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Metal Clusters. 21.[1] Synthesis of Rhodium Phosphite Clusters

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Abstract: Reaction of η^3-C_3H_5Rh-1,5-cyclooctadiene with phosphites and phosphines has through the simple expedient of stoichiometry control yielded a series of quasi-four-coordinate and five-coordinate η^3-allylrhodium complexes, η^3-$C_3H_5RhL_2$ and η^3-$C_3H_5RhL_3$. All members of these two classes exhibited a fast hydrogen cleavage of the allylrhodium bond at 20 °C to form propene (initially) and rhodium hydrides. The cleavage reactions were always preceded or accompanied by ligand exchange so that the reactions typically yielded $HRhL_4$, H_3RhL_3, $\{HRhL_2\}_x$, and an unidentified hydride; the yield of the polynuclear $HRhL_2$ species was highest with the η^3-$C_3H_5RhL_2$ complexes. Fully identified were the polynuclear hydrides: $\{HRh[P(OCH_3)_3]_2\}_3$, $\{HRh[P(OC_2H_5)_3]_2\}_3$, and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. Stability of the phosphine analogues was substantially lower and rhodium metal was a pervasive and significant product in the $H_2 + \eta^3\text{-}C_3H_5Rh[PR_3]_n$ reactions. The polynuclear hydride complexes were very active catalyst precursors for olefin and acetylene hydrogenation reactions. Turnover rates for olefin hydrogenation were greater than ~two/s at 23 °C at olefin to polynuclear hydride ratios of 10 000:1. Because acetylenes competed far more effectively than olefins for coordination sites in the polynuclear hydrides, the catalyzed acetylene hydrogenation reactions, although much slower than olefin hydrogenation, yielded largely olefins. The dimer $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ was a catalyst precursor for arene hydrogenations: the rates were low, the hydrogen addition mode was nonselective (large amounts of *trans*-dimethylcyclohexanes were produced from xylenes), and in D_2-arene reactions there was substantial H-D exchange. In the reactions of $\{HRh[P(OR)_3]_2\}_n$ with hydrogen, there was no detectable cluster fragmentation. The intermediate in the case of the dimer was identified as $H[(i\text{-}C_3H_7O)_3P]_2RhH_3Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ and as $H_5Rh_3[P(OCH_3)_3]_6$ for the trimer. Both these hydrogen adducts were fluxional molecules; hydride ligand migration occurred in each adduct in two mechanistically distinct processes. In the catalytic reaction, the hydrogen addition step and the olefin addition step appear to be largely centered on adjacent rhodium sites.

Introduction

Allylcobalt phosphite and phosphine complexes, η^3-$C_3H_5Co[P\lessdot]_3$, are unique catalysts for the hydrogenation of aromatic hydrocarbons: rates run as high as 1 turnover/min at 20 °C and 1-3 atm and there is complete stereoselectivity with an all cis hydrogen addition.[2,3] However, these complexes all suffer hydrogenolysis of the allyl-cobalt bond.[3] We initiated a general study of allylmetal complexes to establish catalytic scope and the factors that promote the hydrogen cleavage reaction. Generally, we have found that the rates for catalytic hydrogenations and for hydrogenolysis of the allyl group correlate directly in these allylmetal complexes.[3,4] We describe here the synthesis and chemistry of a group of allylrhodium phosphite and phosphine complexes—a study that has led to the isolation of a novel class of coordinately unsaturated and very reactive clusters.[5,6]

Experimental Section

Reagents and Solvents. All operations with air-sensitive materials were effected in a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri Train under an argon or nitrogen atmosphere, or in a conventional vacuum system. Rhodium trichloride hydrate was obtained from Alfa Chemicals and Matthey Bishop, Inc. Trimethyl phosphite, triethyl phosphite, triphenylphosphine, *o*-xylene, *p*-xylene, and 1,5-cyclooctadiene were purchased from Aldrich Chemical Co., Inc.; triisopropyl phosphite and trimethylphosphine from Strem Chemicals; 1-hexene from Phillips Petroleum Co.; trifluoroacetic acid from Eastman Kodak Co.; allylbenzene and *trans*-propenylbenzene from Chemical Samples. Prepurified hydrogen (99.95%), deuterium, CP (99.5% (atom)), ethylene CP, ethane CP, propylene CP, and propane were purchased from Matheson & Co.

Rhodium trichloride hydrate, absolute ethanol, and the gases were used as obtained. The 1,5-cyclooctadiene was purified by passing it down an alumina column and degassing it prior to use. Acetonitrile, 1-hexene, and *trans*-propenylbenzene were stored over calcium hydride for at least 1 week and were vacuum distilled prior to use. Allylbenzene was stored over lithium aluminum hydride and vacuum distilled prior to use. The trifluoroacetic acid was vacuum distilled just before using it. Reagent grade *n*-pentane, benzene, toluene, diethyl ether, tetrahydrofuran, and the xylenes were vacuum distilled from sodium benzophenone ketyl. The trialkyl phosphites were stored over sodium for a minimum of 2 weeks (with periodic degassing) and distilled prior to their usage. Methanol was dried over magnesium methoxide and vacuum distilled prior to use. Allylmagnesium bromide was prepared by standard methods[7] and was isolated as a solid of ~80% activity.

Physical Measurements. ^1H NMR spectra were recorded at 60 MHz with a Varian Associates A-60A, and at 90 MHz with either a Varian Associates EM-390 or a Bruker HX-90 (with a Digilab Fourier accessory). Chemical shifts were referenced to internal tetramethylsilane and are reported in parts per million with increasing field in the positive direction. Solution ^{31}P spectra were recorded on the Bruker HX-90 and chemical shifts were referenced to external H_3PO_4. All NMR spectra were of C_6D_6 solutions except where stated otherwise. Unsaturated hydrocarbons and products of hydrogenations

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were analyzed on a Perkin-Elmer 990 gas chromatograph with a flame ionization detector. Benzene, the xylenes, and their hydrogenated derivatives were separated on a Carbowax 20M (3%, 12 ft) column or on an OV-225 (3%, 6 ft) column. Allylbenzene, *trans*-propenylbenzene, benzene, and their hydrogenated derivatives were separated on OV-17 (15%, 12 ft) and OV-225. Columns of squalane (3%, 12 ft) and ethyl *N*,*N*-dimethyloxamate (20%, 7 ft) joined in series or just the latter were used to separate hexane and the hexene isomers. Mass spectra of organic mixtures were obtained with a Finnegan 3300 GC-MS interfaced with a System Industries System 150. Mass spectra of the rhodium compounds were obtained with an AEI MS-902.

η^3-$C_3H_5Rh[1,5$-$C_8H_{12}]$. To 150 mL of tetrahydrofuran in a 500-mL three-necked round-bottom flask was added $[(1,5\text{-}C_8H_{12})RhCl]_2$[8a] (4.93 g, 10.0 mmol), and the mixture was stirred under an inert atmosphere (the solid did not totally dissolve). The solution was cooled to 0 °C and a solution of allylmagnesium bromide (4.8 g of a 77 wt % active sample, 25 mmol, a slight excess) in tetrahydrofuran (100 mL) was added dropwise over 0.75 h. The solution was stirred for an additional 2 h at 0 °C. The solvent was then removed under vacuum to leave a yellow to brown solid which was extracted with several portions of pentane (25–100-mL volumes were used until the pentane ceased to become strongly colored). The pentane was removed from the extracts under vacuum to leave a yellow solid. (With older samples of allylmagnesium bromide, the yield was reduced to ~40% and the product at this stage varied from yellow through darker yellows to a brown solid which melted to a brown sludge at ~20 °C.) The product was vacuum sublimed at 20 °C to a cold finger at −78 °C. After each day of sublimation, the remaining residue was slurried in a small amount of pentane and washed over the sublimator walls as the pentane was allowed to evaporate. This improved the yield and decreased total sublimation time. The sublimed, yellow, crystalline material (4.2 g, 83% yield) melted with decomposition at 30.5–31 °C. Because the material was thermally unstable, it was stored at ~−30 °C. Mass spectrum: calcd for $C_{11}H_{17}{}^{103}Rh$, 252; found, 252, 211, $Rh(C_8H_{12})$; 144, $Rh(C_3H_5)$. ^1H NMR: −1.82, −2.03, −2.19 (allyl anti doublet superimposed on cyclooctadiene endo and exo methylenic resonances, 10), −3.36 (d, $J_{\text{Hsyn-H}} = 6.8$ Hz, 2), −4.80 and −5.42 ppm (broad singlet upfield of an adjacent multiplet, $J_{\text{H-Hanti}} = 12.8$, $J_{\text{H-Rh}} = 3.2$ Hz, 5).

A solution of η^3-$C_3H_5Rh[1,5$-$C_8H_{12}]$ (252 mg, 1 mmol) in 2.0 mL of $HCCl_3$ darkened over 30 min from yellow to dark orange. The solvent was removed under vacuum. The remaining solid gave a dark orange solution and a pale insoluble solid upon addition of pentane. Both fractions were dried under vacuum. ^1H NMR showed the pentane-soluble fraction to be mostly unreacted starting material. The solid was not characterized but major ^1H NMR peaks at −2.1 and −4.25 ppm, solubility considerations, and its color showed it to be neither the starting material nor thermal decomposition products of the starting material.

η^3-$C_3H_5Rh[P(OCH_3)_3]_2$. Two equivalents of trimethyl phosphite (236 μL, 2 mmol) was added to a pentane solution (5 mL) of η^3-$C_3H_5Rh[1,5$-$C_8H_{12}]$ (252 mg, 1 mmol). After the light yellow solution was stirred for several minutes, the volatile components (pentane and cyclooctadiene) were removed under vacuum to leave a yellow-orange oil. To aid the vacuum removal of the displaced cyclooctadiene, the oil was redissolved in pentane which was again removed under vacuum; this procedure was repeated once. The resulting oily crystals were dissolved in a very small amount of pentane. This pentane solution was cooled to approximately −30 °C to yield a crop of light yellow crystals with orange-red bands running through the mass (379 mg, 97%). Two more like recrystallizations yielded a pale yellow, crystalline product (364 mg, 93%) which was air sensitive and melted at 27.8–28.5 °C. ^1H NMR: −2.09 (d, $J_{\text{Hanti-H}} = 11.4$ Hz, 2), −3.52 (broad s, phosphite and allyl syn proton resonances, 20), −4.96 ppm (m, $J_{\text{H-Hsyn}} = 6.5$, $J_{\text{H-Rh}} = 2$ Hz, 1). Anal. Calcd for $C_9H_{23}O_6P_2Rh$: C, 27.57; H, 5.95. Found: C, 27.58; H, 5.83.

η^3-$C_3H_5Rh[P(OCH_3)_3]_3$. This compound[9] was prepared and characterized in the same manner as η^3-$C_3H_5Rh[P(OCH_3)_3]_2$ except that 3 equiv of trimethyl phosphite (354 μL, 3 mmol) was used. Purification was effected by passing a toluene solution of the crude yellow oil down a 25 × 200 mm column of Bio-Beads S-X2 or Bio-Beads S-X8 followed by removal of the toluene under vacuum and two cycles of dissolution in pentane and vacuum removal of the pentane. On a larger scale (≥5 mmol), the direct recrystallization from pentane gave a pure, waxy, crystalline product. ^1H NMR: −1.93 (d, $J_{\text{Hanti-H}} = 9$ Hz, 2), −2.68 (d, $J_{\text{Hsyn-H}} = 5.5$ Hz, 2), −3.53 (broad singlet, 27), −5.04 ppm (m, 1). Anal. Calcd for $C_{12}H_{32}O_9P_3Rh$: C, 27.92; H, 6.25; P, 18.00; Rh, 19.93. Found: C, 27.72; H, 6.15; P, 18.00; Rh, 19.81.

η^3-$C_3H_5Rh[P(O$-i-$C_3H_7)_3]_2$. This compound was prepared and characterized in the same manner as η^3-$C_3H_5Rh[P(OCH_3)_3]_2$ to give yellow crystals, mp 35.5 °C. ^1H NMR: −1.25 (d, $J_{\text{CH3-CH}} = 6$ Hz, 36), −2.30 (d of t, $J_{\text{Hanti-H}} = 13$, $J_{\text{Hanti-P}} = 4.5$ Hz, 2), −3.70 (d, $J_{\text{Hsyn-H}} = 7$ Hz, 2), −4.80 ppm (m, 7). Anal. Calcd for $C_{21}H_{47}O_6P_2Rh$: C, 45.00; H, 8.45; P, 11.05; Rh, 18.36. Found: C, 45.23; H, 8.43; P, 11.13; Rh, 18.44.

η^3-$C_3H_5Rh[P(O$-i-$C_3H_7)_3]_3$. This compound was prepared and characterized in the same manner as η^3-$C_3H_5Rh[P(OCH_3)_3]_2$, using 3 instead of 2 equiv of the phosphite, to give a yellow, crystalline solid; mp 71.5–72 °C. ^1H NMR −1.25 (d, $J_{\text{CH}_3\text{-CH}} = 6$ Hz, 54), −2.08 (broad d, $J_{\text{Hanti-H}} = 10$ Hz, 2), −3.10 (broad d, $J_{\text{Hsyn-H}} = 6$ Hz, 2), −4.75 ppm (m, 10). Anal. Calcd for $C_{30}H_{68}O_9P_3Rh$: C, 46.88; H, 8.92; P, 12.09; Rh, 13.39. Found: C, 47.19; H, 9.03; P, 11.63; Rh, 12.90.

η^3-$C_3H_5Rh[P(OC_2H_5)_3]_2$. To a 2.0-mL solution of η^3-$C_3H_5Rh[1,5$-$C_8H_{12}]$ (262 mg, 1.04 mmol) in ether was syringed 351 μL of $P(OC_2H_5)_3$ (345 mg, 2.08 mmol). The solution darkened immediately to an orange-brown color. The ether was removed under vacuum leaving an orange-brown oil which became viscous but did not solidify at −30 °C. ^1H NMR: −3.80 (t, $J = 6.8$ Hz, 21.2), −4.72 (d, $J_{\text{Hanti-H}} = 11.2$ Hz, 2), −6.03 (broad s, 1.4), −6.56 (g, $J = 17.0$ Hz, 14.1), −7.55 ppm (m, 1).

η^3-$C_3H_5Rh[P(O$-t-$C_4H_9)_3]_2$. Into a flask containing η^3-$C_3H_5Rh[1,5$-$C_8H_{12}]$ (55 mg, 0.22 mmol) and 10 mL of n-C_5H_{12} was added a pentane solution of $P(O$-t-$C_4H_9)_3$[8b] (100 mg, 0.40 mmol, 20 mL). The pentane was removed under vacuum to leave an orange oil. The oil was dissolved in several 1–3-mL portions of pentane which were subsequently removed under vacuum (to aid in removal of cyclooctadiene) to yield an orange solid. This solid of 145 mg (~93%) was dissolved in ~0.5 mL of n-C_5H_{12} and the solution was cooled to −30 °C. After 24 h, orange crystals formed. The crystals were collected and dried under vacuum. The compound formed was very unstable in solution decomposing in 10 min at 20 °C in benzene-d_6.

η^3-$C_3H_5Rh[P(CH_3)_3]_2$. Pentane solutions (5 mL each) of η^3-$C_3H_5Rh[1,5$-$C_8H_{12}]$ (252 mg, 1 mmol) and $P(CH_3)_3$ (152 mg, 2 mmol) were combined. A slight darkening in color was noted. After vacuum removal of the pentane, the remaining oily solid was redissolved in a minimal amount of pentane (~0.2 mL). The solution was cooled to −30 °C. Pale yellow crystals which formed after 24 h were recovered by decantation and were vacuum dried, mp 36–37 °C. ^1H NMR: −1.33 (d, $J_{\text{CH}_3\text{-P}} = 6.2$ Hz, 18), −1.60 (d, $J_{\text{Hanti-H}} = 11.2$ Hz, 2), −2.59 (d, $J_{\text{Hsyn-H}} = 7$ Hz, 2), −4.55 ppm (sept of d, $J_{\text{H-Rh}} = 2$ Hz, 1). Anal. Calcd for $C_9H_{23}P_2Rh$: C, 36.50; H, 7.83; P, 20.92. Found: C, 36.57; H, 7.87; P, 21.11.

η^3-$C_3H_5Rh[P(CH_3)_3]_3$. After a pentane solution of $P(CH_3)_3$ (228 mg, 3 mmol, 5 mL) was added to a pentane solution of η^3-$C_3H_5Rh[1,5$-$C_8H_{12}]$ (252 mg, 1 mmol), the pentane was removed by rotary evaporation. The remaining waxy solid was redissolved in a minimal amount of pentane. This solution was cooled to −30 °C. Yellow crystals which formed after 24 h were collected by decantation and were then vacuum dried. An additional recrystallization yielded 325 mg (85%) of waxy crystals. Upon heating, the crystals reversibly darkened to orange up to a melting point of 123 °C. Once the material had been heated to this temperature, it remained orange on cooling to ambient temperatures. ^1H NMR: −1.11 (d, $J_{\text{P-C-H}} = 5.4$ Hz, 29), −1.78 (d, $J_{\text{Hsyn-H}} = 5.0$ Hz, 2), −4.64 ppm (m, $J_{\text{H-Rh}} = 2.0$ Hz, 1). Anal. Calcd for $C_{12}H_{32}P_3Rh$: C, 38.72; H, 8.66; P, 24.96. Found: C, 38.54; H, 8.72; P, 25.36.

η^3-$C_3H_5Rh[P(C_6H_5)_3]_2$. Addition of a pentane solution of $P(C_6H_5)_3$ (262 mg, 1.0 mmol, 25 mL) to a pentane solution of η^3-$C_3H_5Rh[1,5$-$C_8H_{12}]$ (126 mg, 0.5 mmol, 2.0 mL) yielded yellow solids. The reaction mixture was cooled and reduced in volume by ~80% by removing some of the solvent under vacuum. Yellow crystals (297 mg, 92% yield) were collected by filtration, washed with pentane, and vacuum dried. ^1H NMR (C_6H_5Cl):[10] −2.12 (d, $J_{\text{Hanti-H}} = 12.7$ Hz, 2), −2.66 (d, $J_{\text{Hsyn-H}} = 6.7$ Hz, 2), −4.86 ppm (m, 1). The analogue complex based on the $(o$-$C_7H_7)_3P$ phosphine was prepared in a similar fashion.

General Procedure for Catalytic Hydrogenations with Allylrhodium Complexes. All catalytic reactions were effected in a reaction tube (~250 mL) equipped with a Kontes high-vacuum stopcock and a polyethylene-coated magnetic stirrer bar. The unsaturated hydrocarbon reactant was the initial solvent in these reactions. Typically, a solution of catalyst (50 mg) in the unsaturated hydrocarbon (100 equiv) was prepared either directly by dissolving a purified allylrhodium complex (50 mg) in the hydrocarbon or indirectly, and in situ, by adding 0-3 equiv of the appropriate phosphine or phosphite to a solution of η^3-$C_3H_5Rh[1,5\text{-}C_8H_{12}]$ (50 mg, 0.198 mmol) in the unsaturated hydrocarbon (19.8 mmol). After these solutions were cooled to −196 °C, the vessel was evacuated thoroughly to remove all traces of nitrogen and then hydrogen was introduced to a pressure of 1 atm. The stopcock was closed and the reaction vessel was allowed to warm to 20 °C. Typically, reaction solutions were magnetically stirred for 24 h. At the end, the reaction tube was cooled to −196 °C and hydrogen was removed by evacuation. The volatile products were then vacuum distilled at room temperature and were analyzed by gas chromatography and by GC-MS. Sustained benzene hydrogenation was not observed unless rhodium metal formed in the reaction with the exception of the η^3-$C_3H_5Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ system where the cleavage product $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ was the active catalyst (see later section of Experimental Section). Olefin (1-hexene) hydrogenations were relatively slow until substantial quantities of the polynuclear hydrides were generated whereupon the rates rose dramatically to greater than about 1-2 turnovers/s.

Rate of Allyl Cleavage in η^3-$C_3H_5Rh[P(OR)_3]_2$ Complexes. The cleavage of the allyl ligand from η^3-$C_3H_5Rh[P(OCH_3)_3]_2$ in the presence of H_2 was monitored by ^1H NMR spectroscopy. A solution of the rhodium complex (795 mg, 2.03 mmol) in benzene-d_6 (5.0 mL) was placed in a 1.0-L round-bottom flask with a side arm fitted with a Kontes high-vacuum stopcock and located near the bottom of the flask. The side arm led, through the stopcock, to a 9-mm Solv Seal greaseless joint. Several NMR tubes were glass sealed to 9-mm Solv Seal joints.

The sampling apparatus and procedure were as follows. An NMR tube was connected to the 9-mm joint on the "out" side of the side-arm stopcock through an adapter which was a T-piece with a 9-mm Solv Seal greaseless joint and a takeoff, through a stopcock, to a source of vacuum. The NMR tube was evacuated through the T-shaped adapter and then closed at the stopcock. Then the reaction vessel was tilted so that the solution covered the source of the side arm and the side-arm stopcock was partially opened to allow some of the solution to enter the NMR tube. The side-arm stopcock was closed. Finally, the solution in the NMR tube was frozen (at −196 °C), and the NMR tube was evacuated and then sealed.

With the reaction solution in the reaction flask, the flask was cooled to −196 °C, evacuated, reclosed, and allowed to warm to 24 °C. The first sample was taken. Vigorous stirring of the solution was begun and hydrogen to 1 atm was admitted to the reaction vessel. The initially yellow solution was orange-yellow after 3 min when the next sample was taken. After 10 min of reaction, the red solution was sampled. Samples were also taken at 24, 100, and 172 min after the admission of hydrogen. The solution was brown at these samplings. The concentration of the allylrhodium complex was determined by integration of the peaks due to the phosphite protons and the allyl anti protons. The half-life of the allylrhodium complex was ~14 min based on a pseudo-first-order specific rate constant of 0.050 ± 0.005 min^{-1} determined from initial reaction stages.

A reaction vessel fitted with a Kontes stopcock and an NMR tube was charged with η^3-$C_3H_5Rh[P(O\text{-}i\text{-}C_3H_7)_3]_3$ (93 mg) and toluene-d_8 (0.5 mL) and the resultant solution was cooled to −196 °C. After the vessel had been evacuated, hydrogen was admitted to a pressure of 61 cm. The solution was stirred magnetically for 21 h at 20 °C. Then the solution was decanted into the NMR tube which was sealed. NMR analysis showed no allylrhodium species to be present; the primary identifiable hydride species detected were $HRh[P(O\text{-}i\text{-}C_3H_7)_3]_4$ (δ 12.46, $J_{Rh-H} = 8.8$ and $J_{P-H} = 33.8$ Hz) and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ (after hydrogen removal). Color changes indicated that cleavage was less rapid than with the trimethyl phosphite analogue.

$HRh[P(OCH_3)_3]_4$. The synthesis of this compound was based on a preparation of the triethyl phosphite analogue.[8c] No attempt was made to optimize the yield or characterize the intermediate $HCl_2Rh[P(OCH_3)_3]_3$. Rhodium trichloride trihydrate (2.6 g, 10 mmol) and 13 mL of trimethyl phosphite were mixed (argon atmosphere) and then heated to 90 °C for 1 h. While hot, the reaction mixture was filtered. The filtrate was reduced under vacuum and yielded an orange-yellow solid that was further vacuum dried at 80 °C (1.8 g, 33% yield of $HCl_2Rh[P(OCH_3)_3]_3$). To a methanol solution of this orange solid (1.64 g) and trimethyl phosphite (0.4 g excess) was added 8.5 g of sodium borohydride. This mixture was refluxed for 2 h and then filtered. The filtrate was evaporated to dryness under vacuum. The residual solid was extracted with 30 mL of pentane. Evaporation under vacuum of the pentane extracts gave 0.56 g (32%) of white, powdery $HRh[P(OCH_3)_3]_4$. ^1H NMR: +11.61 (quintet of d, $J_{H-Rh} = 9.8$, $J_{H-P} = 35.0$ Hz), −3.7 ppm (br s).

$\{HRh[P(OCH_3)_3]_2\}_3$. To a toluene solution of η^3-$C_3H_5Rh[1,5\text{-}C_8H_{12}]$ (252 mg, 1 mmol, 4.0 mL) was added 2 equiv of $P(OCH_3)_3$ (235 μL, 2 mmol). The solution was placed in a 250-mL reaction tube fitted with a Kontes high-vacuum stopcock. The solution was cooled to −196 °C and the tube was evacuated. Hydrogen was then admitted to about 1 atm; the stopcock was closed. The solution was magnetically stirred for 12 h at 20 °C during which time the initially pale yellow solution changed to orange and then to brown. After the solution was cooled to −196 °C, the remaining hydrogen was removed under vacuum. The solvent was then removed under vacuum at ~20 °C. The resulting red-brown solid was slurried in ~2 mL of pentane and the slurry was filtered. The brown filtrate contained $HRh[P(OCH_3)_3]_4$ while the solid was largely $\{HRh[P(OCH_3)_3]_2\}_3$. This solid was dissolved in a minimal amount of toluene and the solution was filtered. After the solution was diluted by ~300% with pentane, the filtrate was cooled to −30 °C. Brown crystals formed within ~12 h. The solution was decanted, and the collected crystals (200 mg, 57%) were washed with cold pentane, mp 114 °C dec. ^1H NMR: +9.56 (23-line m (septet) of quartet, $J_{H-Rh} = 16.5$, $J_{H-P} = 25.0$ Hz), −3.7 ppm (complex resonance 12 Hz wide). $^1H\{^{31}P\}$ NMR: +9.56 (quartet, $J_{H-Rh} = 16.5$ Hz), −3.7 ppm (s). ^{31}P NMR: 148.5 ppm (broad d, $J_{P-Rh} = 241$ Hz). $^{31}P\{^1H\}$: d of very complex halves. Analysis of the CH_3O proton resonance with the assumption of $J_{H(C)-H(Rh)}$ and $J_{H(C)-Rh} \simeq 0$ gave for the X part of an $X_3AA'X'_3$ spin system $J_{PP'} = 32$, $J_{PH} = 10$, and $J_{PH'} = 2$ Hz, values comparable to cis or vicinal phosphorus substituted rhodium complexes. Anal. Calcd for $C_6H_{19}O_6P_2Rh$: C, 20.47; H, 5.44; P, 17.60; Rh, 29.23. Found: C, 20.81; H, 5.45; P, 18.02; Rh, 28.36.

$\{HRh[P(OC_2H_5)_3]_2\}_3$. A 250-mL reaction vessel was charged with a benzene solution of η^3-$C_3H_5Rh[1,5\text{-}C_8H_{12}]$ (126 mg, 0.5 mmol, 4.4 mL). Upon addition of 2 equiv of $P(OC_2H_5)_3$ (160 μL, 1.0 mmol), the color of the solution changed to a dark orange. The reaction tube was cooled to −196 °C, evacuated, filled with H_2 to 1 atm pressure, and then allowed to warm to ~20 °C. Within minutes of thawing, the solution had darkened further to a yellow-brown. After 24 h, the solvent and excess hydrogen were removed under vacuum. A ^1H NMR spectrum showed that the principal component of the brown, pentane-soluble solid which remained was $\{HRh[P(OC_2H_5)_3]_2\}_3$ and the only hydride resonance was that of the trimer. ^1H NMR: +9.70 (23-line overlapping quartet of septets, $J_{H-Rh} = 16.0$, $J_{H-P} = 24.3$ Hz), −1.30 (t, $J_{CH_3-CH_2} = 7.1$ Hz), −4.3 ppm (m).

$\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. A solution of 2 equiv of triisopropyl phosphite (832 mg, 4 mmol) in pentane (5 mL) was added to a pentane solution of η^3-$C_3H_5Rh[1,5\text{-}C_8H_{12}]$ (504 mg, 2 mmol, 5 mL). The resulting pale yellow solution was placed in a 500-mL reaction vessel fitted with a Kontes high-vacuum stopcock and Teflon covered magnetic stirring bar and then cooled to −196 °C. After evacuation, hydrogen was admitted to a pressure of about 1 atm. The vessel was closed and allowed to warm to ~20 °C. There was a rapid color change to red as the solution warmed to room temperature. After the solution was stirred for 12 h, the excess hydrogen and the pentane were removed via a dynamic vacuum through a trap held at −196 °C. As the hydrogen was removed, the color changed from red through brown to brownish-green. The residue was washed from the reaction vessel with pentane which was subsequently removed under vacuum. The resultant green-brown solid was dissolved in a minimal amount of pentane. After filtration, the solution was cooled to −30 °C. Green crystals formed within ~12 h leaving a brown solution. The crystals, recovered by decantation, were washed with cold pentane (783 mg, 75%), mp 123 °C dec. ^1H NMR (toluene-d_8 at 35 °C): +7.11 (overlapping t of quintet), −1.41 (d, $J_{CH_3-CH} = 6$ Hz), −5.11 ppm (m). $^1H\{^{31}P\}$ NMR (toluene-d_8): +7.11 ppm (t, $J_{H-Rh} = 34.2$ Hz). ^1H NMR (toluene-d_8 at 70 °C): +7.11 (t of quintet, $J_{H-Rh} = 34.2$, $J_{H-P} = 36.6$ Hz). ^{31}P NMR (toluene-d_8): broad complex doublet +3.22 ppm from external $P(OCH_3)_3$, $J_{P-Rh} = 249.5$ Hz. Anal. Calcd for $C_{18}H_{43}O_6P_2Rh$: C, 41.55; H, 8.32; P, 11.90; Rh, 19.79. Found: C, 41.60; H, 8.38; P, 12.08; Rh, 19.16. Another product of the hydrogenolysis reaction was *fac*-$H_3Rh[P(O\text{-}i\text{-}C_3H_7)_3]_3$. ^1H NMR (toluene-d_8 at 25 °C): multiplet, +7.2 ppm [J_{HP}(trans) = 120, J_{HP}(cis) = 16 Hz].

Reaction of $\{HRh[P(OCH_3)_3]_2\}_3$ with $P(OCH_3)_3$. One equivalent of trimethyl phosphite (11.3 μL, 0.095 mmol) was added to a toluene solution of $\{HRh[P(OCH_3)_3]_2\}_3$ (100 mg, 0.095 mmol, 1.0 mL). The toluene was removed under vacuum. The remaining brown solid was extracted with 5.0 mL of pentane. Filtration of this pentane slurry gave a brown solid and a brown solution. The insoluble material (the major product) was shown by ^{1}H NMR to be unreacted trimer. Both ^{1}H and ^{1}H{^{31}P} NMR spectra showed the pentane-soluble material to be 30% unreacted trimer, 60% $HRh[P(OCH_3)_3]_4$, and an unidentified dimeric hydride (+7.9 ppm, $J_{H\text{-}Rh}$ = 21 Hz).

When the reaction was repeated with an addition of excess trimethyl phosphite (1.0 mL), the solution immediately discolored to an orange-brown tinted clear solution. Rotary evaporation of the liquid left an off-white, crystalline solid identified as principally $HRh[P(OCH_3)_3]_4$ by its ^{1}H NMR spectrum; there was no other metal hydride resonance.

Reaction of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ with $P(OCH_3)_3$. A Y-shaped reaction vessel was loaded with 500 mg of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ (0.48 mmol) in one arm and 6.0 mL of $P(OCH_3)_3$ (51 mmol) in the other. The phosphite was frozen (at −196 °C), the tube was evacuated (and resealed), and the phosphite was allowed to thaw. Two more freeze-thaw cycles were performed. At the end of the third cycle, the reaction vessel was tilted so that as the phosphite melted it flowed into the arm containing the dimer, which was immersed in an ice bath. There was a dramatic color change to red accompanied by a violent agitation of the solution. The color had paled to an orange-tinted, clear solution by 5 min after the bubbling had ceased. The reaction vessel was cooled to −78 °C and connected to a Toepler pump through a trap held at −196 °C. Cycling the Toepler pump for 1 h produced less than 0.5 μmol of noncondensable gas. The phosphite was removed under vacuum and the orange-tinted, white solid produced was identified by NMR as $HRh[P(OCH_3)_3]_4$, free $P(O\text{-}i\text{-}C_3H_7)_3$, and a hydride (<1%) which had a hydridic resonance nearly coincident with that of $HRh[P(OCH_3)_3]_4$; this hydride was probably $HRh[P(OCH_3)_3]_3[P(O\text{-}i\text{-}C_3H_7)_3]$.

Reaction of $\{HRh[P(OCH_3)_3]_2\}_3$ with F_3CCO_2H Synthesis of $CF_3CO_2Rh[P(OCH_3)_3]_2$. To a flask containing $\{HRh[P(OCH_3)_3]_2\}_3$ (100 mg, 0.094 mmol) were added 20 mL of diethyl ether and 3 equiv of trifluoroacetic acid (21 μL, 0.282 mmol) to give a clear orange solution. The solvent was removed under vacuum. A very small amount of ether was added to the solid to give a dark orange-brown solution containing a yellow solid (major product). This solid was collected and dissolved in a minimal amount of ether. Needle-like, orange crystals formed after the solution was cooled to −30 °C for 12 h. Crystals were collected and vacuum dried. Anal. Calcd for $C_8H_{18}F_3O_8P_2Rh_1$: C, 20.71; H, 3.91; P, 13.35; Rh, 22.2. Found: C, 20.47; H, 3.84; P, 13.81; Rh, 21.7. ^{1}H NMR (CD_2Cl_2): −3.67 ppm (m, two sharp outer peaks broad central peak 11.5 Hz wide). ^{1}H (toluene-d_8): −3.57 ppm (same pattern). ^{31}P (toluene-d_8): doublet 0.4 ppm upfield from external $P(OCH_3)_3$, $J_{P\text{-}Rh}$ = 295 Hz.

Reaction of $\{HRh[P(OCH_3)_3]_2\}_3$ and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ with H_2. A reaction vessel fitted with a Kontes stopcock and an NMR tube was charged with ~150 mg of hydride which was then dissolved or slurried in ~0.6 mL of benzene-d_6, acetone-d_6, or toluene-d_8. After the mixture was cooled to −196 °C, the tube was evacuated, then refilled with hydrogen to a pressure of 0.4–0.8 atm and sealed. The solution was magnetically stirred for several hours and then allowed to remain undisturbed for several hours more. (During the first few minutes there were definite changes in the mixtures: both compounds were solubilized, the trimer solution became red-brown, and the green-tinted dimer (which was less soluble than the trimer) slurry became an intense red solution.) Next the solution was decanted into the NMR tube. The NMR tube was then cooled to −196 °C, sealed, and stored at −196 or −78 °C for NMR analysis. The ^{1}H NMR spectrum of $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ in the hydride region was at <−85 °C (toluene-d_8 or toluene-d_8 and CF_2Cl_2): +7.8 (d of m, J_{HP} = 180 Hz, 2), +11.1 (d of m, J_{HP} = 89 Hz, 1), and 14.5 ppm (broad, s, 1). ^{1}H{^{31}P} at −86 °C: +7.8 (t, J_{HRh} = 16 Hz, 2), +11.1 (t, J_{HRh} = 21.5 Hz, 1), and 14.5 ppm (d, J_{HRh} = 14.5 Hz, 1). The ^{1}H{^{31}P} NMR spectrum of $H_5Rh_3[P(OCH_3)_3]_6$ in the hydride region between −105 and −50 °C (toluene-d_8 or toluene-d_8 and CF_2Cl_2): +12.3 (broad s, 1), +13.1 (t, J_{HRh} = 16 Hz, 2), and +15.0 ppm (d, J_{HRh} = 13.5 Hz, 2). The ^{1}H spectrum was very broad and complex at these temperatures. The terminal IR stretching frequency in $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ was at 2013 cm^{-1} ($\Delta\nu_{1/2}$ = 69 cm^{-1}).

The stoichiometry of these reactions was determined in the following manner: 100 mg of the trimer (dimer) was dissolved in 1.0 mL of toluene (pentane) in one chamber of a two-chambered reaction vessel. The solution (slurry) was cooled to −196 °C and the vessel was evacuated and resealed. The solution (slurry) was allowed to warm to room temperature (0 °C). Two more such "freeze-evacuate-thaw" cycles were performed. Next, 4 (3) equiv of hydrogen was measured into the second chamber which was then sealed. Then the hydrogen was allowed to enter the first chamber while the solution (slurry) at 20 °C (0 °C) was magnetically stirred. The stirring was continued for ~1 h, after which time the solution was cooled to −196 °C and the remaining hydrogen was measured with a Toepler pump and constant-volume manometer. To account for any hydrogen dissolved in the solution, the latter was allowed to melt and then immediately refrozen. Total hydrogen released was collected; in all cases, no significant additional hydrogen was detected by this procedure. The recovery of all the hydrogen present initially was attempted by allowing the solution to warm to room temperature while keeping the second chamber at −196 °C to prevent solvent from entering the Toepler pump. Any hydrogen released was again measured with a Toepler pump and constant-volume manometer. For the dimer, the stoichiometry was 0.91 and 0.92 mol of hydrogen per mol of $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ and 100 and 98% of the added hydrogen was recovered by evacuation at 20 °C. For the trimer, the stoichiometry was 0.90 and 0.79 mol of hydrogen per mol of $\{HRh[P(OCH_3)_3]_2\}_3$ and 83 and 86% of the added hydrogen was recovered at 20 °C.

Reaction of the Hydrogen Adducts of $\{HRh[P(OCH_3)_3]_2\}_3$ and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ with C_2H_4. Toluene-d_8 solutions of the trimer and dimer were reacted with hydrogen as described above. The solutions were decanted into the NMR tubes which were then cooled to −196 °C. The hydrogen was removed by evacuation, and C_2H_4 (1.0 equiv for the trimer and 4.0 equiv for the dimer) was condensed onto the frozen solutions. Then the NMR tubes were sealed and stored at −196 °C prior to NMR analysis. At −80 °C, the characteristic hydrogen adduct resonances were observed as well as free ethylene and also a third species that could be ascribed to an ethylene adduct. Hydrogenation of the ethylene began at about −40 °C and was relatively fast at −30 °C as evidenced by the decrease in the ethylene resonance and the appearance and increase in intensity of the dimer and trimer characteristic resonances.

Hydrogenation of 1-Hexene. The catalyst ($ClRh[P(C_6H_5)_3]_3$, $\{HRh[P(OCH_3)_3]_2\}_3$, or $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$) (10 mg) was placed in a flask with 10 000 equiv of 1-hexene and sufficient tetrahydrofuran to give a total rhodium concentration of 0.55 mmol/L. The resulting solution was transferred to a 1.0-L round-bottom flask fitted with a stopcock side arm capped with a new septum and an adapter with stopcock. The reaction vessel was cooled to −196 °C, evacuated, and allowed to warm back to room temperature, whereupon it was immersed in a constant-temperature water bath, and was magnetically stirred. One sample was withdrawn by opening the side-arm stopcock, piercing the new septum with a needle (the syringe having been flushed with argon), drawing ~250 μL of the reaction soution into the syringe, partially withdrawing the needle, closing the side-arm stopcock, and withdrawing the needle completely. The sample was then transferred into a test tube bottomed glass cylinder affixed to a vacuum line. The cylinder was cooled to −196 °C and evacuated. Volatile products were vacuum transferred at 20 °C and stored prior to gas chromatographic analysis. The reaction flask was quickly charged with hydrogen to a pressure slightly greater than 1 atm. Samples were taken as outlined above except that the pressure in the flask never fell below 1 atm once the septum was pierced. Sampling was continued for ~1 h.

The rate of the hydrogenation was obtained by plotting the percent hexane of total C_6 hydrocarbons vs. time and calculating the turnover number (τ) (in units of cluster^{-1} min^{-1}) from the slope. The rate of isomerization was estimated by the time required to reach an "equilibrium distribution" (as judged by shape of the GC trace) of the hexenes. The percent conversions were determined from peak areas (uncorrected for response factor differences) which were determined by triangulation or by a chart recorder integrator. Data are presented in Table I.

Hydrogenation of Hexynes. The catalytic hydrogenations of the hexynes were conducted in the same manner as the hydrogenation of 1-hexene with the following modifications (made possible by the large difference in rates): (a) a smaller, tubular, reaction vessel was used (~50 mL) in which the side arm did not have a stopcock; (b) no solvent was used, and the acetylene to rhodium molar ratio was either 200:1 or 100:1; (c) the first sample was taken after hydrogen addition; (d) vigorous stirring was initiated after the first sample was taken. There were several notable changes on addition of acetylenes: (a) the dimer, sparingly soluble in hydrocarbons in general, rapidly dissolved in the acetylenes; (b) the solutions of dimer formed were not the characteristic green but transparent orange with internal acetylenes and dark

Table I. Results of Catalytic Hydrogenations of Hexene and Hexyne at 23 °C at 1 Atm of Hydrogen Pressure

catalyst	substrate (solvent)	substrate to rhodium mole ratio	products	rate,[a] min^{-1}
$ClRh[P(C_6H_5)_3]_3$	1-hexene (THF[b])	10 000:1	*n*-hexane	
$\{HRh[P(OCH_3)_3]_2\}_3$	1-hexene (THF[b])	10 000:1	*n*-hexane	72
			(isomeric hexenes)[c]	
	3-hexyne	100:1	*n*-hexane	0.15
			cis-3-hexene (75)[d]	7.2
			(total)[e]	7.4
	2-hexyne	200:1	*n*-hexane	0.18
			cis-2-hexene (70)[d]	2.0
			(total)[e]	2.16
	1-hexyne	100:1	*n*-hexane	0.30
			1-hexene (90)[d]	0.36
			(total)[e]	0.66
$\{HRh]P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$	1-hexene (THF[b])	10 000:1	*n*-hexane[c]	120
			n-hexane	0.14
	3-hexyne	200:1	*cis*-3-hexene (88)[d]	3.2
			(total)[e]	3.3
	2-hexyne	200:1	*n*-hexane	0.08
			cis-2-hexene (82)[d]	1.9
			(total)[e]	2.0
	1-hexyne	200:1	*n*-hexane	0.08
			1-hexene (92)[d]	0.18
			(total)[e]	0.26

[a] Rate is reported as moles of product per mol of complex per min. [b] THF = tetrahydrofuran. [c] Hexenes present as a result of isomerization concurrent with hydrogenation (see text). [d] Major olefinic product (percent of major olefinic product of total olefinic products). [e] Rates opposite this label are total (additive) rates of conversion to olefin and alkane.

orange-brown with 1-hexyne; (c) the trimer gave not the expected dark-brown solution but an orange-brown solution; (d) all the solutions reddened upon addition of H_2. Data are presented in Table I.

Catalytic Hydrogenation of Arenes by $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ and $\{HRh[P(OCH_3)_3]_2\}_3$. The catalytic hydrogenation of the following compounds was effected as outlined in the "General Procedure for Catalytic Hydrogenations" with the modifications noted below. For the compounds benzene, toluene, *o*-xylene, *p*-xylene, *trans*-propenylbenzene, allylbenzene, and *n*-propylbenzene (benzene and toluene in the case of the trimer), the modifications follow: (a) arene:Rh ratios varied from 260:1 to 20:1 with 10–100 mg of cluster; (b) reaction times varied from 1 to 62 days; (c) competitive reactions were run between allylbenzene and benzene (100 arene:1 rhodium) and between *trans*-propenylbenzene and benzene (100 arene:1 rhodium) for 24 h. For the study of H–D exchange catalyzed by this rhodium complex, the above procedure was followed and the unreacted arene and product cyclohexanes were analyzed by GC-MS. Data are presented in Tables II and III.

Reaction of $\{HRh[P(OCH_3)_3]_2\}_3$ and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ with C_2H_4. This reaction was investigated in three ways. In procedure A, a toluene solution of the trimer or dimer was allowed to react with an excess of C_2H_4, at 0 °C, for varying periods of time, at the end of which the remaining C_2H_4 and the solvent were removed under vacuum. The residual solid was either studied directly by NMR or separated into two fractions (by extraction of a pentane-soluble component) each of which was examined by NMR spectroscopy.

In procedure B, 1 and 2 equiv of C_2H_4 were condensed onto a toluene-d_8 solution of the trimer or dimer at -196 °C. The NMR tubes were then sealed and stored at -196 °C prior to an NMR investigation.

In procedure C, the trimer (0.200 g) in toluene-d_8 was allowed to react with 1 equiv of C_2H_4 or C_3H_6. After reaction, the solution was decanted into an NMR tube (glass sealed to the reaction tube) which was then sealed and stored at -196 °C prior to NMR analysis. The remaining volatile products were separated by trap-to-trap distillation; toluene was stopped in a -78 °C trap. C_1, C_2, and C_3 hydrocarbons passed through into a sampling bulb (at -196 °C) and were subsequently analyzed by gas chromatography (Porapak Q) and by mass spectroscopy. Results for the ethylene reactions are as follows: 0.25-h reaction period, 0.3% CH_4, 93.5% C_2H_4, 5.7% C_2H_6; 2.75-h reaction period, 0.5% CH_4, 63% C_2H_4, 31% C_2H_6; 22-h reaction period, 8.1% CH_4, 9.6% C_2H_4, 82% C_2H_6. The results for propylene after 22-h reaction period were 0.2% CH_4, 0.4% C_2H_4, 1.3% C_2H_6, 85.7% C_3H_6, and 12.4% C_3H_8. With C_2D_4 as the reactant, high-resolution mass spectrometric analysis of the methanes showed the ratios of CD_4:CD_3H:CD_2H_2:CDH_3:CH_4 to be approximately 35:30:20:10:5 and 50:35:10:4:1 after reaction periods of 3 and 16 h, respectively.

Results and Discussion

Allylrhodium Chemistry. Allylrhodium-1,5-cyclooctadiene[11] proved a versatile reagent for the synthesis of two classes of allylrhodium phosphite and phosphine complexes. The only minor inconvenience and constraint in the use of this intermediate stem from its thermal reactivity which necessitates storage at low temperatures and from its reactivity toward chlorinated solvents. Stoichiometry control in the allylrhodium-1,5-cyclooctadiene reactions with phosphites and phosphines provided high-yield syntheses of $C_3H_5RhL_2$ and $C_3H_5RhL_3$ complexes which structurally may be described as quasi-square planar and quasi-square pyramidal,[12,13] respectively, with a trihapto allyl ligand effectively occupying two coordination sites. Interconversion of η^3- and η^1-allyl forms was not fast on the NMR time scale at 40 °C for any of these complexes,[14,15] although the η^3-$C_3H_5RhL_3$ species appear to be fluxional or nonrigid on the NMR time scale to -80 °C because the $^{31}P\{^1H\}$ spectra were A_3, not AB_2, patterns from $+20$ to -80 °C.

All allylrhodium phosphite and phosphine complexes underwent relatively rapid hydrogen addition and subsequent reductive elimination of propylene[16] in the presence or absence of a reducible substrate. These cleavage reactions generated a series of rhodium hydride complexes, discussed below. Hydrogenolysis of the allyl–rhodium bond occurred much more rapidly than for allylcobalt phosphine or phosphite complexes.[17] The pseudo-first-order rate constant for hydrogenolysis in η^3-$C_3H_5Rh[P(OCH_3)_3]_2$ was 5×10^{-2} min^{-1} at 24 °C. For comparison, the half-life of this complex was 14 min (1 atm H_2) and for η^3-$C_3H_5Co[P(OCH_3)_3]_3$[17] about 2 days. Cleavage rates rose in going from trimethyl to triisopropyl phosphite ligands in the bis complexes of rhodium as had been observed also in the cobalt system.[17]

Because of the rapid hydrogenolysis of the allyl–rhodium bond, it was difficult to assess the catalytic activity of the allylrhodium complexes for the hydrogenation of arenes and olefins. For arene hydrogenations, there was evidence that the

Table II. Results of Catalytic Hydrogenation of Arenes by $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ at 20 °C at 1 Atm of Hydrogen Pressure

substrate	substrate to dimer mole ratio	rate,[a] day^{-1}	products (% composition)
benzene	20:1	1.0 ± 0.4	cyclohexane
	300:1		
toluene		~0.5	methylcyclohexane
p-xylene	100:1	0.62 ± 0.16	*cis*-1,4-dimethylcyclohexane (67%)
			trans-1,4-dimethylcyclohexane (33%)
o-xylene	100:1	0.35 ± 0.03	*cis*-1,2-dimethylcyclohexane (9)
			trans-1,2-dimethylcyclohexane (9%)
n-propylbenzene	50:1	0.17 ± 0.02	*n*-propylcyclohexane
trans-propenylbenzene	200:1	0.60 ± 0.20	*n*-propylcyclohexane
allylbenzene	200:1	0.78 ± 0.20	*n*-propylcyclohexane
trans-propenylbenzene +	400:1	0.7 ± 0.10	benzene
benzene (equimolar)		0.35 ± 0.05	*n*-propylcyclohexane
allylbenzene + benzene	400:1	1.5	benzene
(equimolar)		0.74	*n*-propylcyclohexane

[a] Rate reported as moles of product per mol of dimer per day. Values are averaged and errors indicated are range of observed rates. [b] Rate is estimated.

Table III. Mass Spectral Data for H-D Exchange in Arenes Catalyzed by $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$

arene[a]	reaction[b] time, days	$(m/e)_{d_6}$	intensity [normalized to $(m/e)_{d_6}$][c]											
			d_0 (d_6)	d_1 (d_7)	d_2 (d_8)	d_3 (d_9)	d_4 d_{10})	d_5 (d_{11})	d_6 (d_{12})	d_7 (d_{13})	d_8 (d_{14})	d_9 (d_{15})	d_{10} (d_{16})	d_{11} (d_{17})
benzene	54	78	100	28.5	11.3	7.4	6.0	3.8	2.6					
	0 (std)	78	100	6.1	0.1									
cyclohexane	(54)	(90)	(100)	(15.6)	(3.5)	(1.9)	(1.7)	(1.7)	(1.4)					
	0 (std)	84	100	6.2	0.1		0.1	0.2						
cyclohexane	54	84	100	5.9										
toluene	62	92	100	9.0	1.3	0.8								
	0 (std)	92	100	7.5	0.3	0.2								
methylcyclohexane	(62)	(104)	(100)	(48.9)	(52.9)	(16.0)	(7.6)	(4.4)	(2.2)					
o-xylene	62	106	100	21.8	8.2	6.7	3.2	2.0	2.7	0.2				
	0 (std)	106	100	9.2		1.2								
cis-1,2-dimethylcyclohexane	(62)	(118)	100	(46.0)	(44.5)	(67.9)	(32.1)	(29.2)	(41.6)	(10.2)	(3.6)	(1.5)		
trans-1,2-dimethylcyclohexane	(62)	(118)	(100)	(109)	(109)	(159)	(109)	(92.2)	(83.3)	(58.9)			(7.8)	
p-xylene	62	106	100	85.8	62.1	65.4	57.4	57.4	59.6	4.7	0.2	1.1	0.2	
	0 (std)	106	100	10.2	0.2		0.2	0.2		0.2		2.9	0.5	
cis-1,4-dimethylcyclohexane	(62)	118	(100)	(154)	(216)	(198)	(202)	(169)	(174)	(21.0)	(9.7)			
trans-1,4-dimethylcyclohexane	(62)	118	(100)	(142)	(268)	(247)	(263)	(201)	(226)	(68.3)	(31.7)			
n-propylbenzene	5	121	100	19.3	6.3	0.8								
n-propylcyclohexane	(5)	(133)	(100)	(68.4)	(49.9)	(17.1)	(3.4)							

[a] Spaces separate different reactions. [b] Data presented for the recovered (nonhydrogenated) arene and for the standard reference (time = 0) spectrum of the arene or the cyclohexane. A number in parentheses indicates that the data are for the (alkyl)cyclohexane recovered from the deuteration of the corresponding (alkyl)benzene run for the number of days indicated in the parentheses. [c] All parenthetical entries for column headings and column entries apply to the deuterated cyclohexanes produced in the D_2 + arene reaction.

$\eta^3\text{-}C_3H_5RhL_2$ complexes were active catalysts. Typically, the hydrogenations of benzene with these complexes yielded cyclohexane but the total conversion was constant after about 1 h—reflecting the destruction of the allyl complex. For $\eta^3\text{-}C_3H_5Rh[P(OCH_3)_3]_2$, the implicated rate of arene hydrogenation was comparable to that established for $\eta^3\text{-}C_3H_5Co[P(OCH_3)_3]_3$, although the precise rhodium analogue, $\eta^3\text{-}C_3H_5Rh[P(OCH_3)_3]_3$, had either no catalytic activity or a very low level of activity. An estimate of catalytic activity for the allylrhodium bis- and tris(isopropyl phosphite) complexes was not realized because a hydrogenolysis product, a dinuclear hydride discussed below, was an active arene hydrogenation catalyst. Of the allylrhodium phosphine complexes, only $\eta^3\text{-}C_3H_5Rh[P(o\text{-}C_7H_7)_3]_2$ showed evidence of significant catalytic activity for arene hydrogenation (>8 turnovers/h). Similar analyses of catalytic activity in the allylrhodium complexes for olefin and acetylene hydrogenations were also complicated because the polynuclear hydrides (see later discussion) produced in the hydrogenolysis reaction were extremely active catalysts for these hydrogenation reactions. For $\eta^3\text{-}C_3H_5Rh[P(OCH_3)_3]_2$, the turnover rate in 1-hexene hydrogenation was ~4/min, which is about 100 times higher than the rate established for $\eta^3\text{-}C_3H_5Co[P(OCH_3)_3]_3$ in this hydrogenation reaction. Unlike the allylcobalt catalysts, the allylrhodium catalysts were selective to olefins over arenes and effected olefin hydrogenation at rates that were minimally 250 times higher than for arene hydrogenation.

For the allylrhodium phosphine derivatives, hydrogenolysis was followed by a process that led to rhodium metal formation especially for those of the $\eta^3\text{-}C_3H_5Rh[PR_3]_2$ class. Hydrogen cleavage was also fast for $\eta^3\text{-}C_3H_5Rh\text{-}1,5\text{-}cyclooctadiene$ whereby rhodium metal was quantitatively formed—interestingly, this form of rhodium metal was less active as an arene hydrogenation catalyst than the allylcobalt phosphite complexes. Cleavage of the allyl-rhodium bond was also fast with protonic acids; here the propylene elision was accompanied by complexation of the counteranion as for trifluoroacetic acid to give the four-coordinate $\eta^2\text{-}CF_3CO_2Rh[P(OR)_3]_2$ complex.

The processes[18] that led to hydrogenative cleavage in the allylrhodium phosphite complexes involved intermediates in which there was significant lability of the phosphite ligands. In every case, there were several rhodium hydride complexes formed: typically, the five-coordinate $HRh[P(OR)_3]_4$ species,

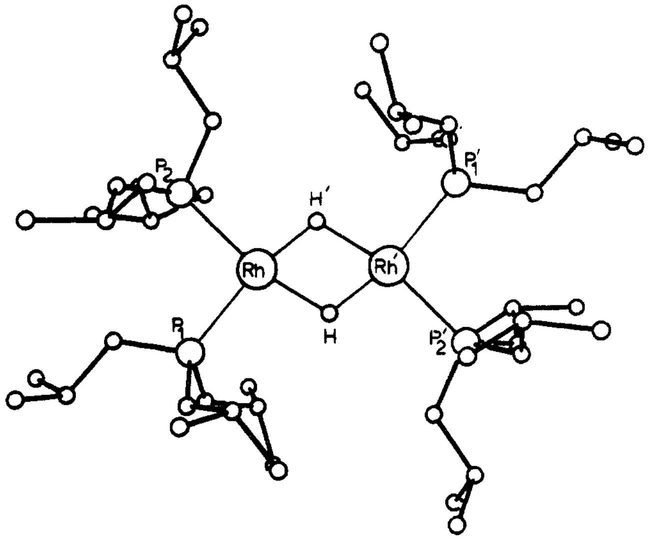


Figure 1. Perspective drawing (adapted from an ORTEP plot) of the nonhydrogen atoms and hydrido ligands for the $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ molecule.[6] Rhodium and phosphorus atoms are represented by large- and medium-sized open circles, respectively; oxygen, carbon, and hydride hydrogen atoms are represented by small open circles. Atomic positions for the nonhydrogen atoms represent least-squares refined values using X-ray diffraction data while those for the two hydride hydrogens were determined by difference-Fourier analyses using neutron diffraction data.

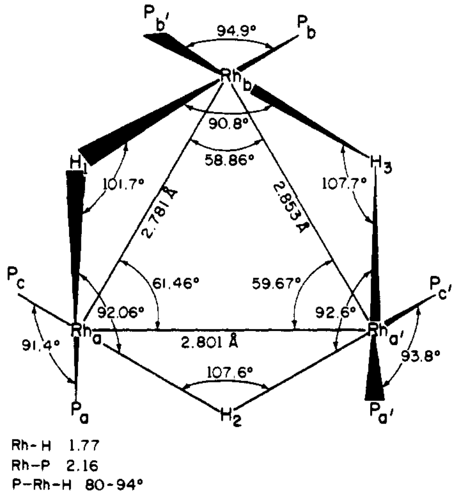


Figure 2. Representation of the rhodium, phosphorus, and hydrogen (hydride) atom positions in $\{HRh[P(OCH_3)_3]_2\}_3$. The nearly square-planar character of the P_2RhH_2 coordination sets is delineated by the bond angle data.

an unidentified hydride, and the $\{HRh[P(OR)_3]_2\}_x$ polynuclear complexes irrespective of the number of phosphites bound in the initial allyl complex, although the yields of the polynuclear complexes were higher for the $\eta^3\text{-}C_3H_5Rh[P(OR)_3]_2$ class. For the $\eta^3\text{-}C_3H_5Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ hydrogen reaction, the predominant products were $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ and a hydride identified as the facial isomer of $H_3Rh[P(O\text{-}i\text{-}C_3H_7)_3]_3$.[19]

Polynuclear Rhodium Hydrides. Both the dimer, $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, and the trimer, $\{HRh[P(OCH_3)_3]_2\}_3$, were isolated in pure form and were fully characterized. The trimer formed dark-brown crystals from toluene-pentane, and the dimer black-green crystals from pentane. Thermal stability in the solution and solid states was substantial for the trimer but was low for the dimer solution state at 20 °C. Both dimer and trimer reacted quantitatively with excess trimethyl phosphite to form $HRh[P(OCH_3)_3]_4$; no hydrogen gas was detected in these reactions. Hence there was only one hydride ligand per rhodium in these polynuclear species. Crystallographic analyses[5,6] based on neutron and X-ray diffraction experiments have established the structural features of the polynuclear rhodium hydrides produced in the hydrogen cleavage reactions. All these hydrides are generated from near square planar $[(RO)_3P]_2RhH_2$ units by edge (hydrogen atom) sharing to form dimers (triisopropyl phosphite derivative) and by vertex sharing to form trimers (trimethyl and triethyl phosphite derivatives) as shown in Figures 1 and 2.[5,6] The trimers were stereochemically nonrigid; hydrogen atom mobility was rapid on the NMR time scale to −120 °C so that each hydrogen atom was magnetically equivalent and spin coupled equivalently with all rhodium and phosphorus atoms.[5] For example, the $\{HRh[P(OCH_3)_3]_2\}_3$ hydride NMR resonance at −80 °C was a quartet (coupling with three rhodium atoms) of septets (coupling with six phosphorus atoms) which reduced to a quartet on ^{31}P decoupling;[5] a similar hydride pattern was observed for the triethyl phosphite analogue. The dimer was also stereochemically nonrigid on the NMR time scale; the hydride ^1H spectrum was a triplet of quintets and the hydride $^1H\{^{31}P\}$ spectrum, a binomial triplet. Activation energies for hydrogen atom migration in these clusters were less than 8 kcal/mol.

All the polynuclear rhodium hydrides were exceptionally active catalyst precursors for olefin hydrogenation reactions. Turnover rates exceeded ~2/s at 23 °C at olefin to complex ratios of 10 000:1. The dimer was about twice as active as the trimer. For comparison, the very active mononuclear rhodium complex, $ClRh[P(C_6H_5)_3]_3$, was under identical conditions about four to six times less active than the polynuclear rhodium hydrides (the comparative studies required tetrahydrofuran solutions because of the low solubility of $ClRh[P(C_6H_5)_3]_3$ in alkanes and alkenes).

Olefin hydrogenation reactions catalyzed by these polynuclear rhodium hydrides were accompanied by an exothermic olefin isomerization process. This same phenomenon was also observed for 1-hexene and $\{HRh[P(OR)_3]_2\}_n$ mixtures in the absence of hydrogen. We presume that the isomerization process does not lie along the major reaction sequence for olefin hydrogenation (vide infra).

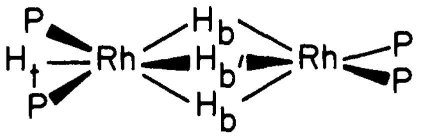
We initially assumed that the olefin hydrogenation reactions catalyzed by the dimeric and trimeric hydridorhodium complexes proceeded through the sequences of (1) hydrogen addition to give mononuclear $H_3Rh[P(OR)_3]_2$, (2) olefin addition, (3) hydrogen atom migration, and (4) reductive elimination of alkane and regeneration of $H_3Rh[P(OR)_3]_2$. However, the experimental data do not support the thesis that this sequence is the *primary* one leading to olefin hydrogenation, although hydrogen addition is clearly the first step in the catalytic sequence. The polynuclear hydrides reacted with ethylene in a slow, complex fashion with the formation of ethane, small amounts of methane, and, in the case of the trimer, a rhodium monohydride presumed to be $\{HRh_3[P(OCH_3)_3]_2\}_3$ because of the quartet $^1H\{^{31}P\}$ hydride resonance. (The source of the methane appeared to be the ethylene based on the observed formation of CD_4 and all the other deuteriomethanes from the reaction of C_2D_4 with $\{HRh[P(OCH_3)_3]_2\}_3$.) Rates of these reactions were more than 10^6 lower than that of the catalytic olefin hydrogenation reaction. In contrast, the polynuclear rhodium hydrides reacted, reversibly and virtually instantaneously, with hydrogen but the stoichiometry was not one molecule of hydrogen per atom of rhodium in the polynuclear complexes but simply one hydrogen molecule per molecule of polynuclear complex, (1) and (2). The hydrogen

$$H_2 + \{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2 \rightleftharpoons H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4 \qquad (1)$$

$$H_2 + \{HRh[P(OCH_3)_3]_2\}_3 \rightleftharpoons H_5Rh_3[P(OCH_3)_3]_6 \quad (2)$$

oxidative addition reactions were visually evident in the extremely fast black-green and black-brown to red color changes for the dimer and trimer solutions, respectively, and the reaction stoichiometries were established by vacuum system hydrogen titrations and by the reversible (20 °C) reaction under vacuum (Toepler pump analysis of hydrogen loss). Both hydrogen adducts exhibited a high solution-state stability; hence hydrogen addition, at least in the case of the dimer, lowered the thermal reactivity (irreversible decomposition) to a substantial degree. No phosphite ligand lability was detected when hydrogen was present in the dimer or trimer solutions. Reaction of these hydrogen adducts with olefins was virtually instantaneous at 20 °C, as evidenced by the red to black-green or black-brown color change, to give alkanes and the dimer or trimer complex which established the polynuclear hydrogen adducts as primary catalytic intermediates. NMR studies of ethylene and $H_5Rh_3[P(OCH_3)_3]_6$ mixtures gave evidence of an ethylene complex at ~−80 °C and showed that ethylene hydrogenation began about −40 °C and was relatively fast at −30 °C.

Solutions of the dimer or trimer hydrogen adducts gave spectroscopic evidence of only one solution species. NMR spectroscopic analysis of the dimer-hydrogen adduct at −80 °C implicated a rhodium-rhodium complex with three bridging hydride ligands. The hydride portion of the ^1H NMR spectrum of $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ consisted of a doublet of multiplets of intensity two, a doublet of multiplets of intensity one, and a broad peak of intensity one which in the $^1H\{^{31}P\}$ experiment became a triplet, a triplet, and a doublet, respectively (due to coupling with two, two, and one rhodium atoms, respectively). In the downfield bridging hydride proton resonances, the large P-H coupling constants are ascribed to essentially (~180°) trans H-Rh-P arrays as typically[20] observed for second- and third-row transition-metal complexes. All the NMR parameters were fully consistent with structure **1** with



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three bridging hydride ligands. In **1**, the right-hand set of phosphite ligands are shown to lie on a mirror plane so as to be consistent with the equivalence of the H_b bridging hydride ligands and a large (presumably trans) coupling of the $H_{b'}$ and P ligand atoms. Attempts to isolate single crystals of **1** are still in progress. There is a protonated analogue precedent for **1**, $H[R_3P]_2IrH_3Ir[PR_3]_2H^+$, for which crystallographic studies[21] established a face (hydrogen) bridged octahedral dimer with a very short, iridium-iridium separation of 2.513 Å.[22] In fact, we found that protonation of **1** yielded $H[(i\text{-}C_3H_7O)_3P]_2RhH_3[P(O\text{-}i\text{-}C_3H_7)_3]_2H^+$ which is apparently isostructural to the established iridium complex.

An extremely important dynamic facet of the $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ structure was the facile hydrogen atom migration evident in the character of the hydride portion of the ^1H DNMR spectra (Figure 3). Rearrangement in this molecule occurred by two distinct processes. The low-temperature process was characterized by a merging and coalescence of the two resonances ascribed to the terminal hydride ligand and to the one unique bridging hydride ligand. In this exchange regime, the resonance ascribed to the two identical bridging hydride ligands was unaltered in the ^1H and $^1H\{^{31}P\}$ experiments. The activation energy, E_a, for this low-temperature process is ~9 kcal/mol. A plausible exchange sequence is a "roll-over" of the terminal and the unique bridging hydride ligands to generate an equivalent configuration **2** wherein environments $H_{b'}$ and H_t are equilibrated. However, the qualitative character of the ^1H spectrum rigorously excludes this process because the ^1H resonance of the H_b hydride ligands should transform from a doublet to a triplet (large trans H-P coupling). The process is permutationally distinguished by a simple transposition of H_t and $H_{b'}$ hydride ligands. Geometrically, this process may be represented as occurring through a transition state or reaction intermediate as shown in **3**.

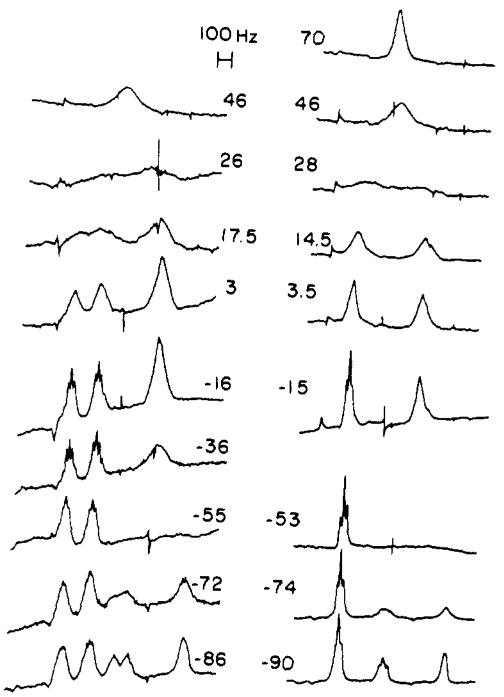
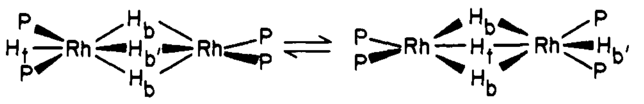


Figure 3. High-field (hydride region) 90-MHz ^1H NMR (left) and phosphorus-31 decoupled ^1H NMR (right) spectra from −90 to +70 °C of a toluene-d_8 or toluene-d_8 + CF_2Cl_2 solution of $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ under an atmosphere of hydrogen.



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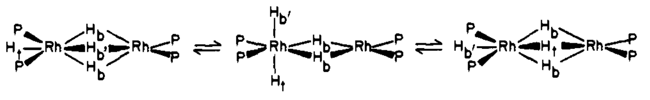

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Thus, the relatively unexpected scenario is encountered in which hydrogen oxidative addition to a d^8-d^8 dinuclear species leads not to fragmentation to mononuclear species, at least as the dominant reaction scheme, but to a relatively robust dinuclear complex. Since the hydrogen adduct **1** reacted instantly with olefins to produce alkanes and the dimer $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, the primary catalytic sequence in olefin hydrogenation must involve dinuclear species as shown in Scheme I. Note that in effect hydrogen adds oxidatively to one rhodium atom and the olefin to the other rhodium atom in this scheme; in effect, this feature *formally* models metal surface catalyzed olefin hydrogenations that would center on two adjacent, active metal atom sites. The structures presented for the olefin and ethyl intermediates are conjectural; several plausible alternatives can be drawn. In this overall mechanistic postulate, we do not intend to exclude mononuclear $H_3Rh[P(OR)_3]_2$ species as viable intermediates in the olefin hydrogenation sequence.[23] We simply note that the very high rates at which the dimer reacts with hydrogen to form the dimer **1** and at which **1** reacts

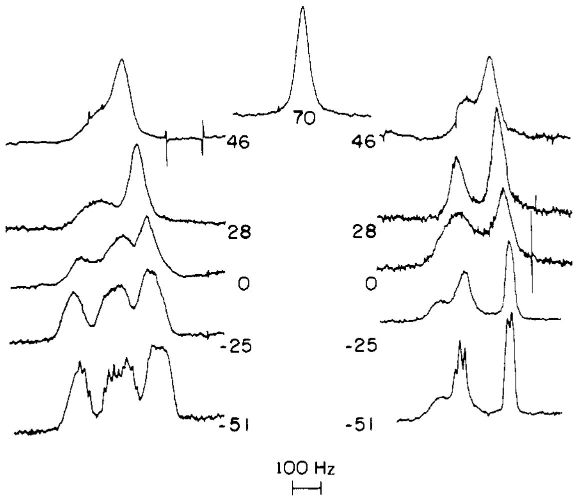
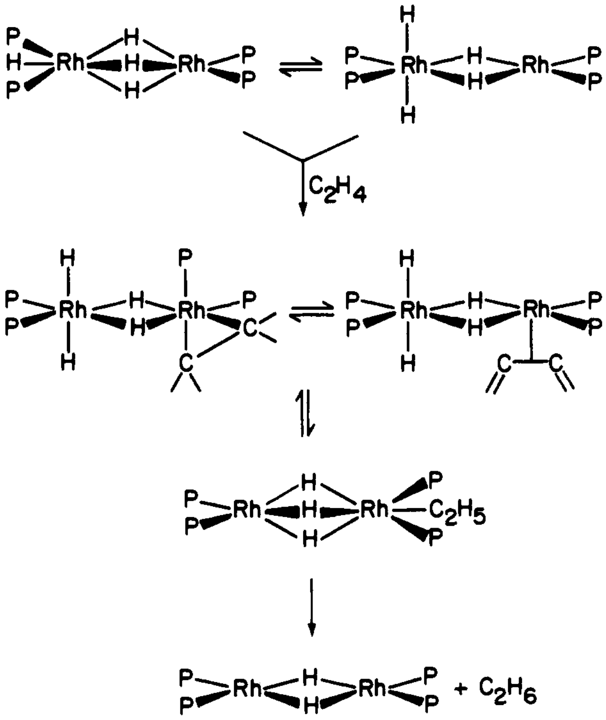


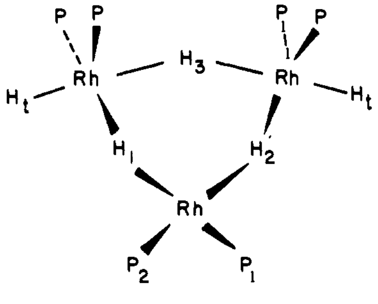
Figure 4. High-field (hydride region) 90-MHz ^1H NMR (left) and phosphorus-31 decoupled ^1H NMR (right) spectra of a toluene-d_8 solution of $H_5Rh_3[P(OCH_3)_3]_6$ under an atmosphere of H_2 from −51 to +70 °C.

Scheme I



with olefins to form alkanes clearly establish the major olefin hydrogenation sequence through dimer species.

The stoichiometry of the hydrogen-$\{HRh[P(OCH_3)_3]_2\}_3$ reaction was also 1:1 and the $^1H\{^{31}P\}$ hydride spectrum of this adduct at −80 °C consisted of a broad peak (lowest field), a triplet, and a doublet (highest field) of relative intensities 1, 2, and 2, respectively. The hydrogen adduct thus has two terminal hydride ligands, two edge-bridging hydride ligands, and one of undetermined stereochemical form. Like the dimer-hydrogen adduct, this trimer-hydrogen adduct was stereochemically nonrigid (Figure 4) with the hydrogen migration occurring in perhaps two distinct steps (collapse temperatures of 0 and 46 °C). The lower temperature process primarily involved the exchange of the two edge-bridging hydride ligands and the unique hydride ligand. The unique low-field hydride resonance may be due to an edge-bridging hydride since the resonance position is close to the resonance set arising from the two edge-bridging hydride ligands. *One* possible stereochemical representation is **4**; the trans relationship of P_1-H_1 and P_2-H_2 is consistent with the large doublet splitting for these two environmentally equivalent hydride ligands. For a structure like **4**, the low-temperature fluxional process would comprise intramolecular exchange among the edge-bridging hydrogen atoms. Olefin addition in **4** should occur at the unique square-planar rhodium site in formal analogy to the dimer chemistry (Scheme I).



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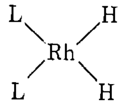
Acetylenes reacted immediately with $\{HRh[P(OCH_3)_3]_2\}_3$ and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ as evidenced by the dissolution of the polynuclear hydrides and the discoloration from black-green or brown to orange or orange-red. In a catalytic mode, these hydrides effected the hydrogenation of the acetylenes to cis olefins at rates much lower than the catalytic olefin hydrogenation reactions. Clearly, the acetylenes prevailed over olefins in the competition for coordination sites on the rhodium hydride catalyst precursors or intermediates. A more detailed spectroscopic and kinetic study of these acetylene hydrogenation reactions is in progress.

The dimer or more accurately the dimer hydrogen adduct $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$ was a catalyst precursor for the hydrogenation of aromatic hydrocarbons. The effective catalytic intermediate could be the dimer hydrogen adduct, $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_3$,[24] or a low-concentration, spectroscopically nondetectable monomer, $H_3Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$. Generation of the second species requires liberation of free phosphite, a process inconsistent with the observations: Free phosphite reacts exothermally with the dimer to ultimately and irreversibly yield $HRh[P(OR)_3]_4$ complexes yet in the presence of hydrogen and an arene the formation of such five-coordinate hydrides was not detected. The third alternative, the mononuclear intermediate, is isoelectronic with an intermediate implicated in allylcobalt-catalyzed reactions. However, the rhodium-catalyzed reactions, unlike the allylcobalt reactions, were not stereoselective (large amounts of *trans*-dimethylcyclohexanes were produced from xylenes), were chemoselective to olefins, not arenes, exhibited extensive H-D exchange in benzene-D_2 mixtures, and were extremely slow. In these respects the hydridorhodium and allylcobalt catalysts sharply differ. Although the mechanistic features of this system are obscure, there is a similarity between the rhodium catalyst and the η^6-$C_6(CH_3)_6Ru$-η^4-$C_6(CH_3)_6$ catalyst[25] in the patterns of the H-D exchange reactions catalyzed for D_2-arene reactions (Table III).[24] There was extensive exchange at ring sites in benzene as evidenced by the range of deuterated species found in the recovered benzene and the product cyclohexanes. For methyl-substituted benzenes, this exchange appeared to be largely limited to aliphatic exchange as evidenced by sharp, near cutoff at toluene-d_3 and methylcyclohexane-d_9 and at xylene-d_6 and dimethylcyclohexane-d_{12}, respectively, in the toluene and xylene (ortho and para) reaction products. For *n*-propylbenzene, the cutoff was at d^2 in the recovered propylbenzene. All these data implicate the formation of benzyl derivatives in the ruthenium and rhodium catalytic systems—an important mechanistic issue that is now under general investigation in our studies of catalytic arene hydrogenation reactions.[2]

Conclusion

The mechanistic features of the chemical and catalytic properties of the polynuclear rhodium hydrides establish an important point vis-à-vis the metal cluster-metal surface analogy.[26] An obvious concern about the validity of the analogy derives from application of the analogy to chemical reactions wherein fragmentation of the cluster into smaller aggregates or even mononuclear species may occur. This concern is especially relevant to the coordinately saturated metal carbonyl clusters in which the *average* metal-metal bond energy is comparable to—not larger than—the *average* metal-carbonyl bond energy.[27,28] There is, in fact, evidence that some first- and second-row metal carbonyl clusters fragment into mononuclear species in chemical and catalytic[29] reactions. Scission of either metal-metal or metal-carbonyl bonds is common simply because many of these "saturated" clusters react in a dissociative fashion with other ligands and with hydrogen. For this reason, we have sought the synthesis of coordinately unsaturated clusters[30] to minimize in the cluster chemistry the possibility of cluster fragmentation and to maximize reactivity and potential catalytic activity. Clearly, the structural, chemical, and catalytic data presented above establish this tack to be effective in this class of "unsaturated" polynuclear rhodium hydrides which are generated by edge or vertex sharing of 15-electron square-planar (**5**) units.



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(12) The isoelectronic allylcobalt tris(trimethyl phosphite) complex has near square pyramidal geometry with a bidentate allyl ligand at two basal positions as in η^3-cyclooctenylcobalt tris(trimethyl phosphite). However, this actual structure is also very close to an alternative idealized geometry of pseudotetrahedral form with a "monodentate" allyl ligand—i.e., a C_3CoP_3 substructure with the allyl C_3 centroid-Co vector along the threefold axis. Tau, D.; Muetterties, E. L.; Thompson, M. R.; Day, V. W. To be published.

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(14) The allylcobalt tris(trialkyl phosphites) did not exhibit fast (NMR time scale) $\eta^3 \rightleftharpoons \eta^1$ interconversion but were fluxional species wherein a transition from AB_2 to A_3 $^{31}P\{^1H\}$ NMR spectra occurred at low temperatures.[15]

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(16) Because the polynuclear rhodium hydrides produced in the hydrogenolysis reaction were extremely active olefin hydrogenation catalysts, the propylene was not detected; only propane was observed in the gaseous product.

(17) Rakowski, M. C.; Hirsekorn, F. J.; Stuhl, L. S.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975,** *97,* 237.

(18) By analogy to reasonably well established sequences[3] for the cobalt series, these processes probably are

$$\eta^3\text{-}C_3H_5RhL_n \rightleftharpoons \eta^1\text{-}C_3H_5RhL_n \xrightleftharpoons{H_2} \eta^1\text{-}C_3H_5RhH_2L_n$$
$$\rightleftharpoons \eta^3\text{-}C_3H_5RhH_2L_{n-1} + L$$

(19) The hydride portion of the ^{1}H NMR spectrum was a doublet of triplets centered at 7.2 ppm upfield from tetramethylsilane with J_{HP}(cis) = 16 and J_{HP}(trans) = 126 Hz and a zero or near-zero Rh–H coupling constant. This observation is not unique and has been made by others for rhodium hydrides; cf. Kaesz, H. D.; Salient, R. B. *Chem. Rev.* **1972,** *72,* 231.

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(21) Crabtree, R. H.; Felkin, H.; Morris, G. E.; King, T. J.; Richards, J. A. *J. Organomet. Chem.* **1976,** *113,* C7.

(22) As in the rhodium-hydrogen adduct, the resonances of the bridging hydride ligands are downfield from the resonances for terminal hydride ligands in this iridium dimer.[21]

(23) (a) In the presence of hydrogen, the dimer or trimer *may* form monomeric species (very small concentrations) and these monomers *may* be the active species in the very slow catalytic hydrogenation of arenes. (b) A full kinetic analysis of the catalytic olefin hydrogenation reaction is in progress. However, the rate expression for the catalytic reaction will add little molecular information to established, qualitative mechanistic features. Key mechanistic studies in progress involve labeled dimers (or trimers) of the type $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ and $\{HRh[P(O\text{-}i\text{-}C_3D_7)_3]_2\}_2$ to assess the extent, if any, of ligand exchange and of cluster fragmentation.

(24) Interestingly, the dimer hydrogen adduct **1** is isoelectronic and apparently structurally similar to an arene hydrogenation catalyst, $[\eta^6\text{-}C_6(CH_3)_6\text{-}RuH_2Ru\text{-}\eta^6\text{-}C_6(CH_3)_6Cl]Cl$, recently reported: Bennett, M. A.; Huang, Tai-Nang; Turney, T. W. American Chemical Society–Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April 5, 1979, Inorganic Division, Abstract 337.

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(29) In the $Fe_3(CO)_{12}$ catalysis of olefin isomerization, mononuclear intermediates are involved. Cf. Casey, C. P.; Cyr, C. *J. Am. Chem. Soc.* **1973,** *95,* 2248.

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