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Reactivity of Electron-Rich Binuclear Rhodium Hydrides. Synthesis of Bridging Alkenyl Hydrides and X-ray Crystal Structure of $[\{((CH_3)_2CH)_2PCH_2CH_2P(CH(CH_3)_2)_2\}Rh]_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$

Michael D. Fryzuk*

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

T. Jones and F. W. B. Einstein

Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada

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The reaction of the electron-rich binuclear rhodium hydride $[\{((CH_3)_2CH)_2PCH_2CH_2P(CH(CH_3)_2)_2\}Rh]_2(\mu\text{-}H)_2$ (**1b**) with ethylene leads to the bridging vinyl hydride derivative $[\{((CH_3)_2CH)_2PCH_2CH_2P(CH(CH_3)_2)_2\}Rh]_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$ (2) whose X-ray crystal structure has been determined. Other simple olefins such as propene, 1-hexene, *cis*-2-pentene, and *trans*-butene generate the analogous bridging alkenyl hydrides in at least two structurally isomeric forms. More bulky olefins such as *tert*-butylethylene and isobutene do not react with **1b** under ambient conditions; similarly, **1b** does not react with cyclooctene. The structurally isomeric bridging alkenyl hydrides thermally transform into mononuclear allyl derivatives with only mild heating (30–50 °C). A mechanism to explain this fragmentation reaction is also presented.

Introduction

Prior coordination of an olefinic substrate to a transition-metal center is a necessary activation step in many catalytic and stoichiometric organic transformations.[1] With *mononuclear* metal derivatives, the nature of the metal–olefin interaction is well-known[2] and numerous complexes containing olefinic ligands have been fully characterized.[3] This contrasts the situation with *polynuclear* metal derivatives for which olefinic ligands are rare,[4] in fact the reaction of olefins with transition-metal clusters can lead to bridging alkenyl hydrides[5-7] (eq 1–3).

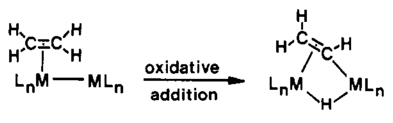
$$[Os_4H_4(CO)_{12}] + CH_2{=}CHR \xrightarrow{h\nu} [Os_4H_3(\mu\text{-}\eta^2\text{-}CH{=}CHR)(CO)_{11}] \quad (1)$$

$$[Os_3H_2(CO)_{10}] + CH_2{=}CH_2 \rightarrow [Os_3H(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(CO)_{10}] \quad (2)$$

$$[Re_2(CO)_{10}] + CH_2{=}CHR \xrightarrow{h\nu} [Re_2H(\mu\text{-}\eta^2\text{-}CH{=}CHR)(CO)_8] \quad (3)$$

The use of substituted olefins can generate, in principle, isomeric bridging alkenyl derivatives; however, in all cases[5,7] studied to date only one structural isomer[8] has been observed (eq 1 and 3).

It has been proposed[4,6-8] that the formation of the alkenyl hydride product involves activation of a coordinated olefin by one metal center followed by oxidative addition of a vinylic C–H bond to an adjacent, coordinatively unsaturated site (eq 4). While other mechanisms[9] may be



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invoked to rationalize the observed products, any sequence requires, at some initial stage, the olefin to interact with a coordinatively unsaturated metal cluster. Since we have had a number of coordinatively unsaturated, catalytically active rhodium hydride clusters[10,11] at our disposal, we have investigated the reaction of a number of simple olefins with the binuclear members of this family. In this paper we report (i) a coordinatively unsaturated binuclear derivative that generates bridging alkenyl hydrides in two or more structurally isomeric forms upon reaction with simple olefins, (ii) the X-ray crystal structure of the parent vinyl hydride complex, and (iii) the thermal decomposition products of these bridging alkenyl derivatives.

Experimental Section

General procedures and instrumentation were as described elsewhere.[11,12] Liquid olefins (Aldrich) such as 1-hexene, *cis*-2-pentene, *tert*-butylethylene, and cyclooctene were distilled, dried over activated 4-Å molecular sieves, and vacuum transferred before use. Gaseous olefins (Matheson) were dried by passage through activated 3-Å molecular sieves.

$((CH_3)_2CH)_2PCH_2CH_2P(CH(CH_3)_2)_2$. The synthesis of this ligand is identical with that described[13] for $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$, starting from $Cl_2PCH_2CH_2PCl_2$ and the Grignard reagent $(CH_3)_2CHMgBr$. Thus 1,2-bis(diisopropylphosphino)ethane (dippe) was obtained as an air-sensitive, colorless liquid (bp 75–80 °C (0.2 mm)): ^1H NMR (C_6D_6, ppm) $P(CH(CH_3)_2)_2$, 1.65 (septet of d, $^2J_P = 1.6$ Hz, $^3J_{CH_3} = 7.2$ Hz), PCH_2CH_2P, 1.62 (d (second order)), $P(CH(CH_3)_2)_2$, 1.10 (d of d, $^3J_P = 13.6$ Hz), 1.07 (d of d, $^3J_P = 10.4$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, relative to external $P(OMe)_3$ at +141.0 ppm) 8.7 (s).

$[(dippe)Rh]_2(\mu\text{-}H)_2$. To a solution of $[\eta^3\text{-}(2\text{-}Me\text{-}C_3H_4)Rh(COD)]$[12] (0.265 g, 1.0 mmol) in hexanes (3 mL) was added a solution of 1,2-bis(diisopropylphosphino)ethane (dippe) (0.263 g, 1.0 mmol) in hexanes (1 mL) to give a dark greenish brown solution of $[\eta^3\text{-}(2\text{-}Me\text{-}C_3H_4)Rh(dippe)]$. The hexanes and 1,5-cyclooctadiene were removed under vacuum, and the oily residue was dissolved in toluene (5 mL), the mixture transferred to a 250-mL thick-walled glass reactor equipped with a magnetic stirring bar and a Teflon needle valve, and the reactor attached to a vacuum line. The solution was degassed, cooled down to −196 °C, and pressurized with H_2 to 1 atm; the reactor was sealed and allowed to warm to room temperature and stirred for 1 week, during which time the solution became dark brown. The toluene and hydrogen were removed under vacuum, and the deep black-green residue was recrystallized from minimum hexanes (3–4 mL) by cooling to −30 °C; deep black-red crystals (0.200 g, 55%) were obtained: mp 178–180 °C dec; ^1H NMR (C_6D_6, ppm) $P(CH(CH_3)_2)_2$, 1.83 (br m, $^3J_{CH_3} = 6.8$ Hz), $P(CH(CH_3)_2)_2$, 1.40 (d of d, $^3J_P = 7.0$ Hz), 1.11 (d of d, $^3J_P = 5.4$ Hz), PCH_2CH_2P, 1.04 (br d, $^3J_P = 12.3$ Hz), RhH, −4.8 (br t of quintets, $^1J_{Rh} = 34.2$ Hz, $^2J_P = 35.2$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, relative to external $P(OMe)_3$ at +141.0 ppm) 104.7 (br complex doublet, $J \approx 165$ Hz); IR (hexane) Rh–H–Rh, 1160 cm^{-1} (m). Anal. Calcd for $C_{14}H_{33}P_2Rh$: C, 45.91, H, 9.08. Found: C, 46.10; H, 9.00.

$[(dippe)Rh]_2(\mu\text{-}D)_2$. Exposing a dark green solution (toluene or hexanes) of the binuclear dihydride to D_2 (1 atm) immediately generated a dark chocolate brown solution; removal of excess D_2 regenerated the dark green color and removal of solvent produces the dideuteride in quantitative yield: IR (hexane) Rh–D–Rh, 850 cm^{-1} (m). Refluxing the dihydride in C_6D_6 or C_7D_8 for extended periods (1–2 days) also yielded the dideuteride.

$[(dippe)Rh]_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)$. A dark green toluene solution (5 mL) of $[(dippe)Rh]_2(\mu\text{-}H)_2$ (0.100 g, 0.137 mmol) was degassed on a vacuum line and ethylene (1 atm) admitted; the solution immediately turned brown then bright orange. After the solution was stirred for 10 min, the toluene was removed and the residue recrystallized from minimum hexanes at −30 °C as red-orange plates; yield 0.095 g (92%); mp 120–121 °C dec; ^1H NMR (C_6D_6, ppm) H_a, 9.48 (dd, $^3J_{ab} = 11.4$ Hz, $^3J_{ac} = 18.6$ Hz), H_b, 6.37 (m, $^2J_{bc} = 3.7$ Hz, $^4J_P = 4$ Hz), H_c, 4.36 (dd), $P(CH(CH_3)_2)_2$, 2.13 (br m), $P(CH(CH_3)_2)_2$ and PCH_2CH_2P, broad overlapping multiplets at 1.20, RhH, −7.00 (m); $^{31}P\{^1H\}$ (C_6D_6, relative to external $P(OMe)_3$ at +141.0 ppm) 95.2 and 91.1 (br m). Anal. Calcd for $C_{15}H_{34}P_2Rh$: C, 47.50; H, 9.04. Found: C, 47.29; H, 9.00.

$[(dippe)Rh]_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}{}^{13}CH{=}{}^{13}CH_2)$. The use of $^{13}CH_2{=}{}^{13}CH_2$ (92.1% ^{13}C, Merck, Sharp and Dohme) generates the ^{13}C labeled μ-vinyl in 90% recrystallized yield: ^1H NMR (C_7D_8, ppm) H_a, $^1J_{13C} = 127$ Hz, H_b, H_c, $^1J_{13C} = 151$ Hz; $^{13}C\{^1H\}$ NMR (C_6D_6, 30 °C, relative to C_6D_6 at 128.0 ppm) $RhCH{=}$, 195.6 (m), $RhCH{=}CH_2$, 79.7 (d, $^1J_{C,C} = 36.0$ Hz), other weak signals in the region 15–30 ppm were observed but not assigned; $^{13}C\{^1H\}$ NMR (C_7D_8, ppm, −30 °C) 79.7 (dd, $J = 14.6$ Hz, either ^{31}P or ^{103}Rh).

$[(dippe)Rh]_2(\mu\text{-}H)_2$ + Propene. This procedure was identical with that described for the preparation of the $\mu\text{-}\eta^2$-vinyl derivative except that the solution was stirred for 30 min at room temp. Removal of the toluene under vacuum gave a dark, brown-orange solid. Recrystallization from minimum hexanes (−30 °C) gave brown-orange crystals (70% yield): mp 107–110 °C dec; ^1H NMR (C_6D_6, ppm) **3a**; R^1 = H, 9.03 (br d, $^3J_{H,H_b} = 9.3$ Hz), H_b, 7.02 (m, $^4J_P = 4.4$ Hz), $R^2 = CH_3$, 1.77 (d, $^3J_{H_b} = 4.8$ Hz), **3b**, H_b, 5.65 (br m, $^4J_P = 4$ Hz), R^2 = H, 4.12 (br d, $^2J_{H,H_b} = 2$ Hz), $R^1 = CH_3$, 2.42 (br s), $P(CH(CH_3)_2)_2$, 2.1 (m), $P(CH(CH_3)_2$ and PCH_2CH_2P, complex multiplet centered at 1.2, RhH, −7.14 (m). Anal. Calcd for $C_{31}H_{70}P_4Rh_2$: C, 48.19; H, 9.13. Found: C, 48.42; H, 9.31.

$[(dippe)Rh]_2(\mu\text{-}H)_2$ + 1-Hexene. $[(dippe)Rh]_2(\mu\text{-}H)_2$ (0.080 g, 0.11 mmol) was dissolved in neat 1-hexene (~2 g) to give a dark brown solution that lightened over a period of 10 min to a bright orange solution. After 10 min of more stirring, the volatiles were removed to give an oily, yellow-orange solid in quantitative yield: ^1H NMR (C_6D_6, ppm) **4a**, R^1 = H, 9.04 (br d, $^3J_{H,H_b} = 9.0$ Hz), H_b, 6.86 (m, $^4J_P = 4$ Hz), $R^2 = CH_2CH_2CH_2CH_3$, 1.78 (m), $R^2 = CH_2CH_2CH_2CH_3$, obscured by phosphine ligand resonances, **4b**, H_b, 5.82 (br s), R^2 = H, 3.94 (br s), $R^1 = CH_2CH_2CH_2CH_3$, 2.89 (br m), $R^1 = CH_2CH_2CH_2CH_3$, obscured by phosphine ligand resonances, $P(CH(CH_3)_2)_2$, 2.4 and 2.1 (m), $P(CH(CH_3)_2)_2$ and PCH_2CH_2P, overlapping multiplets at ~1.2, RhH, −7.10 (m). Anal. Calcd for $C_{34}H_{67}P_4Rh_2$: C, 50.13; H, 9.40. Found: C, 50.50; H, 9.36.

$[(dippe)Rh]_2(\mu\text{-}H)_2$ + *cis*-2-Pentene. The procedure was identical with that described for the reaction with 1-hexene. After the solution turned orange (~45 minutes), the excess *cis*-2-pentene was removed under vacuum to give an oily, yellow-orange material that was analyzed by ^1H NMR only: ^1H NMR (C_6D_6, ppm) **5a**, R^1 = H, 9.15 (br d, $^3J_{H,H_b} = 9.0$ Hz), H_b, 6.88 (m), $R^2 = CH_2CH_2CH_3$, 1.78 (m), $R^2 = CH_2CH_2CH_3$, obscured by phosphine ligand resonances, **5b**, H_b, 5.84 (br s), R^2 = H, 3.94 (br s), $R^1 = CH_2CH_2CH_3$, 2.84 (br m), $R^1 = CH_2CH_2CH_3$, obscured by phosphine ligand resonances, $P(CH(CH_3)_2)_2$, 2.3 and 2.1 (m), $P(CH(CH_3)_2$ and PCH_2CH_2P, overlapping multiplets at ~1.2, RhH, −7.10 (m).

$[(dippe)Rh]_2(\mu\text{-}H)_2$ + *trans*-Butene. This procedure was identical with that described for the reaction with ethylene or propene. After 3 h, the dark brown solution was pumped to dryness to give an oily brown solid that was dissolved in minimum hexanes (~100 mg in ~0.5 mL) and cooled to −30 °C for 12 h. Yellow-orange microcrystals (~50% yield) deposited which, by ^1H NMR, consisted of an intimate mixture of **6a**, **6b**, and **6c**: ^1H NMR (C_6D_6, ppm) **6a**, R^1 = H, 9.00 (br, d, $^3J_{H,H_b} = 9.4$ Hz), H_b, 6.80 (br m), $R^2 = CH_2CH_3$, obscured by ligand resonances, **6b**, H_b, 5.84 (br m), R^2 = H, 3.94 (br s), $R^1 = CH_2CH_3$, 2.90 (br m), $R^1 = CH_2CH_3$, obscured by phosphine ligand resonances, **6c**, H_b, 6.33 (br m), $R^1 = CH_3$, 2.60 (br s), $R^2 = CH_3$, 1.95 (d, $^3J_{H_b} = 5.0$ Hz), $P(CH(CH_3)_2)_2$, ~2.1 and 2.3 (m), $P(CH(CH_3)_2)_2$ and PCH_2CH_2P, complex multiplet centered at ~1.2, RhH, −7.2 and −7.6 (m). The supernatant from the solid obtained above contains mostly **6a**, **6b**, and **6c** and ~20% $[\eta^3\text{-}(1\text{-}Me\text{-}C_3H_4)Rh(dippe)]$ as

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[9] (a) One alternative that we are now investigating involves the possible formation of the bridging alkane-1,2-diyl[9b] intermediate $[(dippe)Rh]_2(\mu\text{-}1,2\text{-}CH_2CHR)$ by (formal) insertion of the olefin into the Rh–Rh bond of $[(dippe)_2Rh_2]$ (formed by initial dehydrogenation of **1b** by the olefin). Subsequent binuclear β-elimination of the alkane-1,2-diyl unit would generate the observed bridging alkenyl hydrides. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 237.

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[14] In fact the dideuteride $[(dippe)Rh]_2(\mu\text{-}D)_2$ is also formed by exchange with C_6D_6 *after* formation of **1b** and **7** in eq 7.

judged by ^{1}H NMR (see following preparation).

[η^3-(1-Me-C_3H_4)Rh(dippe)]. To a hexanes solution (4 mL) of [η^3-(1-Me-C_3H_4)Rh(COD)][12] (0.0256 g, 0.96 mmol) was added dippe (0.252 g, 0.96 mmol) in hexanes (2 mL) dropwise. The resulting dark brown solution was allowed to sit at room temperature for 30 min, and then all of the volatiles were removed under vacuum to give a dark brown oil: ^{1}H NMR (C_6D_6, ppm) syn isomer, $H_{central}$, 4.85 (m), H_{syn} 3.70 (br d, $^3J_{H_{central}} = 7.6$ Hz), H'_{anti}, 3.30 (septet, $^3J_{H_{central}} = 12.0$, $J_P = {}^3J_{CH_3} = 6.0$ Hz), syn-CH_3, 2.20 (dt, $J_P = 6.0$ Hz, $J_{Rh} = 2.5$ Hz), H_{anti}, 1.99 (br dd, $^3J_{H_{central}} =$ 12.0 Hz, $J_P = 6.5$ Hz), $P(CH(CH_3)_2)_2$, ~1.7–2.1 (m), $P(CH(CH_3)_2)_2$, ~0.8–1.2 (m), PCH_2CH_2P, obscured, anti isomer, $H_{central}$, 4.78 (m), H_{syn}, 3.77 (br d, $^3J_{H_{central}} = 7.5$ Hz), H_{anti}, 2.40 (br dd, $^3J_{H_{central}} =$ 13.2 Hz, $J_P = 6.5$ Hz), all other protons are not assignable due to overlap, syn:anti ratio = 2.5:1; $^{31}P\{^1H\}$ NMR (C_6D_6, relative to external $P(OMe)_3$ at +141.0 ppm) syn isomer, P_A, 96.5 (dd, $^2J_{AM}$ = 17.1 Hz, $^1J_{Rh}$ = 195 Hz), P_M, 88.8 (dd, $^1J_{Rh}$ = 196.5 Hz), anti isomer, P_A, 98.7 (dd, $^2J_{AM}$ = 17.1 Hz, $^1J_{Rh}$ = 192 Hz), P_M, 91.2 (dd, $^1J_{Rh}$ = 197 Hz).

[(η^3-C_3H_5)Rh(dippe)]. To a hexanes solution (2 mL) of [(η^3-C_3H_5)Rh(COD)][24] (0.126 g, 0.5 mmol) was added a hexanes solution (1 mL) of dippe (0.131 g, 0.5 mmol) dropwise; the initial bright yellow solution darkened to a brown-green. After 10 min at ambient temperature, the volatiles were removed under vacuum and the brown-green oil was analyzed by spectroscopic techniques: ^{1}H NMR (C_6D_6, ppm) $H_{central}$, 4.85 (m, $^3J_{H_{syn}} = 7.5$ Hz, $^3J_{H_{anti}} =$ 13.0 Hz, $^2J_{Rh} = 2.0$ Hz), H_{syn}, 3.94 (d), H_{anti}, 2.32 (dd, $J_P = 5.0$ Hz), $P(CH(CH_3)_2)_2$, 1.90 (br sep, $^3J_{CH_3} = 7.0$ Hz), 1.80 (br sep, $^3J_{CH_3}$ = 7.0 Hz), PCH_2CH_2P, 1.23 (m), $P(CH(CH_3)_2)_2$, overlapping doublets, ~1.0 ppm ($^3J_P = 7.0$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6, relative to external $P(OMe)_3$ at +141.0 ppm) 95.5 (d, $^1J_{Rh}$ = 193 Hz).

Thermal Transformation of Bridging Alkenyl Hydrides. These reactions were carried out in sealed NMR tubes (5 or 10 mm) in C_6D_6 or C_7D_8 and monitored periodically by ^{1}H or $^{31}P\{^1H\}$ NMR. Two different methods were used; an example of each is outlined below.

Method 1. A C_7D_8 solution (2.5 mL) of [(dippe)Rh]$_2$(μ-H)$_2$ (0.130 g, 0.18 mmol) in a 10-mm NMR tube attached to a Teflon needle valve was degassd and cooled to −70 °C (dry ice–CH_2Cl_2); *trans*-butene (~70 equiv) was condensed in and the tube sealed with a torch. The resultant dark green solution was warmed slowly to room temperature and the $^{31}P\{^1H\}$ spectrum taken periodically. After ~3 h at room temperature, the starting dihydride had been consumed and a very complicated, unsymmetrical set of lines (overlapping ABCDXY spectra for the isomeric butenyl hydrides) between +80 and +100 ppm was observed. After 1 day, characteristic lines of [η^3-(1-Me-C_3H_4)Rh(dippe)] (~50% conversion) were observed. After 3 days, the tube was opened under N_2, the volatiles were removed, and the orange-brown residue was analyzed by ^{1}H NMR; the syn:anti isomer ratio was 7:1.

Method 2. A C_6D_6 solution (0.4 mL) of the pure propenyl hydrides (from the reaction of propene and [(dippe)Rh]$_2$(μ-H)$_2$ followed by removal of excess propene) (0.050 g, 0.06 mmo) was heated to ~50 °C (probe temperature) under N_2 in a sealed NMR tube (5 mm). The formation of [(η^3-C_3H_5)Rh(dippe)] and [(dippe)Rh]$_2$(μ-H)$_2$ was followed by $^{31}P\{^1H\}$ NMR; after 3 h, approximately 50% conversion had occurred. Because of the overlap of resonances, accurate rate data could not be obtained.

For the analogous thermal decomposition of the isomeric hexenyl hydrides, the following AMX spectra could be gleaned from the $^{31}P\{^1H\}$ data in analogy to [η^3-(1-Me-C_3H_4)Rh(dippe)] (C_6D_6, relative to external $P(OMe)_3$ at +141.0 ppm): major isomer, *syn*-[η^3-(1-Pr-C_3H_4)Rh(dippe)], P_A 96.6 (dd, $^2J_{AM}$ = 17.1 Hz, $^1J_{Rh}$ = 194 Hz), P_M, 89.2 (dd, $^1J_{Rh}$ = 195 Hz), minor isomer, *anti*-[η^3-(1-PrC_3H_4)Rh(dippe)], P_A, 98.1 (dd, $^2J_{AM}$ = 17.1 Hz, $^1J_{Rh}$ = 191 Hz), P_M, 91.6 (dd, $^1J_{Rh}$ = 197 Hz); another minor isomer was observed, but full analysis as an AMX pattern was not possible due to overlap of resonances. The syn:anti ratio could only be estimated at 4–5:1.

Structure Determination of [(dippe)Rh]$_2$(μ-H)(μ-η^2-CH=CH_2). Crystals suitable for data collection were obtained by cooling a hexanes solution of 2 to −30 °C. An orange crystal (0.14 × 0.19 × 0.11 mm) was mounted in a Lindemann glass capillary and sealed under N_2. Precession and Weissenberg photographs were used to obtain approximate unit cell dimensions and to assign the space group as *Cc* or *C*2/*c* (systematic absences: *hkl*, $h + k = 2n + 1$; *hol*, $l = 2n + 1$). Subsequent structure solution uniquely defined the space group as *C*2/*c*. Accurate cell dimensions (Table I) were determined by least-squares refinement of the diffractometer angles of 34 independent reflections (2θ = 35.7–42.3; λ(Mo Kα_1) = 0.70926 Å) chosen from a variety of points in reciprocal space. Data were collected at 293 K, by using a Picker FACS-I four-circle diffractometer with a graphite monochromater and a scintillation detector with pulse height discrimination. The takeoff angle was 3°, and symmetrical θ–2θ scans (2° min^{-1}) of $(1.4 + 0.692 \tan \theta)°$ were used. Stationary-crystal–stationary-counter counts of 10% of the scan time were taken at each side of the scan. A peak profile analysis was performed on each reflection, and the intensity and its associated error were determined by the method of Grant and Gabe.[15] Measurement of two standards every 40 reflections showed there to be a slight variation in intensity (±2%) which was corrected appropriately.

Table I. Crystal Data

$C_{30}H_{69}P_4Rh_2$	mol wt 759.590
space group: *C*2/*c*	
$a = 38.209$ (2) Å	$\mu = 10.52$ cm^{-1}
$b = 14.596$ (2) Å	$\rho_{obsd}{}^a = 1.33$ g cm^{-3}
$c = 13.472$ (2) Å	$\rho_{calcd}(Z = 8) = 1.346$ g cm^{-3}
$\beta = 93.98$ (1)°	final $R^b = 0.025$
$U = 7495.24$ Å^3	final $R_w{}^c = 0.027$

[a] Flotation in a CH_2Cl_2–CH_2I_2 mixture. [b] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [c] $R_w = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2)^{1/2}$.

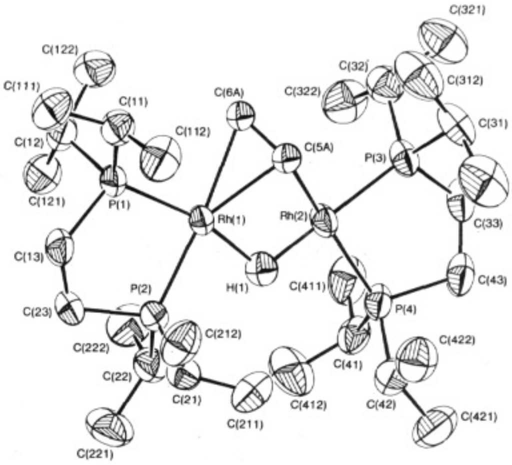

Figure 1. Molecular geometry and labeling for **2** (ORTEP diagram; 50% probability contours for all atoms).

Intensities were measured for 5892 independent reflections (2θ < 45.0°), of which 4728 were classed observed [$I \geq 2.3\sigma(I)$]. Lorentz–polarization and absorption corrections were made (transmission coefficients varied from 0.675 to 0.792).

Determination and Refinement of Structure. The structure was solved by using conventional Patterson and Fourier methods. All atoms of the molecule were clearly revealed by difference Fourier syntheses apart from the hydrogen atoms associated with the bridging ethylene moiety. Initial refinement of the complete molecule (with the exception of the aforementioned hydrogens), with anisotropic temperature factors for all non-hydrogen atoms, gave rise to exceptionally large U_{11} and U_{22} values and a small interatomic distance (ca. 1.1. Å) for the ethylene carbon atoms. Further examination of the ethylene region led to the disordered model shown in Figure 1, with fractional occupancies of 0.69 for C(5A)–C(6A) and 0.31 for C(5B)–C(6B). The fractional hydrogens associated with these carbons were not located. Block-diagonal least-squares refinement of the atomic coordinates of all the atoms with anisotropic temperature factors for all non-hydrogen atoms (except the ethylene carbon atoms), variable isotropic temperature factors for H(1) and the ethylene carbons, and fixed isotropic temperature factors (B_{iso} = 6.0 for methylene hydrogens; B_{iso} = 9.0 for methyl hydrogens) for all other hydrogen atoms gave final

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(15) Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1977**, *11*, 114.

Table II. Positional and Thermal Parameters[a] for $[\{((CH_3)_2CH)_2PCH_2CH_2P(CH(CH_3)_2)_2\}Rh]_2 \cdot (\mu\text{-}\eta^2\text{-}CH{=}CH_2)(\mu\text{-}H)$

atom	x	y	z	B_{iso},[b] Å^2
Rh(1)	0.35506 (1)	0.17106 (2)	0.30654 (2)	3.17 (1)
Rh(2)	0.37514 (1)	0.29978 (2)	0.46071 (1)	3.93 (2)
P(1)	0.32026 (3)	0.09256 (7)	0.19855 (7)	3.40 (4)
P(2)	0.39900 (3)	0.10815 (7)	0.23227 (7)	3.54 (5)
P(3)	0.35413 (3)	0.39037 (7)	0.57247 (7)	4.00 (5)
P(4)	0.42846 (3)	0.35218 (8)	0.51510 (7)	3.89 (5)
C(11)	0.2850 (1)	0.0186 (3)	0.2433 (3)	4.5 (2)
C(111)	0.2655 (1)	−0.0397 (3)	0.1638 (4)	5.9 (3)
C(112)	0.2992 (1)	−0.0409 (4)	0.3297 (3)	6.5 (3)
C(12)	0.2960 (1)	0.1596 (3)	0.0982 (3)	4.2 (2)
C(121)	0.3211 (1)	0.2126 (3)	0.0370 (3)	5.3 (2)
C(122)	0.2692 (1)	0.2230 (4)	0.1401 (4)	6.0 (3)
C(13)	0.3458 (1)	0.0104 (3)	0.1274 (3)	4.1 (2)
C(21)	0.4255 (1)	0.0207 (3)	0.3039 (3)	4.6 (2)
C(211)	0.4451 (1)	0.0615 (4)	0.3952 (4)	6.2 (3)
C(212)	0.4028 (1)	−0.0581 (3)	0.3337 (4)	6.3 (3)
C(22)	0.4329 (1)	0.1846 (3)	0.1860 (3)	4.7 (2)
C(221)	0.4599 (1)	0.1375 (4)	0.1257 (4)	7.5 (4)
C(222)	0.4165 (1)	0.2657 (4)	0.1307 (4)	6.4 (3)
C(23)	0.3832 (1)	0.0441 (3)	0.1193 (3)	4.3 (2)
C(31)	0.3353 (1)	0.3401 (3)	0.6835 (3)	5.4 (3)
C(311)	0.3621 (3)	0.2810 (4)	0.7412 (4)	8.4 (4)
C(312)	0.3020 (2)	0.2868 (4)	0.6553 (4)	8.1 (4)
C(32)	0.3189 (1)	0.4703 (3)	0.5274 (3)	5.2 (2)
C(321)	0.3056 (2)	0.5349 (4)	0.6054 (4)	7.6 (4)
C(322)	0.3296 (1)	0.5239 (4)	0.4373 (4)	6.9 (3)
C(33)	0.3886 (1)	0.4670 (3)	0.6295 (3)	4.7 (2)
C(41)	0.4518 (1)	0.4342 (3)	0.4364 (3)	4.9 (3)
C(411)	0.4285 (1)	0.5152 (4)	0.4065 (3)	6.2 (3)
C(412)	0.4648 (2)	0.3874 (4)	0.3462 (4)	8.2 (4)
C(42)	0.4641 (1)	0.2701 (3)	0.5555 (3)	5.2 (3)
C(421)	0.4986 (1)	0.3124 (5)	0.5970 (4)	7.6 (4)
C(422)	0.4504 (1)	0.1998 (4)	0.6257 (4)	6.7 (3)
C(43)	0.4246 (1)	0.4233 (3)	0.6286 (3)	4.9 (2)
C(5A)	0.3258 (1)	0.2728 (4)	0.3898 (4)	4.1 (1)
C(5B)	0.3313 (3)	0.2250 (8)	0.4401 (8)	3.2 (2)
C(6A)	0.3079 (2)	0.1931 (4)	0.4003 (5)	4.8 (1)
C(6B)	0.3058 (3)	0.2362 (8)	0.3686 (8)	3.0 (2)
H(1)	0.392 (1)	0.234 (3)	0.375 (3)	6.0 (1)

[a] See Table D for remaining hydrogen atom coordinates. [b] $B_{iso} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

agreement factors of $R = 0.025$ and $R_w = 0.027$ for 519 variables. The largest shift to error ratio during the final cycle was 0.14 for the y coordinate of C(6A). The final difference map showed no significant residual electron density. Unit weights were deemed adequate on the basis of error analyses which monitored trends in $|F_o|$, $(\sin \theta)/\lambda$, and Miller indices. Atomic scattering factors including anomalous dispersion were taken from ref 16. Final positional parameters and B_{iso} thermal parameters are given in Table II. The computer programs used here are those belonging to "the PDP-8e crystal structure system."[17]

Results and Discussion

Formation of Bridging Alkenyl Hydrides. Binuclear rhodium hydride complexes of the formula $[\{R_2PCH_2CH_2PR_2\}Rh]_2(\mu\text{-}H)_2$ (**1**) are effective catalysts for the hydrogenation and isomerization of simple olefins under one atmosphere pressure of hydrogen.[11,18] In the absence of hydrogen, however, only **1b**, which contains the electron-rich isopropyl substituents, reacts with olefinic substrates directly; **1a**, the related complex which contains isopropoxy substituents, does not interact measurably with simple monoolefins.[11]

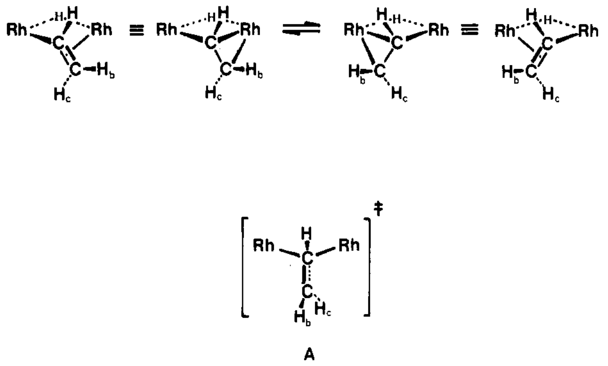
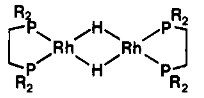
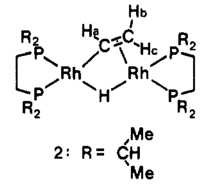


Figure 2. Proposed oscillation of the bridging vinyl ligand to generate equivalent rhodium centers at 25 °C. At lower temperatures (<−30 °C) this process is slow on the NMR time scale.



1a: $R = OCHMe_2$
1b: $R = CHMe_2$

A deep green toluene solution of **1b** reacts rapidly with ethylene (1 atm) even at −20 °C to give a clear orange solution from which **2** can be isolated as orange crystals



in nearly quantitative yield; the only other product formed is ethane (vide infra). Reaction of the deuteride $[(dippe)Rh]_2(\mu\text{-}D)_2$ in C_6D_6 with ethylene generates **2** with no evidence of deuterium incorporation (by ^1H NMR) in the product; $C_2H_4D_2$ was detected[6] in the volatiles (by mass spectrometry). Characteristic of a bridging vinyl ligand in **2** is the especially low-field resonance for H_a in the ^1H NMR at 9.48 ppm. The signal for H_b has additional coupling from two phosphorus nuclei (on the basis of decoupling experiments[19]), presumably those phosphorus donors which are trans to the bridging vinyl moiety. The $^{13}C\{^1H\}$ NMR of **2** at 25 °C (made from $^{13}CH_2{=}^{13}CH_2$, 92.1% ^{13}C enriched) consists of a complex multiplet at 195.6 ppm for the α-carbon σ bonded to rhodium and a doublet at 79.7 ppm ($^1J_{^{13}C,^{13}C} = 36.0$ Hz) for the β-carbon. At lower temperatures both resonances show more coupling; at −30 °C the resonance for the β-carbon is a doublet of doublets ($J = 14.7$ Hz) due to coupling to another nucleus (either ^{103}Rh or ^{31}P) while the α-carbon resonance becomes even more complex. This behavior is indicative of the previously noted[20] fluxional process whereby the vinyl ligand oscillates between the two rhodium centers as shown in Figure 2. The ^1H NMR also shows this temperature dependent behavior in that the vinyl proton resonances and the bridging hydride resonance broaden and become more complex at lower temperature; no changes in chemical shifts are observed upon raising or

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(16) "International Tables for X-Ray Crystallography"; Kynock Press: Birmingham, England, 1974; Vol. IV.

(17) Gabe, E. J.; Larson, A. C.; Lee, F. L.; Wang, Y. "The NRC PDP-8e Crystal Structure System"; Chemistry Division, NRC: Ottawa, Ontario, 1979.

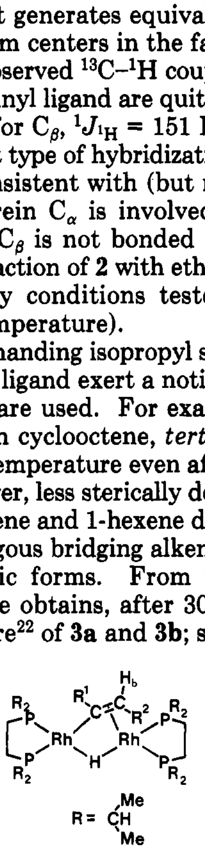
(18) Fryzuk, M. D.; Jones, T.; Einstein, F. W. B., manuscript in preparation.

(19) $^1H\{^{31}P\}$ experiments were performed on a homemade decoupler attached to a Varian XL-100 spectrometer. Due to the limitations of this configuration, full decoupling was not achieved; the resonance for H_b of **2** at 6.37 ppm, with phosphorus decoupled, appeared as a broadened doublet of doublets.

(20) Burch, R. R.; Shusterman, A. J.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 3546.

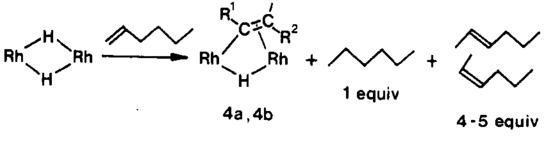
lowering the probe temperature. Whatever mechanism is invoked to rationalize this process, it must be noted that equilibration of the H_b and H_c sites is not occurring; therefore, we favor a symmetrical transition state such as A (Figure 2) since it generates equivalent environments around both rhodium centers in the fast exchange limit. Interestingly, the observed ^{13}C–^1H coupling constants for the carbons of the vinyl ligand are quite different: for C_α, $^1J_{^1H} = 127$ Hz and for C_β, $^1J_{^1H} = 151$ Hz. Normally this suggests[21] a different type of hybridization for each carbon and therefore is consistent with (but not proof of) transition state A wherein C_α is involved in a 3-center–2-electron bond and C_β is not bonded to either rhodium nucleus. Further reaction of 2 with ethylene has not been observed under any conditions tested (i.e., increased pressure and/or temperature).

The sterically demanding isopropyl substituents on the ancillary phosphine ligand exert a noticeable effect when substituted olefins are used. For example, **1b** does not appear to react with cyclooctene, *tert*-butylethylene, or isobutene at room temperature even after extended reaction periods. However, less sterically demanding terminal olefins such as propene and 1-hexene do react slowly with **1b** to give the analogous bridging alkenyl hydrides in two structurally isomeric forms. From the reaction with propene (1 atm) one obtains, after 30 min, an approximately equal mixture[22] of **3a** and **3b**; similarly, **1b** reacts with neat 1-hexene to give **4a** and **4b**, also in a nearly 1:1 ratio. The isomeric structures of these new complexes were determined on the basis of their ^1H NMR as follows: **3a** and **4a** exhibit a downfield doublet (~9.0–9.5 ppm) for R^1 = H with a splitting of 9–10 Hz, typical of a cis vicinal coupling[23] to H_b through the alkenyl fragment; **3b** and **4b** having R^2 = H display broadened singlets at chemical shifts comparable to those observed for H_b and H_c in the parent vinyl complex 2.



3a, R^1 = H, R^2 = CH_3
b, R^1 = CH_3, R^2 = H
4a, R^1 = H, R^2 = C_4H_9
b, R^1 = C_4H_9, R^2 = H
5a, R^1 = H, R^2 = C_3H_7
b, R^1 = C_3H_7, R^2 = H
5c, R^1 = CH_3, R^2 = C_2H_5
d, R^1 = C_2H_5, R^2 = CH_3
6a, R^1 = H, R^2 = C_2H_5
b, R^1 = C_2H_5, R^2 = H
c, R^1 = CH_3, R^2 = CH_3

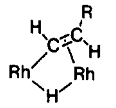
To determine the exact stoichiometry of this reaction type, a known excess of 1-hexene was added to **1b** and the volatiles were analyzed by GC; the results are shown in eq 5. Exactly 1 equiv of hexane is produced along with variable ratios of *cis*- and *trans*-2-hexene (4–5 equiv total). In a separate experiment, a mixture of **4a** and **4b** did not isomerize 1-hexene, thus indicating that the isomerization occurs during the formation of the observed products.

 (5)

4a,4b
4-5 equiv

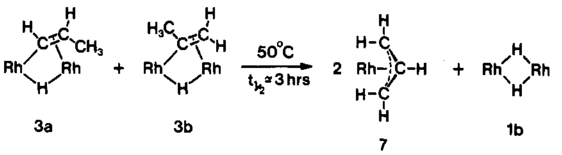
Internal olefins such as *cis*-2-pentene and *trans*-butene do generate similar products, but the reaction times are much longer and other side products are observed. Most notably, the major products derived from the internal olefins are the alkenyl hydrides that would result from the reaction with the corresponding *terminal* olefins. Thus the interaction of **1b** with *cis*-2-pentene generates the structurally isomeric alkenyl hydrides **5a** and **5b**; other products, presumed to be **5c** and/or **5d**, are detected (~10% by ^1H NMR), but their small concentrations have precluded full characterization. *trans*-Butene generates a similar set of derivatives with the bridging alkenyl hydrides **6a** and **6b** as the major products (~60–70% by ^1H NMR; the presence of the 2-butenyl hydride **6c** (<20% by ^1H NMR), which results from the unrearranged internal olefin, is inferred from the similarity of its ^1H NMR spectrum (see Experimental Section) to that of the mixture of isomers **3a** and **3b** which are produced from the reaction of propene with **1b**. The identity of the major products derived from internal olefins is consistent with an initial isomerization of *cis*-2-pentene to 1-pentene and *trans*-butene to 1-butene. This reflects the steric influence of the bulky isopropyl substituents on phosphorus which impedes, to some extent, the formation of the bridging alkenyl hydrides from the internal olefins so that reaction with the terminal olefins is more facile.

One structural isomer, with the rhodium and the substituent trans disposed across the alkenyl fragment (i.e., **3c** or **4c**) is noticeably absent. This can be attributed, once again, to the presence of the bulky isopropyl substituents which might destabilize this particular product or an intermediate in its formation.



	R
3c	CH_3
4c	C_4H_9

Thermal Transformation of Bridging Alkenyl Hydrides. In the reaction of substituted olefins with **1b**, small amounts of other side products are observed (by ^1H NMR analysis of the crude reaction mixture), especially if long reaction times are utilized. We have identified these side products as mononuclear allylrhodium derivatives spectroscopically by comparison to other work from our laboratory.[12] These mononuclear allyl complexes are *not* one of the primary products of the reaction of **1b** with olefins nor are they intermediates in the formation of the bridging alkenyl hydrides. This is evident by the following experiment (eq 6). Heating a C_6D_6 solution of the isomeric propenyl hydrides **3a** and **3b** to ~50 °C in the *absence* of propene leads to the formation of $[(\eta^3\text{-}C_3H_5)Rh(dippe)]$, **7**, and generation of the starting binuclear hydride[21] **1b** (~50% conversion after 3 h); no reaction between propene and **7** is observed. The identity of **7** was checked by its unambiguous synthesis from $[(\eta^3\text{-}C_3H_5)Rh(COD)]$[24] (COD = 1,5-cyclooctadiene) and dippe. Thus the observed formation of **7** during extended reaction times between **1b** and propene is due to the thermal decomposition of **3a** and **3b**; the **1b** so formed is recycled back to **3a** and **3b** by

 (6)

3a 3b 7 1b

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(21) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.

(22) Attempts to separate or enrich either structural isomer **3a** or **3b** by fractional crystallization have not met with success.

(23) Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience: New York, 1972; p 272.

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

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[\{((CH_3)_2CH)_2PCH_2CH_2P(CH(CH_3)_2)_2\}Rh]_2(\mu\text{-}\eta^2\text{-}CH{=}CH_2)(\mu\text{-}H)$

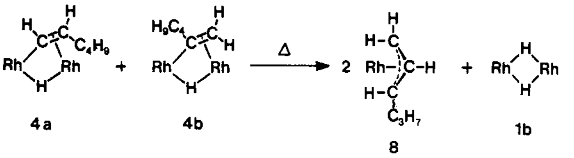
Distances

Rh(1)-H(1)	1.86 (4)	Rh(2)-H(1)	1.66 (4)
Rh(1)-C(5A)	2.210 (6)	Rh(2)-C(5A)	2.091 (6)
Rh(1)-C(5B)	2.216 (11)	Rh(2)-C(5B)	2.004 (11)
Rh(1)-C(6A)	2.295 (6)	Rh(2)-P(3)	2.197 (1)
Rh(1)-C(6B)	2.314 (11)	Rh(2)-P(4)	2.250 (1)
Rh(1)-P(1)	2.220 (1)	P(3)-C(31)	1.855 (4)
Rh(1)-P(2)	2.213 (1)	P(3)-C(32)	1.852 (5)
P(1)-C(11)	1.858 (4)	P(3)-C(33)	1.853 (4)
P(1)-C(12)	1.863 (4)	P(4)-C(41)	1.868 (4)
P(1)-C(13)	1.855 (4)	P(4)-C(42)	1.866 (5)
P(2)-C(21)	1.857 (4)	P(4)-C(43)	1.862 (4)
P(2)-C(22)	1.849 (4)	C(33)-C(43)	1.518 (7)
P(2)-C(23)	1.851 (4)	C(5A)-C(6A)	1.362 (8)
C(13)-C(23)	1.522 (6)	C(5B)-C(6B)	1.33 (2)
Rh(1)-Rh(2)	2.8655 (5)		

Angles

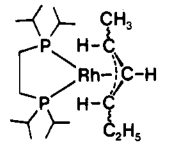
C(5A)-Rh(1)-P(1)	112.2 (2)	C(5A)-Rh(2)-P(3)	93.8 (2)
C(5B)-Rh(1)-P(1)	117.0 (3)	C(5B)-Rh(2)-P(3)	94.6 (3)
C(5A)-Rh(1)-P(2)	159.1 (2)	C(5A)-Rh(2)-P(4)	168.5 (2)
C(5B)-Rh(1)-P(2)	151.8 (3)	C(5B)-Rh(2)-P(4)	163.7 (3)
C(5A)-Rh(1)-C(6A)	35.1 (2)	P(3)-Rh(2)-P(4)	86.44 (4)
C(5B)-Rh(1)-C(6B)	34.1 (4)	P(1)-Rh(1)-P(2)	85.89 (4)
		Rh(1)-H(1)-Rh(2)	109 (2)
		Rh(1)-C(5A)-Rh(2)	83.5 (2)

reaction with the excess propene. The analogous thermal transformation of the hexenyl hydrides **4a** and **4b** is more complicated to analyze, in that isomeric substituted allyl derivatives are formed (eq 7). The major isomeric product



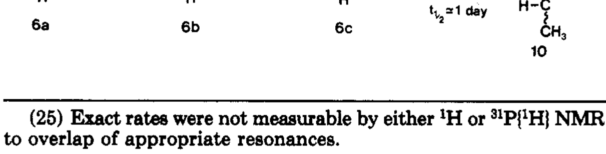
(7)

(60–70%) is the syn isomer of **8** on the basis of ^{1}H and ^{31}P{^{1}H} NMR; characteristic[12] of species such as **8** is the AMX ^{31}P{^{1}H} spectrum, an eight-line pattern, due to the chemically inequivalent phosphorus nuclei coupled to ^{103}Rh. We presume that the anti isomer is also formed in small amounts (<20%) based on the observation of one or more overlapping AMX patterns in the ^{31}P{^{1}H} NMR; isomers such as **9** (syn–anti mixtures) may also be present,



9

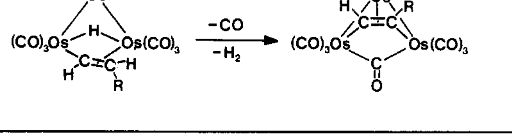
but the complexity of these spectra do not allow unambiguous assignment. A simpler system to analyze is the thermal decompositon of the butenyl hydrides **6a**, **6b**, and **6c**. In the presence of excess *trans*-butene (the rates[25] do not appear to be affected by excess olefin), a syn–anti mixture of [η^3-(1-Me-C_3H_4)Rh(dippe)], **10** (syn:anti ≈ 7:1 as measured by ^{31}P{^{1}H}), is cleanly produced at 30 °C with an approximate $t_{1/2}$ of 1 day (eq 8).



(8)

Monitoring the thermolysis of a particular mixture of alkenyl hydrides by ^{1}H NMR indicates that no isomer is preferentially converted to the corresponding mononuclear allyl product(s), that is, the isomeric alkenyl hydrides decrease in concentration at approximately the same rate.[25]. Either each isomer thermally rearranges to the mononuclear allyl complex(s) at nearly the same rate, or all of the isomers are in equilibrium[22] and the allyl derivative(s) is formed via preferential thermolysis of one isomer; Scheme I illustrates both of these possibilities and includes probable transition states to the observed thermolysis products. Both proposed intermediates (B and C in Scheme I) have precedent in mononuclear chemistry; conversion of a coordinated olefin to an allyl hydride such as B has been observed for the reaction of propene with [Mo(dppe)$_2$(N$_2$)$_2$][26] (dppe = 1,2-bis(diphenylphosphino)ethane) and the reaction of allylbenzene with *trans*-Ir(N$_2$)Cl(PPh$_3$)$_2$, while β-elimination of the 1,1-alkenyl hydride to the allenyl hydride C has been reported[28] for vinyliridium(I) complexes. It should be noted that the identities of B and C and their subsequent decomposition pathways to the allyl derivatives and **1b** can only be speculation at this point.

The thermal transformations of these alkenyl hydrides of rhodium are quite unique. Related osmium clusters thermally rearrange[5,8] by C–H transfer from the vinyl portion of the bridging alkenyl unit without cluster fragmentation (eq 9). Undoubtedly both the presence of an additional metal center and different geometries of the bridging alkenyl ligands can account for this difference in reactivity.



(9)

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(25) Exact rates were not measurable by either ^{1}H or ^{31}P{^{1}H} NMR due to overlap of appropriate resonances.

(26) Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871.

(27) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201.

(28) Schwartz, J.; Hart, D. W.; McGiffert, B. *J. Am. Chem. Soc.* **1974**, *96*, 5613.

(29) Orpen, A. G.; Rivera, A. V.; Brian, E. G.; Pippard, D.; Sheldrick, G. M.; Rouse, K. D. *J. Chem. Soc. Chem. Commun.* **1978**, 723.

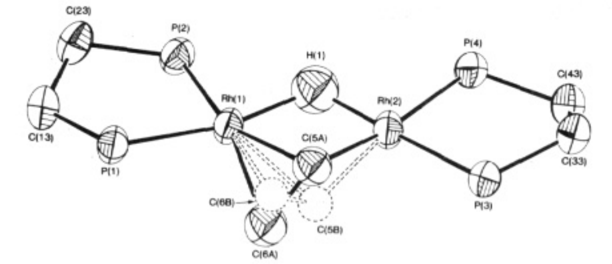
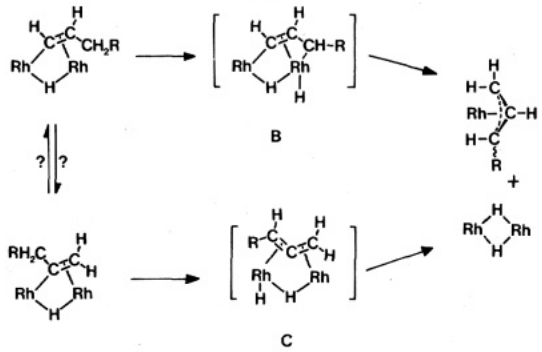


Figure 3. A view depicting the disordered vinyl group of **2** (ORTEP diagram; 50% probability contours for all atoms).

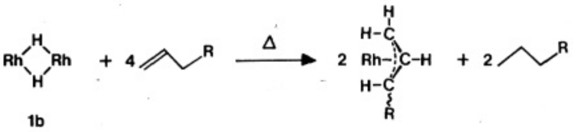
Scheme I



Description of Structure. The structure and numbering scheme of **2** is shown in Figure 1. Selected bond parameters are given in Table III. There are no unusual intermolecular contacts. The bidentate dippe ligands are quite normal in bond lengths and bond angles. The binuclear rhodium core of the molecule, depicting the disordered vinyl group, is shown clearly in Figure 3. The bridging hydride ligand is asymmetrically bound with a Rh(1)–H(1) bond distance of 1.85 (4) Å which is significantly longer than the Rh(2)–H(1) distance of 1.66 (4) Å; this is exactly opposite to that predicted if this molecule was considered, albeit simplistically, as the combination of the two 14-electron fragments [(dippe)RhH] and [(dippe)Rh(η^1-CH=CH$_2$)]. The related derivatives[20] {P(O-*i*-Pr)$_3$}$_4$Rh$_2$(μ-H)(μ-η^2-CR=CHR) (R = Me and *p*-tol) show symmetrical rhodium–hydride bonds. The carbon–carbon bond lengths, 1.362 (8) and 1.33 (2) Å, for the disordered vinyl ligand, appear to be somewhat shorter than the equivalent distance of 1.396 (3) Å found in [Os$_3$H(μ-η^2-CH=CH$_2$)(CO)$_{10}$][29] and the 1.40 (1) Å reported[20] for {P(O-*i*-Pr)$_3$}$_4$Rh$_2$(μ-H)(μ-η^2-CR=CHR) (R = Me and *p*-tol) but, in our opinion, are not significantly different from these literature values. The Rh–P distances of 2.197 (1)–2.250 (1) Å and the P–Rh–P angles of 85.89 (4)–86.44 (4)° lie within ranges consistent with related rhodium bis(phosphine) comlexes.[30] The Rh–Rh separation of 2.8655 (5) Å is comparable to the observed[20] distance of 2.889 (1) Å found for {P(O-*i*-Pr)$_3$}$_4$Rh$_2$(μ-H)(μ-η^2-CMe=CHMe).

Conclusions

We have shown that simple olefins will react with the binuclear rhodium hydride cluster [(dippe)Rh]$_2$(μ-H)$_2$ (**1b**) to generate a series of binuclear alkenyl hydride complexes; most notable is the formation of structural isomers for substituted olefins. These bridging alkenyl hydride clusters cleanly fragment to mononuclear allyl derivatives and the starting hydride **1b** with mild heating. This overall reaction can be represented as a combination of both cluster fragmentation and hydrogen transfer (eq 10)



(10)

whereby 4 equivalents of olefin are transformed by **1b** to 2 equiv each of the corresponding alkane and the allyl derivative. The reaction of other small molecules with this and related electron-rich binuclear rhodium hydrides is a continuing theme in our research effort.

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Registry No. 1b, 87532-56-7; **2**, 87532-57-9; **3a**, 87532-58-9; **3b**, 87532-59-0; **4a**, 87532-60-3; **4b**, 87532-61-4; **5a**, 87532-62-5; **5b**, 87532-63-6; **5c**, 87532-64-7; **5d**, 87532-65-8; **6a**, 87532-66-9; **6b**, 87532-67-0; **6c**, 87532-68-1; ((CH$_3$)$_2$CH)$_2$PCH$_2$CH$_2$P(CH(CH$_3$)$_2$)$_2$, 87532-69-2; Cl$_2$PCH$_2$CH$_2$PCl$_2$, 28240-69-9; (CH$_3$)$_2$CHBr, 75-26-3; η^3-(2-MeC$_3$H$_4$)Rh(COD), 81177-96-0; [(dippe)Rh]$_2$(μ-D)$_2$, 87532-70-5; [(dippe)Rh]$_2$(μ-H)(μ-η^2-^{13}CH=^{13}CH$_2$), 87532-71-6; *syn*-[η^3-(1-Me-C$_3$H$_4$)Rh(dippe)], 87532-72-7; *anti*-[η^3-(1-Me-C$_3$H$_4$)-Rh(dippe)], 87637-45-4; (η^3-C$_3$H$_5$)Rh(COD), 12176-45-3; (η^3-C$_3$H$_5$)Rh(dippe), 87532-73-8; *syn*-[η^3-(1-Pr-C$_3$H$_4$)Rh(dippe)], 87585-09-9; *anti*-[η^3-(1-Pr-C$_3$H$_4$)Rh(dippe)], 87532-74-9.

Supplementary Material Available: Table C, anisotropic thermal parameters, table D, positional and thermal parameters for hydrogen atoms of **2**, table F, additional bond parameters, and Table G, structure factor listings (38 pages). Ordering information is given on any current masthead page.

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