism of Solvolysis of 1,1-Dihaloethylbenzenes in Dioxane-Water Mixtures

Sir:

Secondary deuterium isotope effects are used extensively as probes into mechanisms of solvolytic reactions.¹ The magnitude of the $\beta\text{-D}$ effect reflects changes in the proportion of elimination product(s) with changes of solvent or of leaving group.² Two important questions arise where the elimination/substitution ratio changes with solvent or leaving group: (a) is there a change in the rate-limiting step(s) in the solvolytic scheme and (b) what is the identity of the species acting as a base in the elimination process?³ Several examples in the literature clearly point to formation of elimination products from intimate ion-pair or from solvent separated ion-pair intermediates.⁴ However, the identity of the species that abstracts the

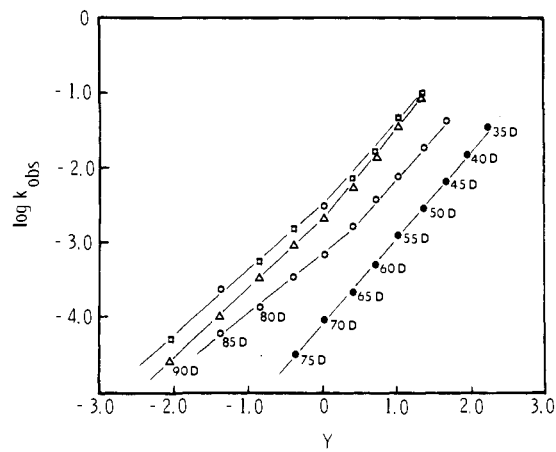
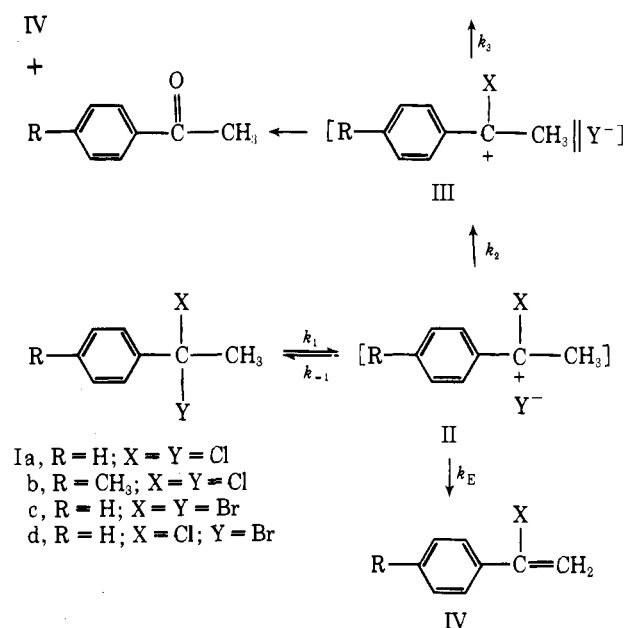


Figure 1. First-order rate constants for solvolysis of 1,1-dihaloethylbenzenes determined spectrophotometrically by monitoring the appearance of acetophenone at 241 nm or *p*-methylacetophenone at 249 nm at 25 °C as a function of solvent polarity, Y .^{6b} Solvent composition is given in volume percent dioxane, e.g., 80D = 80 mL of dioxane + 20 mL of water: filled circles ($\text{PhC}(\text{Cl})_2\text{CH}_3$), $m = 1.18 (\pm 0.02)$; open circles ($\text{PhC}(\text{Br})_2\text{CH}_3$), $m = 1.12 (\pm 0.01)$ (solvent, 45D-60D) and $m = 0.58 (\pm 0.08)$ (60D-85D); filled squares ($\text{PhC}(\text{Cl},\text{Br})\text{CH}_3$), $m = 1.24 (\pm 0.09)$ (50D-65D) and $m = 0.87 (\pm 0.02)$ (65D-90D); triangles (*p*- $\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{Cl})_2\text{CH}_3$), $m = 1.26 (\pm 0.07)$ (50D-65D) and $m = 0.95 (\pm 0.07)$ (65D-90D).

Scheme I



proton from the carbonium ion in an ion-pair intermediate is a more subtle problem.

As part of our continuing study of the solvolysis of benzal halides,⁵ we have determined the $\beta\text{-D}_3$ isotope effects and product distributions in the solvolysis of 1,1-dihaloethylbenzenes in dioxane-water mixtures. This reaction yields two products as shown in Scheme I. In this communication, we propose that in the more polar solvents k_2 is rate-limiting and in the less polar solvents k_E and k_2 are similar in magnitude ($k_{-1} \gg k_E$ and k_2) and most or all of the elimination product is derived from the intimate ion pair (II). We also propose that elimination from II (k_E) involves the counterion as base and that it is the relative stability of the tight ion pair, and hence the relative magnitudes of k_2 and k_E , rather than the intrinsic basicity of the halide ion, Y^- , that decides the extent of elimination from II.

The observed $\beta\text{-D}_3$ kinetic isotope effects are reported in Table I for Ia and Ib in addition to the product distributions