stable, agostic bond-containing clusters are formed when M = Ru and R = Et or $CHPhCH_2Ph$ and when M = Os and R = Me but when M = Ru and R = H, Cl, Br, or Ph or when M = Os and R = H immediate cluster decomposition is observed. Clearly, tautomers having agostic M-H-C interactions may be implicated in many stoichiometric and catalytic reactions of hydrocarbons with polymetallic systems. The fundamental chemistry of such species remains an important area for investigatigation.

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Registry No. $(\mu\text{-H})_3Ru_3(\mu_3\text{-CEt})(CO)_9$, 98799-10-1; $[(\mu\text{-H})_3Ru_3(\mu_3\text{-HCEt})(CO)_9]SO_3CF_3$, 109672-64-2; $(\mu\text{-H})_3Os_3(\mu_3\text{-CMe})(CO)_9$, 51158-87-3; $[(\mu\text{-H})_3Os_3(\mu_3\text{-HCMe})(CO)_9]SO_3CF_3$, 109701-89-5; $[(\mu\text{-H})_3Os_3(\mu_3\text{-HCMe})(CO)_9]SO_3F$, 127972-69-4; $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCHPhCH}_2Ph)(CO)_9$, 86409-47-4; $[(\mu\text{-H})_3Ru_3(\mu_3\text{-HCCHPhCH}_2Ph)(CO)_9]SO_3CF_3$, 127972-67-2; $(\mu\text{-D})_3Ru_3(\mu_3\text{-CCDPhCHDPh})(CO)_9$, 127972-68-3; $H_3Ru_3(CPh)(CO)_9$, 73746-99-3; $(\mu\text{-H})_4Ru_4(CO)_{12}$, 34438-91-0; $(\mu\text{-H})_3Ru_3(\mu_3\text{-CH})(CO)_9$, 63280-43-3; $(\mu\text{-H})_3Ru_3(\mu_3\text{-CCl})(CO)_9$, 73746-97-1; $(\mu\text{-H})_3Ru_3(\mu_3\text{-CBr})(CO)_9$, 73746-95-9; $Ru_3(CO)_{12}$, 15243-33-1; $[HRu(CO)_5]SO_3CF_3$, 127972-70-7; $CH_3CHPhCH_2Ph$, 5814-85-7; CH_3Ph, 108-88-3; $[Ph_3PCH_2Ph]Cl$, 1100-88-5; $[Ph_3PCH_3]Br$, 1779-49-3; acetophenone, 98-86-2; *cis*-1,2-diphenylpropene, 1017-22-7; *trans*-1,2-diphenylpropene, 833-81-8; 2,3-diphenylpropene, 948-97-0; deoxybenzoin, 451-40-1.

Supplementary Material Available: Descriptions of syntheses and listings of ^1H and ^{13}C NMR data for 1,2-diphenylpropane, 1,2-diphenylpropene, and 2,3-diphenylpropene standards used for comparison with products of decomposition of $[(\mu\text{-H})_3Ru_3(\mu_3\text{-}\eta^2\text{-HCCHPhCH}_2Ph)(CO)_9]^+$ (3 pages). Ordering information is given on any current masthead page.

Metallacarboranes in Catalysis. 9. Catalytic Hydrosilanolysis of Alkenyl Acetates by Triethylsilane

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Reaction of an alkenyl acetate, $[CH_3CO_2CR{=}CH_2]$ (R = CH_3, C_6H_5), with triethylsilane in the presence of either the *closo*-rhodacarborane [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (I) or the *exo-nido*-rhodacarborane [*exo-nido*-$(PPh_3)_2$Rh-7,8-$(\mu\text{-}(CH_2)_3)$-7,8-$C_2B_9H_{10}$] (II) as catalyst precursors in CH_2Cl_2 at 40 °C for 42 h yielded triethylsilyl acetate and the alkene derived from the alkenyl acetate rather than the hydrosilylation product. The closo complex I was shown to be a superior catalyst precursor, giving over 80 turnovers, which corresponds to 80% conversion of alkenyl acetate to trialkylsilyl acetate under experimental conditions. The exo-nido complex II, however, showed limited catalytic activity and formed the closo bidentate acetato complex [*closo*-3-(PPh_3)-3,3-$(\eta^2\text{-}CH_3CO_2)$-1,2-$(\mu\text{-}(CH_2)_3)$-3,1,2-$RhC_2B_9H_9$] (III) as a detectable reaction intermediate. Under mild conditions, tris(triphenylphosphine)chlororhodium, $[(PPh_3)_3RhCl]$ (IV), was found to catalyze the hydrosilanolysis as well as the hydrosilylation of isopropenyl acetate. However, hydrosilanolysis predominated over hydrosilylation in a ratio of 20:1. Reaction of III with triethylsilane gave triethylsilyl acetate and the *exo-nido*-rhodacarborane II in the presence of triphenylphosphine. The mechanisms of the hydrosilanolysis and related reactions of alkenyl acetates are discussed.

Introduction

The *closo*-rhodacarborane [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (I)[1] and the *exo-nido*-rhodacarborane [*exo-nido*-$(PPh_3)_2$Rh-7,8-$(\mu\text{-}(CH_2)_3)$-7,8-$C_2B_9H_{10}$] (II)[2] have been shown to be effective alkene hydrogenation and isomerization catalysts, and detailed kinetic and mechanistic studies of these systems have been presented.[3] During the course of our investigation of the further potential of rhodacarboranes in catalytic processes, it was discovered that when alkenyl acetates were employed as substrates for catalytic hydrogenation, the expected saturated esters were not obtained. Instead, quantitative hydrogenolysis of the ester C-O bond occurred to produce acetic acid and alkene.[4] The mechanism of these catalytic hydrogenolyses has been examined in detail.[3c] The cleavage of C-O bonds of alkenyl acetates such as vinyl acetate and allyl acetate, which was promoted by transition-metal complexes, has been previously reported in the literature. Zerovalent Mo,[5] Ni,[6] and Pd[7] complexes afforded the corresponding (η^3-

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Table I. Hydrosilanolysis of Alkenyl Acetates with Triethylsilane by Use of Rhodacarboranes in CH_2Cl_2 at 40 °C

catalyst precursor	[precursor], M	alkenyl acetate	10[acetate], M	10[silane], M	time	% yield[a]	turnovers of Rh[b]
I	9.6×10^{-3}	isopropenyl acetate	9.6	9.6	6 h	13	13
					12 h	33	33
					24 h	60	60
					42 h	81	81
					2 d	86	86
					3 d	95	95
					5 d	96	96
I	4.8×10^{-3}	isopropenyl acetate	9.6	9.6	42 h	58	116[c]
I	2.4×10^{-3}	isopropenyl acetate	9.6	9.6	42 h	32	128[d]
I[e]	9.6×10^{-3}	isopropenyl acetate	9.6	9.6	4 h	96	96
I	2.0×10^{-2}	1-phenylvinyl acetate	7.5	7.5	24 h	19	7[f]
					3d	42	16[f]
II	9.6×10^{-3}	isopropenyl acetate	9.6	9.6	42 h	17	17
					5 d	22	22
II[e]	9.6×10^{-3}	isopropenyl acetate	9.6	9.6	4 h	67	67
I-*3-d*	9.6×10^{-3}	isopropenyl acetate	9.6	9.6	42 h	82	82

[a] Yield of trialkylsilyl acetate based on alkenyl acetate; determined by quantitative GC. [b] 100% yield corresponds to 100 turnovers unless otherwise noted. [c] 100% yield corresponds to 200 turnovers. [d] 100% yield corresponds to 400 turnovers. [e] Sample sealed under vacuum kept in an oil bath at 80 °C. [f] Measured by ^1H NMR spectroscopy; 100% yield corresponds to 50 turnovers.

allyl)(acetato)metal species in reactions with allyl acetate. Low-valent hydrido complexes of late transition metals[8] (Fe, Co, Ru, Rh, and Pd) reacted with alkenyl acetates, to produce free alkene and metal acetates as a consequence of hydride transfer followed by the scission of the intermediate. In all of these cases, metal complexes were employed as one of the reactants and were converted to acetato complexes in stoichiometric reactions. However, in the facile catalytic hydrogenolyses of alkenyl acetates,[3c,4] rhodacarboranes I and II were employed as catalyst precursors and recovered unchanged.

As part of our ongoing effort to enhance the utility of rhodacarborane catalysts, we became interested in examining trialkylsilanes as substitutes for H_2 in catalytic reactions with alkenyl acetates similar to those described above. In reactions involving alkenes, rhodium complexes have long been known to function as effective hydrosilylation catalysts.[9] In a different vein, Lappert et al.[10] reported that hydrosilylanolysis, resulting in triethylsilyl acetate and propene, occurred when allyl acetate reacted with triethylsilane in the presence of catalytic amounts of rhodium(3+) acetylacetonate. However, when isopropenyl acetate was treated with triethylsilane in the presence of the same catalyst, no reaction occurred.[10] In contrast, we have observed that rhodacarboranes I and II and tris(triphenylphosphine)chlororhodium(1+) (IV)[11] catalyze the hydrosilanolyses of alkenyl acetates by triethylsilane as shown in eq 1. Here we report a detailed investigation

$$CH_2{=}C(R)OCCH_3 + R'_3SiH \xrightarrow{\text{catalyst}} CH_2{=}CHR + R'_3SiOCCH_3 \quad (1)$$

$R = CH_3, C_6H_5 \quad R' = C_2H_5$

of selected examples of this novel catalytic process involving the rhodacarboranes I and II and Wilkinson's catalyst, IV.

Results

General Experimental Considerations. The hydrosilanolysis reactions were carried out with use of alkenyl acetates, triethylsilane, and rhodacarboranes at initial concentrations of 9.6×10^{-1}, 9.6×10^{-1}, and 9.6×10^{-3} M (100:100:1), respectively, in degassed CH_2Cl_2 at 40 °C, as listed in Table I. The reactions were monitored by 200.133-MHz ^1H FT NMR spectroscopy. New peaks were observed due to the formation of propene (1.72 ppm, doublet of triplets; 5.0, 5.8 ppm, ABX type) or styrene (5.1, 5.6, 6.6 ppm, ABX type) and the acetate group of trialkylsilyl acetate (2.03 ppm, singlet) as reactions proceeded. A change in chemical shift of the methylene protons of the triethylsilyl moiety (0.2 ppm downfield) due to conversion of triethylsilane to triethylsilyl acetate was observed. All products were confirmed by GC–mass spectral analysis. The rate of decrease in the integration ratios of peaks assigned to the vinyl protons and methyl protons of alkenyl acetate was also used for the estimation of reaction rates in small-scale NMR experiments. The yield of triethylsilyl acetate was calculated from the area ratio of triethylsilyl acetate to that of the unreacted alkenyl acetate in GC with use of predetermined response factors for triethylsilyl acetate and alkenyl acetate. Although true rate measurements were not carried out, product yields can be considered to approximate reaction rates when reactions are compared under identical conditions. The experimental results of the alkenyl acetate hydrosilanolysis reactions are summarized in Table I.

Hydrosilanolysis of Alkenyl Acetates with Rhodacarborane I as a Catalyst Precursor. From Table I it is evident that the yield of products increased with increasing duration of the hydrosilanolyses catalyzed by I. Reaction of isopropenyl acetate with triethylsilane was essentially complete after 3 days at 40 °C in CH_2Cl_2 when the substrate was employed in a 100-fold excess relative to the catalyst. With 1-phenylvinyl acetate as the substrate at an initial concentration of 7.5×10^{-1} M and with 2.0×10^{-2} M I, the hydrosilanolysis occurred more slowly than in the case of isopropenyl acetate. Presumably, the greater steric requirements of the substrate lead to a reduced hydrosilanolysis rate. When the deuterated analogue of I [*closo*-3,3-$(PPh_3)_2$-3-D-3,1,2-$RhC_2B_9H_{11}$] (I-*3-d*)[1c,3c,12] was

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employed in the catalytic hydrosilanolysis of isopropenyl acetate, the catalyst recovered after 40 turnovers retained 85% of the Rh–D label as shown by the ^1H FT NMR spectrum of the reaction mixture.[13] When smaller amounts of I were employed under the same reaction conditions, lower conversions, but more rhodium turnovers, were observed. The absence of a radical mechanism was substantiated by the fact that when the rhodacarborane-catalyzed hydrosilanolysis of isopropenyl acetate was carried out under identical conditions in the presence of galvinoxyl radical (2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy) as a radical scavenger, no reduction in the yield of the product was observed.[9c] As expected, an acceleration in the reaction rate and essentially complete reaction was observed after 4 h when hydrosilanolysis was carried out at 80 °C in a system sealed under vacuum.

When triphenylphosphine was added to the reaction mixture with I, a marked decrease in the reaction rate roughly proportional to the concentration of added triphenylphosphine was observed. For example, addition of triphenylphosphine at initial concentrations of 9.6×10^{-3}, 3.8×10^{-2}, and 9.6×10^{-2} M to reaction mixtures consisting of isopropenyl acetate (9.6×10^{-1} M), triethylsilane (9.6×10^{-1} M), and I (9.6×10^{-3} M) in CH_2Cl_2 led to the formation of triethylsilyl acetate in a decreasing yield of 11, 4.4, and 1.2%, respectively, after 42 h at 40 °C. A similar effect caused by the addition of triphenylphosphine was previously observed in the hydrogenation of olefins catalyzed by I.[3]

The course of selected reactions was further monitored by 81.02-MHz $^{31}P\{^1H\}$ FT NMR spectroscopy.[14] During triethylsilanolysis of isopropenyl acetate and up to 2 weeks thereafter at 40 °C, only a sharp resonance assigned to I at 39.5 ppm (doublet, $J_{Rh-P} = 125$ Hz) was observed when I was employed as the catalyst precursor. After 81 turnovers, the catalyst precursor I was recovered in 81% yield. Although no intermediates were detected by NMR spectroscopy during the course of the reaction, it is obvious that reactive intermediates are present in concentrations too low to be observed spectroscopically.

Hydrosilanolysis of Isopropenyl Acetate with Rhodacarborane II as a Catalyst Precursor. The rate of hydrosilanolysis of isopropenyl acetate with triethylsilane catalyzed by II at initial concentrations of 9.6×10^{-1}, 9.6×10^{-1}, and 9.6×10^{-3} M, respectively, in CH_2Cl_2 at 40 °C was considerably slower than that of the corresponding reaction which employed precursor I.

The progress of the reaction of isopropenyl acetate with triethylsilane in the presence of II was followed by NMR spectroscopy. When 9.6×10^{-3} M II was employed in the hydrosilanolysis of isopropenyl acetate (9.6×10^{-1} M) with triethylsilane (9.6×10^{-1} M) in CH_2Cl_2 at 40 °C, two new resonances were observed in the $^{31}P\{^1H\}$ FT NMR spectrum after 3 h of reaction. One is a singlet at −6.0 ppm due to free triphenylphosphine, and the other resonance is a doublet at 37.4 ppm ($J_{Rh-P} = 168.6$ Hz). These new resonances disappeared after 2 days of reaction, and thereafter only the resonance assigned to II was detected.

Table II. Hydrosilanolysis of Isopropenyl Acetate (9.6×10^{-1} M) with Triethylsilane (9.6×10^{-1} M) by Use of Rhodium Complexes (9.8×10^{-3} M) in CH_2Cl_2 at 40 °C and Effects of Added Triphenylphosphine (9.8×10^{-2} M) on the Reaction Rate

catalyst precursor	time	% yield[a]	turnovers of Rh[b]	% yield of hydrosilylated product
$[(PPh_3)_3RhCl]$ (IV)	12 h	9.6	9	
	24 h	25.0	24	1.2
	42 h	38.0	37	1.9
	3 d	71.0	69	4.3
	4 h[c]	77.0	75	5.3
$Rh(acac)_3$[d]	42 h	0.0	0	
$[(PPh_3)_3RhCl]$ (IV) with 9.8×10^{-2} M PPh_3	42 h	7.5	7	
	4 h[c]	34.0	33	1.6

[a] Yield of triethylsilyl acetate based on isopropenyl acetate by GC. [b] 100% yield corresponds to 98 turnovers. [c] Reaction at 80 °C. [d] acac = acetylacetonate.

Species II was isolated in 69% yield in similar experiments. The doublet at 37.4 ppm was identified as arising from the novel closo bidentate acetato complex III. After 1 day of reaction, when the intensity of the new doublet had reached a maximum, measurement of the integrals for the ^{31}P resonances of II and III revealed that III was present at a concentration approximately equal to that of II. Complex III was independently prepared from the reaction of II with isopropenyl acetate over a period of 3 days at 25 °C and characterized by spectroscopic data and elemental analyses. In the 200.133-MHz ^1H FT NMR spectrum of III in CD_2Cl_2 measured at 25 °C, resonances attributable to the protons of the phenyl groups and μ-trimethylene groups as well as a sharp singlet at 1.11 ppm due to the methyl protons in the acetate group were observed. The $^{11}B\{^1H\}$ FT NMR spectrum exhibited six resonances with an area ratio of 1:1:2:2:2:1, indicating the presence of a closo-carborane cage containing nine boron atoms in a symmetric environment. The infrared spectrum of III displayed a carbonyl stretching band at 1647 cm^{-1}, indicating the presence of a bidentate acetate ligand, since the carbonyl stretching bands in the monodentate acetoxyrhodacarboranes have been observed at higher frequencies (~1650 cm^{-1}).[4b] Further, the elemental analysis of III confirmed its identity as [*closo*-3-(PPh_3)-3,3-$(\eta^2$-$CH_3CO_2)$-1,2-$(\mu$-$(CH_2)_3)$-3,1,2-$RhC_2B_9H_9$].

Complex III was found to regenerate complex II and form triethylsilyl acetate in its reaction with triethylsilane in the presence of triphenylphosphine. The pathway for the reaction of this acetato complex with triethylsilane and its possible relevance to the hydrosilanolysis cycle will be discussed below.

Reaction of Isopropenyl Acetate and Triethylsilane with Tris(triphenylphosphine)chlororhodium as a Catalyst Precursor. During the course of the investigation of hydrosilanolysis catalyzed by rhodacarboranes, we compared the catalytic activity of the rhodacarboranes I and II with that of other simple rhodium species which were well-known as catalysts. Tris(triphenylphosphine)-chlororhodium (IV) has been commonly employed in the catalysis of a variety of reactions,[9-11] and its catalysis of alkene hydrosilylation with trialkylsilanes has been well documented.[9d] Although this catalyst has been employed in the cleavage of benzyl esters,[16] its use as a catalyst for the hydrosilanolysis of alkenyl acetates is without precedent.

Treatment of isopropenyl acetate (9.6×10^{-1} M) with trialkylsilane (9.6×10^{-1} M) in the presence of IV ($9.8 \times$

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(13) Percent Rh–H (and percent Rh–D by difference) was determined by integrating the hydride resonance (−8.4 ppm) vs the phenyl resonances (7.27 ppm) in the 200-MHz ^1H FT NMR spectrum in CD_2Cl_2.

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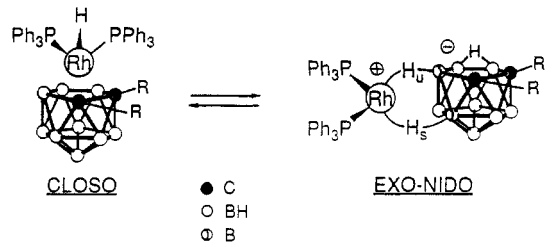
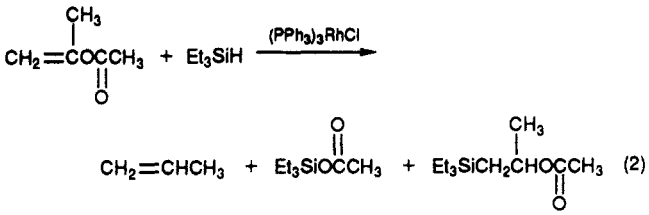


Figure 1. Proposed scheme for rapid closo/exo-nido tautomerism. The equilibrium lies far to the left when R = H and far to the right when R-R = $-(CH_2)_3-$ and PPh_3 ligands are attached to rhodium.

10^{-3} M) in CH_2Cl_2 at 40 °C led to the hydrosilanolysis of the substrate (Table II). However, unlike the reaction with rhodacarboranes I and II, the hydrosilylation product was also obtained in low yield, as shown in eq 2. The



hydrosilylated material was found to be a β-adduct[9c] from the analysis of the GC–mass spectrum. Though the product yield increased with reaction time, the rate of hydrosilanolysis was slower than that observed in the case of I and somewhat faster than that observed in the case of II. As shown in Table II, the addition of triphenylphosphine to the system caused a decrease in the reaction rate similar to that observed with I under similar conditions.

The oxidative addition of the Si–H bond of triethylsilane to the rhodium in IV is believed to be the initial step in this reaction.[17] Within 2 h after the initiation of the reaction, two new sharp resonances were observed in the $^{31}P\{^1H\}$ FT NMR spectrum. One was a singlet at −6.0 ppm due to free triphenylphosphine, and the other resonance was a doublet at 38.7 ppm (J_{Rh-P} = 127.9 Hz) assigned to $[(Ph_3P)_2RhH(SiEt_3)Cl]$ (V).[18] Since the silyl complex is unstable with respect to the reductive elimination of the silane, this complex is only observed in the presence of the latter reagent. As triethylsilane was consumed in this hydrosilanolysis reaction, the silyl complex was found to regenerate IV as shown in the $^{31}P\{^1H\}$ FT NMR spectrum of the reaction mixture.[19]

On the basis of the data presented thus far and the previously reported information regarding the mechanisms of alkene hydrogenation and isomerization involving I and II,[1-3] it is possible to propose pathways for the hydrosilanolysis of alkenyl acetates brought about by these rhodacarborane precursors. Possible mechanisms for the reaction of acetoxyrhodacarborane III with trialkylsilanes can be inferred, as can the approximate role of Wilkinson's catalyst, IV, in the competing hydrosilanolysis and hydrosilylation reactions of alkenyl acetates.

Discussion

Mechanism of Alkenyl Acetate Hydrosilanolysis with Catalyst Precursor I. The reversible formation of a catalytically active exo-nido species in solution and the associated existence of rapid closo/exo-nido tautomerism (Figure 1)[2,3] were demonstrated to be essential in both the alkene hydrogenation and isomerization reactions involving I.[3] This exo-nido species was also shown to be the reactive intermediate necessary for carborane ligand-exchange reactions.[1b,20,21] Very recent work[3c] has more clearly defined the mechanisms of alkene isomerization and hydrogenation catalyzed by *closo*- and *exo-nido*-rhodacarboranes. Thus, the exo-nido tautomers of the rhodacarboranes serve as precursors that supply the catalytically active B–Rh–H intermediates formed by reversible and regiospecific oxidative addition of their Rh^+ centers to terminal B–H bonds. The fact that the deuterated analogue of I [*closo*-3,3-$(PPh_3)_2$-3-D-3,1,2-$RhC_2B_9H_{11}$] (I-*3-d*) retained 85% of the Rh–D label after 40 turnovers in the catalytic hydrosilanolysis of isopropenyl acetate is in agreement with this scheme. It should be noted that 1 turnover would remove the deuterium label if isopropenyl acetate were cleaved by the closo tautomer of I to give propene and the *closo*-acetoxyrhodacarborane which subsequently reacted with the silane. Consequently, closo/exo-nido tautomerism initiates the hydrosilanolysis cycle, which may proceed as outlined in Figure 2 by involving B–Rh–H catalytic centers as in **2**.[3c]

The experimental data indicate that the rate of hydrosilanolysis has an inverse dependence upon added triphenylphosphine concentration. This is in agreement with earlier work,[3] and we suggest that *closo*- and *exo-nido*-rhodacarboranes undergo rapid and reversible replacement of one triphenylphosphine ligand by the substrate, forming **1**. As previously suggested,[2,3] Rh^{3+} closo and Rh^+ exo-nido substrate PPh_3 complexes may be directly interconverted by closo/exo-nido tautomerization as in the case of the bis(triphenylphosphine) precursors.[3c] As shown in Figure 2, the proposed catalytic cycle proceeds through a series of rapid steps beginning with the B–Rh–H species **2**, previously established as a constituent of corresponding hydrogenolysis reactions.[3c] Formation and decomposition of **3**, as shown, forms propene and the reactive species **4**. Metathesis of **4** with Si–H in triethylsilane would rapidly form triethylsilylacetate and the hydride species **5**, which initiates a new catalytic cycle.

Mechanism of Alkenyl Acetate Hydrosilanolysis Catalyzed by II and the Reaction of the Intermediate III with Triethylsilane. An entirely analogous B–Rh–H pathway is amenable to the rhodacarborane precursor II in its catalysis of the hydrosilanolysis process. However, this process alone cannot account for the initial accumulation of large amounts of the intermediate III followed by its slow conversion to products. Therefore, it is necessary to consider the closo pathway depicted in Figure 3 as the principal reaction sequence or as an important side reaction. The catalytic cycle initiated by the dissociation of triphenylphosphine and coordination of the alkene substrate leads to the formation of the exo-nido species **6**, which can be converted to species **7** via closo/exo-nido tautomerization. Insertion of the alkene into the rhodium–hydrogen bond is accompanied by chelation of the carbonyl oxygen to complete the metal coordination sphere, affording **8**. The C–O bond scission[5-8] in the system **8** occurs through the intermediacy of a cyclic six-membered intermediate or transition state. An alternative mode for the insertion of the alkene into the Rh–H bond

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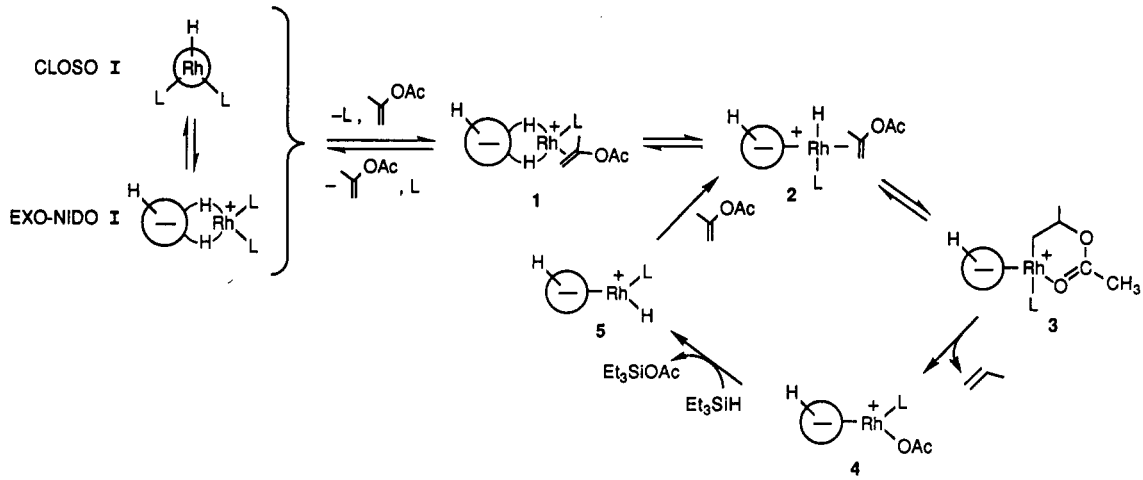

Figure 2. Proposed catalytic pathway for the hydrosilanolysis of isopropenyl acetate with the catalyst precursor I.

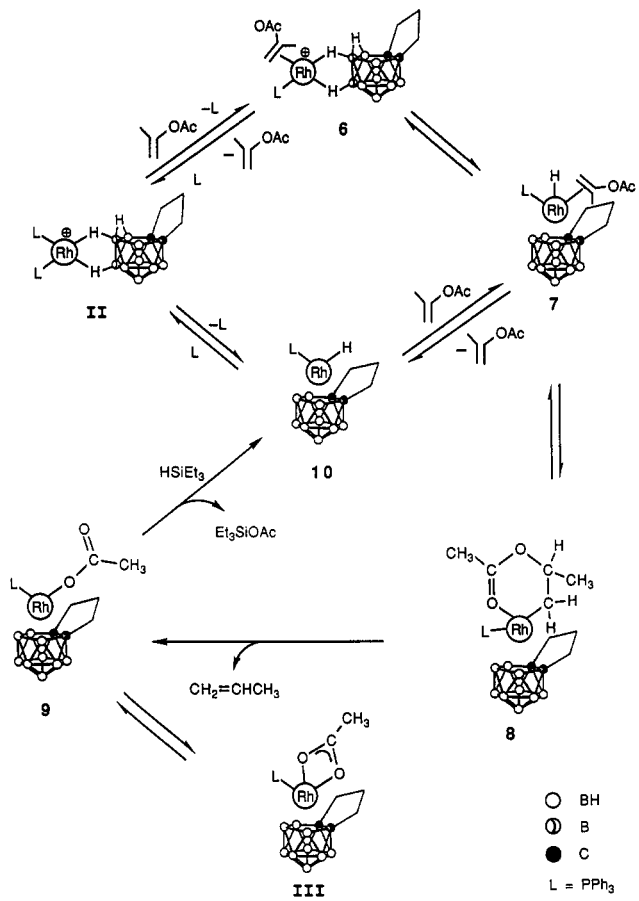

Figure 3. Proposed pathway for the formation and further reaction of III.

and subsequent chelation of the carbonyl oxygen to the metal would result in the formation of a cyclic five-membered species wherein the α-carbon of the substrate is bonded to rhodium. However, formation of this sort of species is unlikely, since such an intermediate has no accessible concerted cleavage process and would be expected to be sufficiently stable to allow observation.[22] After the loss of propene, the resulting closo monodentate acetato complex **9** (16e species) rapidly forms the more stable closo bidentate acetato complex III.

The reaction of the monodentate acetoxyrhodacarborane **9**, derived from III, with triethylsilane may involve hete-

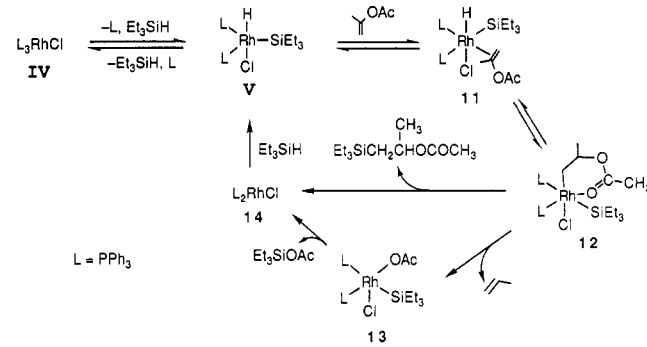

Figure 4. Proposed catalytic pathway for the hydrosilanolysis of isopropenyl acetate with IV as a catalyst precursor.

rolytic cleavage of the Si–H bond as suggested above. The heterolytic cleavage is considered to be more favorable than the oxidative addition of the silane to the rhodium center of the monodentate acetoxyrhodacarborane intermediate, since oxidative addition of silane requires the generation of a formal rhodium(+5) intermediate.[23,24]

Following the formation of the triethylsilyl acetate by this process, the probable coordinatively unsaturated intermediate [*closo*-3-(PPh_3)-3-H-1,2-(μ-$(CH_2)_3$)-3,1,2-$RhC_2B_9H_9$] (**10**) can react with triphenylphosphine to regenerate II or with isopropenyl acetate to produce intermediate **7**.

Proposed Mechanism of Hydrosilanolysis of Isopropenyl Acetate Involving IV as a Catalyst Precursor. Figure 4 depicts one set of proposed mechanisms for the hydrosilanolysis and the hydrosilylation of isopropenyl acetate catalyzed by IV. The spectroscopically observable trigonal-bipyramidal complex [$(PPh_3)_2RhH(SiEt_3)Cl$] (V),[18] formed via the oxidative addition of triethylsilane to IV in the initial step,[17] activates the alkenyl acetate substrate to produce the octahedral species **11**. Insertion of alkene into the rhodium–hydrogen bond accompanied by chelation of the carbonyl oxygen to the rhodium metal would produce a cyclic six-membered intermediate or transition state **12**, from which propene can be formed through C–O bond scission,[5-8] to be followed

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by the reductive elimination of triethylsilyl acetate from **13**. The direct reductive elimination of the silyl and alkyl groups derived from the substrate from **12** would yield the hydrosilylated product. Both of these processes would result in the production of the coordinately unsaturated trigonal intermediate $[(PPh_3)_2RhCl]$ (**14**),[9d] which can oxidatively add triethylsilane to continue the catalytic cycle.

Experimental Section

General Comments. All reactions were carried out in dry Schlenk equipment under an atmosphere of dry argon, with use of standard techniques.[25] Specially designed reactors with Teflon valves and ball joints were used to facilitate the degassing process before reaction and separation of liquid for gas chromatographic analysis after reaction. Benzene, heptane, pentane, and dichloromethane were purified according to literature methods,[26] distilled under argon, and argon-purged immediately prior to use. Isopropenyl acetate was distilled over CaH_2 before use. 1-Phenylvinyl acetate and triethylsilane were distilled prior to use. Triphenylphosphine was recrystallized twice from absolute ethyl alcohol. Compounds I,[2c] II,[2a] I-3-*d*,[1c,12] and IV[27] were prepared according to published methods. The ^1H and $^{31}P\{^1H\}$ FT NMR spectra were obtained with a Bruker WP-200 FT NMR spectrometer at 200.133 and 81.02 MHz, respectively. Proton chemical shifts were referenced to residual protons in the solvent (CD_2Cl_2, 5.32 ppm; C_6D_6, 7.15 ppm; both vs Me_4Si). Phosphorus chemical shifts were referenced to external 85% H_3PO_4 with downfield shifts taken as positive.[28] The 160.463-MHz ^{11}B FT NMR spectra were obtained by using a Bruker AM-500 spectrometer. Boron chemical shifts were referenced to external $BF_3{\cdot}OEt_2$ with downfield shifts taken as positive. Infrared spectra were obtained as Nujol mulls with a Beckman Model FT 1100 FT-IR spectrometer GC–mass spectral analyses were performed with a Kratos Model MS 25 instrument. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5880A instrument equipped with a 40-m SE-30 capillary column and a flame ionization detector.

Hydrosilanolysis of Isopropenyl Acetate with I and II. General Procedure. A Teflon-valve reactor was charged with either the *closo*-rhodacarborane I (49.0 mg, 0.0645 mmol) or the *exo-nido*-rhodacarborane II (51.6 mg, 0.0645 mmol) and 5 mL of dichloromethane. Triethylsilane (1.03 mL, 6.45 mmol) and 0.71 mL of isopropenyl acetate (6.45 mmol) were introduced through a rubber septum by syringe. The mixture was degassed with three freeze–pump–thaw cycles. The reactor was then placed in a 40 °C oil bath and heated for 42 h. After reaction, the volatile components of the reaction mixture were separated by vacuum distillation. The distillate was analyzed by GC (Table I). In the case of I, the yellow residue was washed with pentane and dried. ^1H and $^{31}P\{^1H\}$ FT NMR spectra showed that this residue was rhodacarborane I. Species I (39.7 mg) was recovered (81%). In the case of II, the red residue was treated similarly to recover 35.6 mg of the catalyst (69%). Propene and triethylsilyl acetate were detected by ^1H FT NMR spectroscopy and GC. The yield of triethylsilyl acetate was determined with use of GC.

For high-temperature experiments, the reaction vessel was placed in an 80 °C oil bath. The relevant reaction conditions are given in Table I.

Hydrosilanolysis of Isopropenyl Acetate with [*closo*-3,3-$(PPh_3)_2$-3-D-3,1,2-$RhC_2B_9H_{11}$] (I-3-*d*). Using the method described above, 49.1 mg (0.0645 mmol) of I-3-d was employed in the reaction of isopropenyl acetate with triethylsilane. After the reaction, the volatile components were analyzed by GC and the yellow residue was dissolved in CD_2Cl_2 and analyzed by ^1H FT NMR for deuterium content.

Hydrosilanolysis of Isopropenyl Acetate with IV. Using the method described above, 60.8 mg (0.0657 mmol) of IV was employed in the reaction of isopropenyl acetate with triethylsilane. The products were analyzed by GC–Mass spectra. Table 2 lists the pertinent reaction conditions.

Preparation of [*closo*-3-(PPh_3)-3-$(\eta^2$-$CH_3CO_2)$-1,2-$(\mu$-$(CH_2)_3)$-3,1,2-$RhC_2B_9H_9$] (III). A 100-mL flask equipped with a magnetic stir bar was charged with II (0.30 g, 0.377 mmol), 4.2 mL of isopropenyl acetate (38.2 mmol), and 20 mL of benzene. The mixture was stirred under argon at 25 °C for 3 days. The color of the mixture changed from red to pale reddish brown. The mixture was filtered with a cannula filter. The filtrate was reduced in volume, and heptane was added. The mixture was reduced in volume again until a solid was formed on the surface and then placed in the refrigerator overnight. Both a white solid and a red solid were formed. The red solid was isolated by washing away the white solid with pentane and then recrystallized from benzene/heptane and dichloromethane/heptane to give III (0.095 g, 0.16 mmol, 42% yield). IR: 3057 (m), 2560 (s), 1516 (m), 1437 (s), 1190 (w), 1094 (m), 1075 (w), 1004 (w), 750 (m), 690 (m) cm^{-1}. ^1H NMR (ppm, CD_2Cl_2, 298 K): 7.5–7.7 (envelope, 6 H), 7.3–7.5 (envelope, 9 H), 3.16 (br qrt, 2 H, $-CH_2-$), 2.3–2.6 (envelope, 4 H, $-CH_2-$), 1.11 (sh s, 3 H, CH_3CO_2). $^{31}P\{^1H\}$ NMR (ppm, 10% CD_2Cl_2/90% CH_2Cl_2, 298 K): 37.4 (d, J_{Rh-P} = 168.6 Hz). $^{11}B\{^1H\}$ NMR (ppm, CH_2Cl_2, 298 K): 10.3, 8.7, −4.1, −8.4, −9.8, −15.8 (1:1:2:2:2:1). Anal. Calcd for $C_{25}H_{33}B_9PRhO_2$: C, 50.32; H, 5.57; B, 16.31; P, 5.19; Rh, 17.25. Found: C, 51.04; H, 5.72; B, 16.88; P, 4.93; Rh, 16.17.

Reaction of Acetoxyrhodacarborane III with Triethylsilane. All reactions were performed in 10- or 5-mm NMR tubes attached to glass joints. Acetoxyrhodacarborane, triphenylphosphine, and triethylsilane were charged in NMR tubes in a molar ratio of 1:1:100. After NMR solvents were added, CD_2Cl_2 for ^1H FT NMR spectra and 10% CD_2Cl_2/90% CH_2Cl_2 for ^{31}P FT NMR spectra via vacuum transfer, the mixtures were degassed with three freeze–pump–thaw cycles under high vacuum and sealed in vacuo. Only compound II was observed in the $^{31}P\{^1H\}$ FT NMR spectrum of these reaction mixtures after 1 day at 40 °C ($^{31}P\{^1H\}$ NMR: d, 44.4 ppm, J_{Rh-P} = 186.0 Hz).

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Registry No. I, 53687-46-0; I-3-*d*, 82808-04-6; II, 127916-00-1; III, 127943-61-7; IV, 14694-95-2; $Rh(acac)_3$, 14284-92-5; $Et_3SiCH_2CH(CH_3)OC(O)CH_3$, 34291-82-2; isopropenyl acetate, 108-22-5; 1-phenylvinyl acetate, 2206-94-2; propene, 115-07-1; triethylsilyl acetate, 5290-29-9; styrene, 100-42-5.

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