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REACTIONS AT THE RHODIUM VERTEX OF ISOMERIC *closo*-BIS(TRIPHENYLPHOSPHINE)HYDRIDORHODACARBORANES, ALKENYL ACETATE CLEAVAGE AND SUBSEQUENT REACTIONS *

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Summary

The isomeric hydridophosphinorhodacarboranerhodium(III) clusters, [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1a**); [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (**1b**); and [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$] (**1c**) react with isopropenyl acetate and vinyl acetate under mild conditions to give ester C–O bond scission, expulsion of alkene, and formation of bidentate or monodentate acetate complexes of the form $(PPh_3)(\eta^2\text{-}CH_3COO)RhC_2B_9H_{11}$ or $(PPh_3)_2(\eta^1\text{-}CH_3COO)RhC_2B_9H_{11}$. These acetate complexes react readily with hydrogen to regenerate the parent compounds. A very stable alkyl complex chelated through the carbonyl oxygen could be isolated from the reaction of **1b** with vinyl acetate at lower temperatures, whereas the reaction of **1a** with either isopropenyl acetate or vinyl acetate at higher temperatures led to the formation of an *ortho*-metallated complex whose crystal structure is reported. When allyl acetate was employed as substrate, complexes of the form $(PPh_3)(\eta^3\text{-}C_3H_5)RhC_2B_9H_{11}$ resulted with concomitant elimination of acetic acid. The relevance of the novel compounds reported here to the catalytic hydrogenolysis of alkenyl acetates using **1a**–**1c** as catalyst precursors is discussed.

Introduction

As part of our continuing investigation of metallacarboranes, we have extensively studied the reactions which occur at discrete metal vertices of metallacarborane clusters. We have recently reported the reactions of the rhodium vertex of *closo*-hydridophosphinorhodacarborane clusters with sulfuric [1,2] and nitric [2,3] acids, bases such as hydride and hydroxide ions [4], amine oxides and peroxides [5], and phosphines, chlorinating agents, and acrylate esters [6].

The *closo*-hydridophosphinorhodacarboranes (**1a**–**1c**) (see Fig. 1) have also been shown to be effective alkene hydrogenation and isomerization catalysts, and a

* Dedicated to Prof. J. Halpern on the occasion of his 60th birthday.

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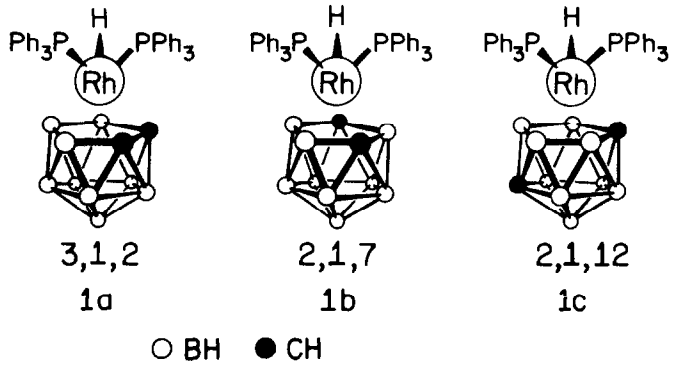


Fig. 1. The isomeric 12-vertex *closo*-$(PPh_3)_2$-$HRhC_2B_9H_{11}$ complexes (**1a–1c**).

detailed kinetic and mechanistic study of these systems has recently been published [7]. During the course of our investigation of the catalytic potential of rhodacarboranes, it was discovered that when alkenyl acetates such as vinyl acetate, isopropenyl acetate, and allyl acetate were employed as substrates for catalytic hydrogenation, the expected saturated esters were not obtained. Instead, hydrogenolysis of the ester C–O bond occurred to produce acetic acid and alkene [8]. Cleavage of unsaturated esters by transition metals has been reported previously, for instance, a molybdenum(0) complex has been observed to react with allyl acetate to produce an allylmolybdenum acetate complex [9], and similar reactions have been demonstrated for palladium [10] and nickel [11]. Other unsaturated esters such as vinyl acetate are less likely to undergo simple cleavage of the ester C–O bond to form transition metal complexes since the hydrocarbon fragment formed is less stable than the allyl ligand produced by the splitting of allyl acetate; however, transition metal hydride complexes are able to effect the scission of unsaturated esters to give metal acetates and free alkene, presumably through an intermediate alkyl complex. This reaction has been reported for complexes of iron, ruthenium, cobalt, palladium [12], and rhodium [12,13]; but the metals are usually in low oxidation states in contrast to the formal rhodium(III) present in rhodacarboranes **1a–1c**. Our study of the reaction of alkenyl acetates with the rhodium vertex of these metallacarborane clusters has resulted in the isolation of a number of interesting new rhodacarboranes. Their characterization and relevance to the mechanims of catalytic hydrogenolysis of alkenyl acetates is discussed below.

Results and discussion

Reactions of closo-bis(triphenylphosphine)hydridorhodacarboranes with isopropenyl acetate

The three isomeric rhodacarboranes, [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1a**), [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (**1b**), and [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$] (**1c**) illustrated in Fig. 1, were allowed to react with isopropenyl acetate in either tetrahydrofuran or benzene solvent at 40 °C. Over a 2-day period **1a** generated a mixture of two compounds, **2a** and **3**, which could be isolated in reasonably pure form by fractional crystallization of the benzene reaction mixture using heptane as the precipitant. Monitoring of the course of the reaction using

$^{31}P\{^1H\}$ NMR revealed a temperature dependence of the distribution of the two products. At 300 K a sharp resonance assigned to **2a** was observed at 42.2 ppm, (doublet, J(Rh–P) 166 Hz) along with a resonance for free PPh_3. At 200 K, the appearance of a new species **3** centered at 29.5 ppm (doublet, J(Rh–P) 134 Hz) coincided with the disappearance of the other two resonances implying that complex **2a** was quantitatively binding PPh_3 to produce complex **3**. The infrared spectra of **2a** and **3** contained carbonyl stretching bands at 1480 and 1650 cm^{-1}, respectively, indicating the presence of a bidentate acetate ligand in **2a** and a monodentate acetate ligand in **3**. Elemental analysis of **2a** confirmed its identity as a mono(triphenylphosphine)acetatorhodacarborane (see Fig. 2). We were unable to obtain an analytically pure sample of **3** due to contamination with **2a**; however, the NMR and IR data presented above and the reactions of **3** described later in this paper unambiguously identify it as the bis(triphenylphosphine)acetatorhodacarborane shown in Fig. 2.

The other two hydridophosphinorhodacarborane isomers, **1b** and **1c**, also reacted with isopropenyl acetate in benzene or tetrahydrofuran, but in contrast to the reaction of **1a** with isopropenyl acetate, only one product, the bidentate acetate complex **2b** or **2c**, was observed in each case. Monitoring of the reaction using $^{31}P\{^1H\}$ NMR showed the presence of the bidentate acetate complexes and free PPh_3 only. Even at 180 K, **2b** and **2c** did not bind PPh_3. We have previously observed significant differences among **1a**, **1b**, and **1c** in metal vertex rotation [14], metal vertex transfer [15], and chemical reactivity [6], presumably due to the differences in symmetry and electron density created by the relative positions of the carbon and boron vertices adjacent to the rhodium vertex. Consequently, the differences observed here were not unexpected.

When **1a** was allowed to react with isopropenyl acetate at the reflux temperature of benzene instead of at 40 °C, a new complex **4**, was generated in high yield. The $^{31}P\{^1H\}$ NMR of this material at 200 K exhibited two sets of resonances centered at −33.3 ppm (doublet of doublets, J(Rh–P(1)) 98 Hz, J(P(1)–P(2)) 31 Hz) and 37.1

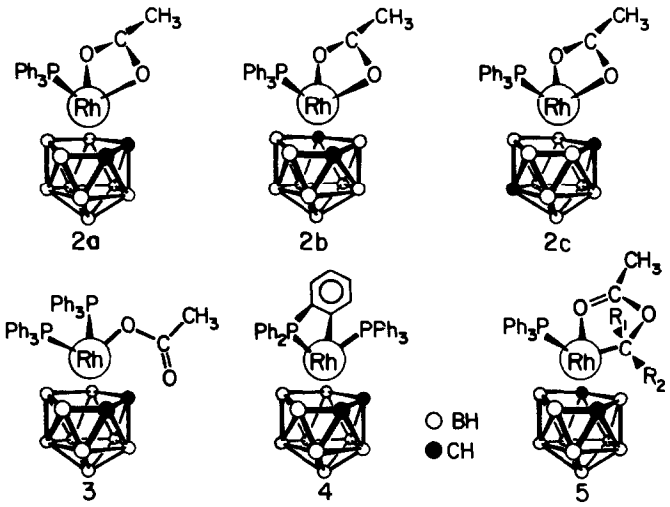


Fig. 2. Representations of complexes prepared in this study.

ppm (doublet of doublets, J(Rh–P(2)) 114 Hz). The $^{13}C\{^1H\}$ NMR of **4** at 200 K displayed an extremely complex set of resonances in the phenyl region although the elemental analyses indicated that **4** was a bis(triphenylphosphine)rhodacarborane. An X-ray crystallographic study was performed to confirm the suspected ortho-metallated nature of **4** (see Fig. 2 and 6). The structure and proposed mechanism for the formation of **4** are discussed later in this paper. Complex **4** could also be generated by heating **3** alone, or **2a** with excess PPh_3 in toluene; however, thermolysis of a bisulfate complex similar to **3**, [*closo*-3,3-$(PPh_3)_2$-3-(HSO_4)-3,1,2-$RhC_2B_9H_{11}$] [2], did not produce **4**. Also, attempts to prepare analogs of **4** starting with **1b** and **1c** were unsuccessful, regardless of the temperature employed. Only **2b** and **2c** were isolated, indicating the greater stability of **2b** and **2c** compared to **2a**.

Reactions of closo-bis(triphenylphosphine)hydridorhodacarboranes with vinyl acetate

When vinyl acetate was used as a reactant instead of isopropenyl acetate, the course of the reaction with **1a** was identical. The complexes **2a** and **3** were formed at 40 °C and **4** resulted when an 80 °C reaction temperature was employed. Also, the reaction of **1c** with vinyl acetate at either temperature led to the quantitative formation of **2c**, and the reaction of **1b** at 80 °C gave **2b** in high yield; however, when **1b** was allowed to react with vinyl acetate at 40 °C, a new complex **5** was produced quantitatively. Complex **5** could be converted to **2b** by heating in solution at 80 °C.

Complex **5** was identified as a mono(triphenylphosphine)alkylrhodacarborane based on elemental analyses and NMR data (see Experimental). The proposed structure of **5** illustrated in Fig. 2 indicates the possibility of diastereomers (R^1 = Me, R^2 = H or R^1 = H, R^2 = Me), and these were observed in the ^1H and $^{31}P\{^1H\}$ NMR spectra in a ratio of approximately 2/1. It is assumed that the sterically less constrained diastereomer with the methyl group directed up and away from the carborane is the predominant species. The infrared spectrum of **5** displayed a carbonyl stretching frequency ν(CO) 1600 cm^{-1} consistent with chelation of the carbonyl group of the rhodium bound alkyl ligand.

Complex **5** proved to be surprisingly stable. It could be prepared from **1b** and vinyl acetate under an atmosphere of hydrogen without further reaction occurring, whereas the other derivatives obtained from isopropenyl acetate and vinyl acetate, except **4**, reacted readily with hydrogen at 40 °C. The chelating carbonyl group is apparently very tightly bound since no evidence for displacement by PPh_3 was observed in ^{31}P NMR experiments, even at 180 K. Recrystallization of **5** could be accomplished with no decomposition in contrast to the structurally similar acrylate ester derivative, (whose preparation and crystal structure we recently reported [6]), which can only be recrystallized in the presence of a large excess of acrylate ester. The stability of **5** is typical of many transition metal complexes containing five-membered rings derived from the intramolecular coordination of a donor atom to the metal center [16].

Reactions of closo-bis(triphenylphosphine)hydridorhodacarboranes with allyl acetate

The reaction of **1a** with allyl acetate in benzene or tetrahydrofuran at 40 °C generated [*closo*-3-(η^3-C_3H_5)-3-PPh_3-3,1,2-$RhC_2B_9H_{11}$] (**6**). Complex **6** has been prepared in these laboratories by a different method and has been structurally characterized by X-ray crystallography to confirm the trihapto bonding mode of the

allyl group [17]. It is interesting to note that in the isopropenyl acetate and vinyl acetate reactions, the C–O scission resulted in the formation of free alkene and an acetate ligand, whereas in the case of allyl acetate, free acid and an η^3-allyl complex were produced. Komiya and Yamamoto have used *cis*-$RuH_2(PPh_3)_4$ and $RhH(PPh_3)_4$ to promote the cleavage of allyl acetate, but in their work, free propene and the acetate complexes *mer*-$RuH(OAc)(PPh_3)_3$ were formed. They did not report the formation of allyl complexes [12].

Reactions of **1b** or **1c** with allyl acetate produced mixtures of **2b** or **2c**, analogs of **6**, and alkyl complexes chelated through the carbonyl oxygen, again demonstrating the effect of structural diversity of the metallacarborane cluster on reactivity at the metal vertex.

Reactions of complexes 2–6 with hydrogen

Figure 3 illustrates the formation of complexes **2a**, **3**, **4**, and **6** from **1a** and their reactions with hydrogen. Solutions of the bidentate acetate complex **2a** or its analogs, **2b** and **2c**, rapidly produced acetic acid when hydrogen was passed through them at ambient temperature. If added PPh_3 were present, complexes **1a–1c** were regenerated. In the absence of added PPh_3, the solutions rapidly darkened upon exposure to hydrogen due to the formation of the dark purple dimer [*closo*-3-PPh_3-3,1,2-$RhC_2B_9H_{11}]_2$ (**7**) or the analogous dimers derived form **2b** and **2c**. Complex **7** has been structurally characterized [5] and has the geometry shown in Fig. 3. The dimers derived from **2b** and **2c** are assumed to be similar but may differ in the orientation of the carborane fragments with respect to each other.

Like **2a–2c**, the *ortho*-metallated species **4** also reacts with hydrogen to regenerate **1a**, but the reaction is slow, even at 80 °C. This reversibility of *ortho*-metallation has been observed previously; for instance, $(Ph_2P\text{-}o\text{-}C_6H_4)Rh(PPh_3)_2$ reacts with hydrogen at ambient temperature to produce $HRh(PPh_3)_3$ [18]; and $(Ph_2P\text{-}o\text{-}$

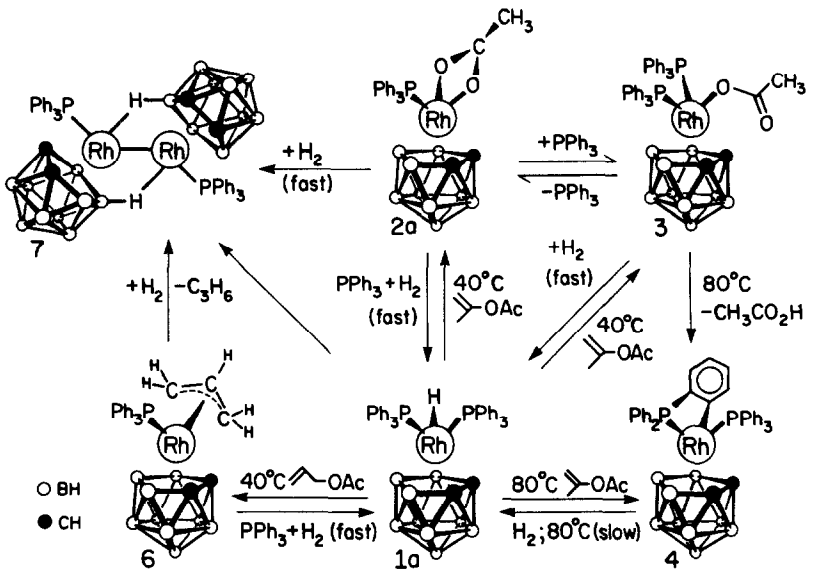


Fig. 3. Reaction sequence originating from complex **1a**.

C_6H_4)RuCl(PPh_3) reacts with hydrogen at room temperature in the presence of one equivalent of PPh_3 to regenerate the complex from which it was prepared, $HRuCl(PPh_3)_3$ [19].

In contrast to the other derivatives mentioned above, the alkyl complex **5** derived from the reaction of **1b** with vinyl acetate is inert toward hydrogen except at temperatures high enough to decompose the complex to **2a** and ethylene.

Mechanism for the hydrogenolysis of alkenyl acetates

The postulated mechanism for the cleavage of the ester C–O linkage in alkenyl acetates by rhodacarboranes (**1a–1c**) in the absence of hydrogen is shown in Fig. 4. The first step is the dissociation of PPh_3 and the coordination of the substrate. Insertion of the alkene into the rhodium–hydrogen bond is rapidly followed by chelation of the carbonyl oxygen to complete the metal coordination sphere. Insertion can occur in two different ways to create either a five-membered or six-membered ring upon chelation [20]. Five-membered rings are in general more stable, and this is borne out by the isolation of the extremely stable five-membered chelate ring compound **5**. Six-membered rings are less stable, and we presume that most C–O bond scission in our system occurs through the intermediacy of a six-membered ring complex. This mechanism is similar to the one proposed by Komiya and Yamamoto for the cleavage of alkenyl carboxylates by *cis*-$RuH_2(PPh_3)_4$

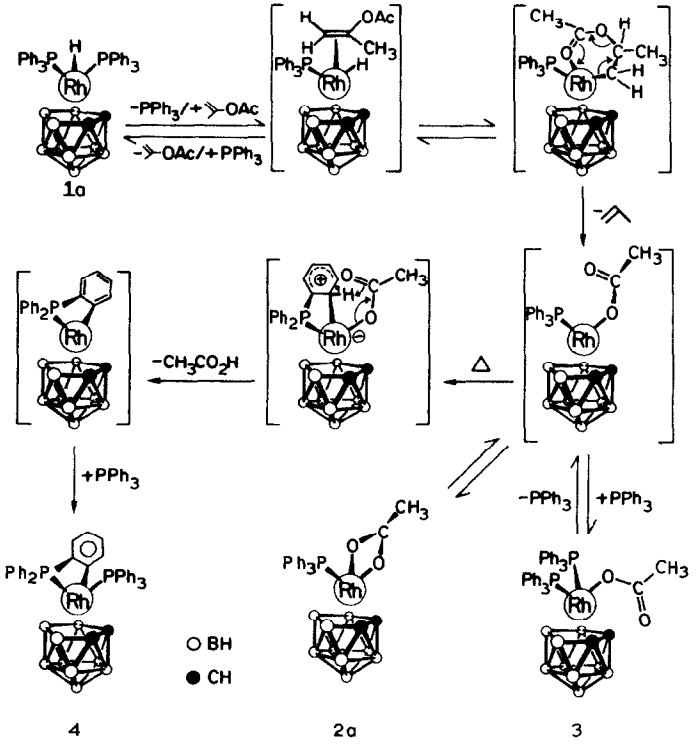


Fig. 4. Proposed mechanisms for alkenyl acetate cleavage and the formation of *ortho*-metallated rhodacarborane (**4**).

[12]. Following C–O cleavage and expulsion of alkene, the monodentate acetate intermediate can convert to a bidentate acetate complex, adduct a second PPh_3, or *ortho*-metallate with concomitant elimination of acetic acid as shown in Fig. 4.

A proposed pathway for the reaction of **2a** with hydrogen is shown in Fig. 5. Dissociation of one of the Rh–O bonds produces the monodentate acetate intermediate which can heterolytically split hydrogen [21] between the electrophilic rhodium and the nucleophilic carbonyl oxygen leading to elimination of acetic acid. The resulting coordinatively unsaturated complex $[(PPh_3)HRhC_2B_9H_{11}]$, can then dimerize with loss of hydrogen to give **7** or regenerate **1a** if excess PPh_3 is present. Previously, we intuitively favored this heterolytic cleavage of hydrogen over oxidative addition since oxidative addition of hydrogen would require the generation of a formal rhodium(V) intermediate [2]; however, recent work by Maitlis et al. has shown that iridium(V) and rhodium(V) complexes can be prepared including an air-stable rhodium(V) hydride species, $[\eta^5\text{-}C_5Me_5)Rh(H)_2(SiEt_3)_2]$ [22]. Maitlis has also obtained evidence that iridium(V) and rhodium(V) alkyl hydrides are intermediates in aromatic substitution reactions he has observed [23]. Also, James et al. have postulated that the reaction of a ruthenium *ortho*-metallated species proceeds through a ruthenium(IV) dihydride intermediate [19], isoelectronic with a rhodium(V) dihydride which one could invoke for the reaction of our *ortho*-metallated species **4**

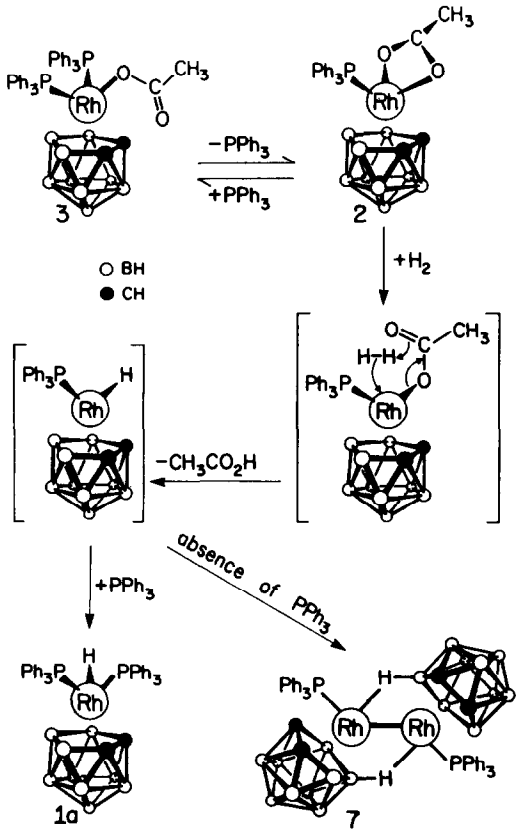
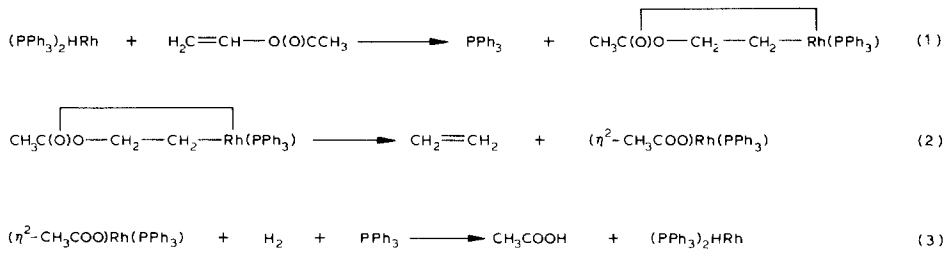


Fig. 5. Proposed heterolytic hydrogen activation process.

with hydrogen. We cannot rule out either heterolytic cleavage or oxidative addition as the mechanism of hydrogen activation in our systems on the basis of our present evidence, and it is quite possible that both mechanisms may be utilized, depending on the nature of the complex involved.

The three major steps discussed above, which together constitute a potential catalytic cycle for the hydrogenolysis of alkenyl acetates by the rhodium vertex of **1a**–**1c**, are summarized in eq. 1–3 using vinyl acetate as the substrate and omitting the carborane ligand in these equations.



We have prepared a chelated alkyl complex (**5**) closely related to the metal species postulated in eq. 1, and we have isolated the bidentate acetate complex shown in eq. 2, and we have verified that the acetate complex reacts readily with hydrogen to produce acetic acid and regenerate the starting metal hydride.

Interestingly, we have strong evidence that the above cycle is not a significant pathway in the catalytic hydrogenolysis of alkenyl acetates using **1a**–**1c** as catalyst precursors. When the deuterated analog of **1a**, (*closo*-3,3-$(PPh_3)_2$-3-D-3,1,2-$RhC_2B_9H_{11}$]) was employed in the catalytic hydrogenolysis of isopropenyl acetate, the catalyst recovered after 25 turnovers retained 89% of the Rh–D label as shown by ^1H NMR. One turnover by the above mechanism would remove the label. This demonstrates that the deuterium is being sequestered at a relatively unreactive site during the hydrogenolysis, and therefore the catalytically active species is probably a rhodium(I) *exo-nido*-metallacarborane as was the case in the hydrogenation of alkenes [7]. These results indicate the risk involved in inferring mechanisms based on the observation of models for individual steps. A somewhat similar situation was encountered by James et al. in their study of the stoichiometric hydrogenation of alkenes using $HRuCl(PPh_3)_3$ [19]. Alkene was hydrogenated in the absence of hydrogen gas to give the *ortho*-metallated complex, $(Ph_2P\text{-}o\text{-}C_6H_4)RuCl(PPh_3)$, which reacted with hydrogen in the presence of PPh_3 to regenerate the starting complex; however, the rates of these reactions were much too slow to account for the catalytic hydrogenation of alkenes under hydrogen using $HRuCl(PPh_3)_3$ as catalyst precursor.

The molecular structure and mechanism of formation of [closo-3-(PPh_3)-3,3-$(Ph_2P$-o-$C_6H_4)$-3,1,2-$RhC_2B_9H_{11}\cdot C_6H_6$]

The reaction of **1a** with isopropenyl acetate at 80 °C gave an interesting side product (**4**). The elemental analyses and NMR spectra of **4** indicated the presence of an *ortho*-metallated phosphine ligand, and an X-ray crystallographic structure determination, which will be reported elsewhere, was undertaken to elucidate its nature. The molecular structure of complex **4** (see Fig. 6) consists of one *ortho*-metal-

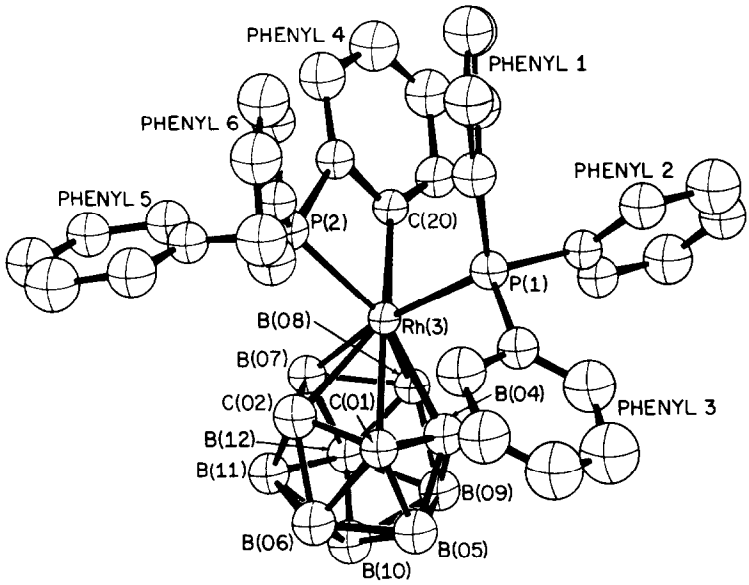


Fig. 6. Molecular structure of **4**, details to be published elsewhere.

lated phosphine ligand and one normal triphenylphosphine. The rhodacarborane cluster does not contain any significant distortions, and requires no comment.

The proposed mechanism for the formation of complex **4** is illustrated in Fig. 4. The C–O bond scission of the isopropenyl acetate substrate generates an electron-deficient rhodium(III) monodentate acetate intermediate. The rhodium initiates electrophilic attack on the phenyl ring of the coordinated triphenylphosphine followed by elimination of acetic acid and coordination of a second phosphine. Electrophilic attack by an electron-deficient metal has previously been proposed as a possible mechanism for orthometallation [24].

Experimental

Materials and methods

Reactions were carried out under argon (Liquid Carbonic), and all manipulations of the solutions were performed in Schlenkware. Solvents (Mallinckrodt) were freshly distilled from potassium metal (Mallinckrodt) under argon immediately before use. Isopropenyl acetate, allyl acetate (Eastman), and vinyl acetate (Matheson, Coleman and Bell) were distilled from calcium hydride (Alfa) under argon before use.

Literature methods were used to prepare [*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1a**), [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (**1b**) [6], and [*closo*-2,2-$(PPh_3)_2$-2-H-2,1,12-$RhC_2B_9H_{11}$] (**1c**) [25].

Infrared spectra were measured as Nujol mulls on sodium chloride plates using a Perkin–Elmer 137 spectrometer. The ^1H (200.133 MHz), $^{31}P\{^1H\}$ (81.02 MHz), and $^{13}C\{^1H\}$ (64.10 MHz) NMR spectra were recorded on a Bruker WP-200 Fourier transform instrument utilizing a deuterium lock and a B-VT-1000 temperature

controller for variable temperature measurements. The residual protons in the deuterated solvents were used as an internal reference in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, and $^{31}P\{^{1}H\}$ NMR spectra were externally referenced to 85% H_3PO_4 and corrected for solvent effects [26]. The ^{11}B and $^{11}B\{^{1}H\}$ (126.7 MHz) NMR spectra were measured on an instrument designed and built by F.A.L. Anet of this department utilizing $BF_3 \cdot OEt_2$ as an external reference. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories (Woodside, NY).

All of the reactions were screened by ^{31}P NMR experiments to determine the nature of the reaction before bench scale preparations were performed. The NMR samples were prepared by distilling the solvent (which had undergone three freeze/pump/thaw cycles) onto the compound in a 10 mm NMR tube. The samples were sealed at 77 K under vacuum. The NMR reactions conducted under hydrogen were performed by dissolving the compound in argon-saturated NMR solvent under argon purge, sealing the tube with a rubber septum covered with Parafilm, and introducing an atmosphere of hydrogen via a long needle inserted through the septum.

*[closo-(PPh$_3$)-3,3-(η^2-CH$_3$COO)-3,1,2-RhC$_2$B$_9$H$_{11}$] (**2a**) and [closo-3,3-(PPh$_3$)$_2$-3-(CH$_3$COO)-3,1,2-RhC$_2$B$_9$H$_{11}$] (**3**)*

[*closo*-3,3-$(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1a**) (1.00 g, 1.31 mmol) was allowed to react with isopropenyl acetate (5.00 ml, 45.4 mmol) in benzene (60 ml) at 40 °C for 3 days resulting in a yellow to dark red color change. Addition of heptane and reduction of volume in vacuo led to the precipitation of an orange powder. Repeated recrystallizations of this powder gave dark red crystalline blocks of **2a**, (0.54 g, 0.96 mmol, 73% yield). ^{1}H NMR (C_6D_6): δ(ppm) 7.5–7.8 (envelope, 6 H), 6.9–7.2 (envelope, 9 H), 4.7 (br s, 2 H, carborane C–H), 1.15 (sh s, 3 H, CH_3–COO). $^{11}B\{^{1}H\}$ NMR (C_6D_6) 8.9, 7.3, −4.4, −12.1, −24.5 (1/1/4/2/1). $^{31}P\{^{1}H\}$ NMR (20% C_6D_6/ THF) 42.2 (d, J(Rh–P) 166 Hz). Anal. Found: C, 47.37; H, 5.23; B, 17.22; P, 5.64; Rh, 18.22; O, 6.32. $C_{22}H_{29}B_9PRhO_2$ calcd.: C, 47.46; H, 5.25; B, 17.49; P, 5.56; Rh, 18.48; O, 5.75%.

When the orange powder initially obtained above was fractionally recrystallized from benzene/heptane, large orange crystals of **3** were obtained contaminated with red crystals of **2a**. Attempts to separate crystals of **3** and recrystallize them led to further conversion of **3** to **2a**.

*[closo-2-(PPh$_3$)-2,2-(η^2-CH$_3$COO)-2,1,7-RhC$_2$B$_9$H$_{11}$] (**2b**)*

[*closo*-2,2-$(PPh_3)_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (**1b**) (0.80 g, 1.05 mmol) was allowed to react with isopropenyl acetate (1.00 ml, 9.1 mmol) in benzene (75 ml) at 80 °C for 2.5 h, resulting in a color change from light yellow to orange. Repeated additions of heptane and volume reduction on a rotary vacuum evaporator gave an orange powder which was recrystallized from benzene/heptane to give bright orange crystals of **2b** (0.53 g, 0.96 mmol, 91% yield). ^{1}H NMR (C_6D_6): δ(ppm) 7.4–7.6 (envelope, 5 H), 6.9– 7.2 (envelope, 10 H), 2.5 (br s, 2 H, carborane C–H), 1.15 (sh s, 3 H, CH_3–COO). $^{11}B\{^{1}H\}$ NMR (C_6D_6): 8.3, 2.8, −7.7, −15.9, −18.1 (1/2/2/2/2). $^{31}P(^{1}H)$ NMR (20% C_6D_6/thf): 38.6 (sh d, J(Rh–P) 129 Hz). Anal. Found: C, 47.68; H, 5.37; B, 17.61; P. 5.59; Rh, 18.37; O, 5.38. $C_{22}H_{29}B_9PRhO_2$ calcd.: C, 47.46; H, 5.25; B, 17.49, P, 5.56; Rh, 18.48; O, 5.75%.

*[closo-2-(PPh_3)-2,2-(η^2-CH_3COO)-2,1,12-$RhC_2B_9H_{11}$] (**2c**)*

Using [*closo*-2,2-(PPh_3)$_2$-2-H-2,1,12-$RhC_2B_9H_{11}$] (**1c**) **2c** could be prepared as bright orange crystals (0.54 g, 0.98 mmol, 93% yield) by the procedure described for the preparation of **2b** above. ^{1}H NMR (C_6D_6): δ(ppm) 7.6–7.8 (envelope, 5 H), 6.9–7.2 (envelope, 10 H), 3.8 (br s, 1, H, carborane C–H), 2.3 (br s, 1 H, carborane C–H), 1.14 (sh s, 3H, CH_3COO). ^{11}B{^{1}H} NMR (C_6D_6): 3.9, −9.4, −18.6, −20.1 (3/2/2/2). ^{31}P{^{1}H} NMR (20% C_6D_6/THF): 38.5 (sh d, J(Rh–P) 134 Hz). Anal. Found: C, 47.65; H, 5.39; B, 17.23; P, 5.83; Rh, 18.06; O, 5.84. $C_{22}H_{29}B_9PRhO_2$ calcd.: C, 47.46; H, 5.25; B, 17.49; P, 5.56; Rh, 18.48, O, 5.75%.

*[closo-3-(PPh_3)-3,3-(PPh_2-o-C_6H_4)-3,1,2-$RhC_2B_9H_{11}$] (**4**)*

[*closo*-3,3-(PPh_3)$_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1a**), (3.83 g, 5.00 mmol) was allowed to react with isopropenyl acetate (12.0 ml, 129.0 mmol) in benzene (150 ml) at 80 °C for 6 h. A yellow to dark red color change was observed. The solution was cooled to 10 °C for 1 h, and the yellow microcrystalline material (2.93 g, 3.85 mmol, 77% yield) was isolated by filtration. Recrystallization from either CH_2Cl_2/heptane or benzene/ethanol afforded analytically pure yellow crystals of **4**. ^{1}H NMR (C_6D_6): δ(ppm) 8.0 (br s, 5 H), 7.0–7.3 (envelope, 15 H), 6.6 (br s, 5 H), 5.7 (br s, 4 H), 2.68 (br s, 1 H, carborane C–H), 1.20 (br s, 1 H, carborane C–H). ^{11}B{^{1}H} NMR (C_6D_6): −0.8, −0.9, −4.3, −7.9, −8.6, −21.3 (1/1/1/1/1/4). ^{31}P{^{1}H} NMR (20% C_6D_6/THF): 37.1 (sh dd, J(Rh–P(1)) 114 Hz, J(P(1)–P(2)) 31 Hz), −33.3 (sh dd, J(Rh–P(2) 98 Hz). Anal. Found: C, 62.94; H, 5.71; B, 11.64; P, 7.38; Rh, 12.69. $C_{44}H_{46}B_9P_2Rh$ calcd.: C, 63.13; H, 5.54; B, 11.63; P, 7.40; Rh, 12.29%.

*[closo-2-(PPh_3)-2,2-(CH_3CH-O(O)CCH_3)-2,1,7-$RhC_2B_9H_{11}$] (**5**)*

[*closo*-2,2-(PPh_3)$_2$-2-H-2,1,7-$RhC_2B_9H_{11}$] (**1b**) (1.00 g, 1.31 mmol) was stirred with vinyl acetate (10 ml, 108.0 mmol) in benzene (60 ml) at 40 °C for 7 d. Only a slight color change occurred. Addition of heptane and reduction of the volume in vacuo caused the precipitation of a yellow powder (0.73 g, 1.24 mmol, 95% yield). Recrystallization from benzene/heptane gave greenish-yellow crystals of analytically pure **5**. ^{1}H NMR (C_6D_6): δ(ppm) 7.7–7.9 (envelope 5 H), 7.1–7.3 (envelope 10 H), 6.32 (dqrt, 1 H, J(Rh–H) 21.7 Hz, J(CH_3–H) = 6.1 Hz), 2.9 (br s, 1 H, carborane C–H), 2.16 (d, 3 H, J(H–CH_3 5.4 Hz), 1.8 (br s, 1 H, carborane C–H), 1.25 (sh s, 3 H, CH_3–COO); (Other diastereomer: 2.6 (br s, 1 H, carborane C–H), 2.06 (d, 3 H, J(H–CH_3) 5.3 Hz), 1.6 (br s, 1 H, carborane C–H), 1.18 (sh s, 3 H, CH_3–COO). ^{11}B{^{1}H} NMR (C_6D_6): 2.8, −4.9, −19.1, (2/4/3). ^{31}P{^{1}H} NMR (20% C_6D_6/THF): 44.6 (sh d, J(Rh–P) 159 Hz), (other diastereomer: 43.6 (sh d, J(Rh–P) 164 Hz). Anal Found: C, 49.40; H, 5.59; B, 16.36; P, 5.76; Rh 17.31; O, 5.22. $C_{24}H_{33}B_9PRhO_2$ calcd.: C, 49.29; H, 5.69; B, 16.65; P, 5.30; Rh, 17.60; O, 5.47%.

*[closo-3-(PPh_3)-3-(η^3-C_3H_5)-3,1,2-$RhC_2B_9H_{11}$] (**6**)*

[*closo*-3,3-(PPh_3)$_2$-3-H-3,1,2-$RhC_2B_9H_{11}$] (**1a**) (1.40 g, 1.84 mmol) was allowed to react with allyl acetate (3.00 ml, 27.8 mmol) in benzene (80 ml) at 40 °C for 5 d resulting in a slight color change from yellow to greenish-yellow. Addition of heptane and reduction of the volume in vacuo precipitated a dull yellow powder (0.90 g, 1.67 mmol, 91% yield) which gave bright yellow crystals on recrystallization from benzene/heptane.

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References

1 W.C. Kalb, R.G. Teller and M.F. Hawthorne, J. Am. Chem. Soc., 101(1979) 5417.
2 W.C. Kalb, Z. Demidowicz, D.M. Speckman, C. Knobler, R.G. Teller and M.F. Hawthorne, Inorg. Chem., 21(1982) 4027.
3 Z. Demidowicz, R.G. Teller and M.G. Hawthorne, J. Chem. Soc., Chem. Commun., (1979) 831.
4 J.A. Walker, C.B. Knobler and M.F. Hawthorne, J. Am. Chem. Soc., 105(1983) 3368.
5 R.T. Baker, R.E. King III, C.B. Knobler, C.A. O'Con and M.F. Hawthorne, J. Am. Chem. Soc., 100 (1978) 8266.
6 R.T. Baker, M.S. Delaney, R.E. King III, C.B. Knobler, J.A. Long, T.B. Marder, T.E. Paxson, R.G. Teller and M.F. Hawthorne, J. Am. Chem. Soc., 106 (1984) 2965.
7 P.E. Behnken, J.A. Belmont, D.C. Busby, R.E. King III, C.W. Kreimendahl, T.B. Marder, J.J. Wilczynski and M.F. Hawthorne, J. Am. Chem. Soc., 106 (1984) 3011.
8 R.E. King III, D.C. Busby and M.F. Hawthorne, 182nd National Meeting of the American Chemical Society, New York, N.Y., August 1981, Abstract INOR 8; R.T. Baker, Ph.D. Dissertation, UCLA, 1980.
9 M.L.H. Green, L.C. Mitchard and W.E. Silverthorn, J. Chem. Soc., Dalton Trans., (1973) 1404.
10 T. Yamamoto, O. Saito and A. Yamamoto, J. Am. Chem. Soc., 103(1981) 5600.
11 T. Yamamoto, J. Ishizu and A. Yamamoto, J. Am. Chem. Soc., 103(1981) 6863.
12 S. Komiya and A. Yamamoto, J. Organometal. Chem., 87(1975) 333.
13 A.G. Abatjoglou, D.R. Bryant and L.C. D'Esposito, J. Molec. Catal., 18(1983) 381.
14 T.B. Marder, R.T. Baker, J.A. Long, J.A. Doi and M.F. Hawthorne, J. Am. Chem. Soc., 103(1981) 2988.
15 T.B. Marder, J.A. Long and M.F. Hawthorne, J. Chem. Soc., Chem. Commun., (1980) 677; J.A. Long, T.B. Marder and M.F. Hawthorne, J. Am. Chem. Soc., 106 (1984) 3004.
16 I. Omae, Coord. Chem. Rev., 32(1980) 235.
17 J.A. Walker and M.F. Hawthorne, to be submitted.
18 W. Keim, J. Organometal. Chem., 14(1968) 179.
19 B.R. James, L.D. Markham and D.K.W. Wang, J. Chem. Soc., Chem. Commun., (1974) 439.
20 G.H. Olivé and S. Olivé, Top. Cur. Chem., 67(1976) 107.
21 P.J. Brothers, Prog. Inorg. Chem., 28(1981) 1.
22 K. Isobe, P.M. Bailey and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1981) 808; M.-J. Fernandez and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1982) 310; Organometallics, 2(1983) 164.
23 M. Gomez, D.J. Robinson and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1983) 825.
24 J.P. Collman and L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley (CA), (1980) 215.
25 D.C. Busby and M.F. Hawthorne, Inorg. Chem., 21(1982) 4101.
26 The chemical shift of PPh_3 was taken as -6.0 ppm; B.E. Mann, J. Chem. Soc., Perkin Trans., 2(1972) 30.