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Preparation of Monoatomic and Diatomic Rhodium Sites on Carbon Surface

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The methods for preparation of two new types of rhodium-on-carbon catalysts, *A* and *B*, *A* from four different mononuclear organorhodium precursors and *B* from six different binuclear organorhodiums, are described. At metal loadings less than 0.02 wt% on 300 m^2/g carbon surface (<1 atom/250 nm^2), these catalysts show behaviors distinctly different from one another and from those of the corresponding higher loading catalysts. At temperatures above 200°C, sintering occurs, altering *A* properties to those characteristic of high loading. Poisoning experiments with trimethylphosphine indicate that *A* and *B* catalysts are free of aggregated sites and that high-loading catalysts are free of *A*- and *B*-type sites. These low-loading catalysts are postulated to have the following active sites: monoatomic rhodium for *A* and diatomic Rh_2 for *B*. Catalyst *A* is strikingly unique in the hydrogenation of 1,3-butadiene, making *cis*-2-butene uncontaminated by *trans*. Generalization to other metals is anticipated. © 1990 Academic Press, Inc.

INTRODUCTION

It is widely accepted that the properties and reactivity of metal atoms are substantially different from those of bulk metal. It has been demonstrated that metal atoms provide routes to novel organometallic compounds by direct reaction with substrates (alkenes, arenes, etc.), whereas the bulk metals are inert to the same reactants (*1*). Analogously, it is expected that a catalyst with atomically dispersed active sites might exhibit distinctly different properties from those of conventional catalysts containing active sites essentially those of bulk metal particles. All earlier attempts to prepare such catalysts have failed.

Several investigators concluded from chemisorption and electron microscopy studies of "highly dispersed" catalysts on alumina or silica that rhodium is present in two-dimensional raft-like structures (*2–4*). But there had been assertions, based on infrared spectra of chemisorbed CO, that Rh/Al_2O_3 was atomically dispersed (*5–8*). However, EXAFS studies revealed rafts of 12–15 atoms (*9, 10*). The claim of formation of a stable, catalytically active, allylmonohydride complex of rhodium-on-silica, linked through one oxygen atom, Si-ORh(H)(allyl) (*11*) has been disputed with an electron microscopy study which revealed the presence of small metal aggregates (*12*). All of these catalyst studies had employed loadings $\geq 0.6\%$ metal on oxidized supports, Al_2O_3 or silica. Although there are a few reports of catalysts on active carbon, metal loadings used in these studies were also high (*13*).

The purpose of the present study was to find the conditions for the preparations of atomically dispersed catalysts. We report here that the catalytic properties of low-loading ($<0.02\%$) rhodium catalysts on carbon ($<10^{-3}$ mmol/m^2, or <1 atom/250 nm^2) are distinctly different from those of high-loading conventional catalysts prepared by an identical procedure, on the same support.

The main problem in assigning structural details to these new catalysts is that commonly used physical methods have not been

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TABLE 1

Catalytic Behavior as a Function of Flow Rates of Reaction Gases

Flow rates of gases (ml/min)			r_{H}[a]	r_{t}[b]	r_{c}[c]	r_{T}[d]	I/H[e]
Helium	Hydrogen	1-Butene					
89	10	1	231.	680.	611.	1522.	5.6
45	5	0.5	237.	689.	621.	1547.	5.5
178	20	2	238.	623.	566.	1427.	5.0

Note. Precursor: $Rh(Allyl)_3$. Loadings: 0.0068% Rh/C. Activation: 125°C, H_2. Catalysis at 30°C.

[a] Rate of hydrogenation (mol product)(mol Rh)$^{-1}$ h^{-1}.

[b] Rate of *trans*-butene formation (mol product)(mol Rh)$^{-1}$ h^{-1}.

[c] Rate of *cis*-butene formation (mol product)(mol Rh)$^{-1}$ h^{-1}.

[d] $r_{\mathrm{H}} + r_{\mathrm{t}} + r_{\mathrm{c}}$.

[e] $(r_{\mathrm{t}} + r_{\mathrm{c}})/r_{\mathrm{H}}$.

developed for these low loadings. Thus, the approach has been to employ a suitable chemical reaction for the comparison of the catalytic properties of the low-loading catalysts with those of high-loading conventional catalysts, using both specific rates and selectivities for competitive processes to distinguish the different types of catalysts. This and selective poisoning and sintering properties give support to the hypothesis that these preparations have atomic dispersions.

CATALYTIC BEHAVIOR AS A FUNCTION OF LOADING

Rhodium in the presence of hydrogen is active for both isomerization and hydrogenation of 1-butene; these reactions were used to evaluate the effect of metal loading on the rates of the competitive hydrogenation (butane) and isomerizations (*cis*- and *trans*-2-butenes). Catalysis was studied at 30°C under atmospheric pressure in a plug-flow, differential microreactor system, with periodic, noninterruptive sampling of the gas outflow and product analysis with gas chromatography. The catalysts were dry-diluted with fresh support material, as required, to reduce the conversions to less than 10% (usually 3–5%) in order to limit the study to primary reactions. The observed rates were not diffusion-limited (see Table 1). Similarly, a second test reaction employed was that of 1,3-butadiene in the presence of hydrogen, comparing the rates of formation of 1-butene, *cis*-, *trans*-2-butene, and butane. For neither of these reactions did the support alone (handled also in O_2 free environment) show any activity.

RHODIUM OVER ALUMINA CATALYST; AGGREGATED ACTIVE SITES; "STRUCTURE INSENSITIVE" BEHAVIOR

D. C. Yates graciously provided two of his well-characterized Rh/Al_2O_3 catalysts which had been shown to have active sites consisting of rafts of 8–12 atoms (*2*). Two low-loading catalysts were prepared in this laboratory according to his procedure (activated at 200°C in H_2). The activities and selectivities of these catalysts with the hydrogenation/isomerization reaction of 1-butene were examined. Results are shown in Table 2. The selectivity is constant for all loadings, but the specific activity decreases with decreasing metal loading, indicating only a loss of active sites with diminished loading (*16*); there is no change in type of site. The constant selectivity is consistent with the conclusion of the EXAFS study

TABLE 2

Catalytic Evaluation of Rhodium on Al_2O_3

Rh metal loading (%)	r_{H}[a]	r_{t}[b]	r_{c}[c]	r_{T}[d]	I/H[e]
0.20[f]	423.	846.	600.	1870.	3.4
0.020[f]	98.6	134.	117.	350.	2.5
0.0080	50.7	96.4	81.2	228.	3.5
0.0020	24.7	42.6	35.9	103.	3.2

[a] Rate of hydrogenation (mol product)(mol Rh)$^{-1}$ h^{-1}.

[b] Rate of *trans*-2-butene formation (mol product) (mol Rh)$^{-1}$ h^{-1}.

[c] Rate of *cis*-2-butene formation (mol product) (mol Rh)$^{-1}$ h^{-1}.

[d] $r_{\mathrm{H}} + r_{\mathrm{t}} + r_{\mathrm{c}}$.

[e] $(r_{\mathrm{t}} + r_{\mathrm{c}})/r_{\mathrm{H}}$.

[f] Sample from D. C. Yates.

that there is no fundamental difference between high and low loadings (9): rafts of 8–12 atoms have the same catalytic properties as bulk metal.

These reactions, catalyzed by rhodium-on-alumina, appear to give an excellent example of structure-insensitive behavior (*14*), showing no difference in selectivity in going from small rafts to highly aggregated systems.

Catalysts prepared on carbon (Monarch 880) show a sharply different response to loading from that of those found with alumina support.

RHODIUM ON CARBON CATALYSTS PREPARED FROM MONO AND DINUCLEAR ORGANORHODIUM COMPOUNDS

Catalysts were prepared and handled in an oxygen-free atmosphere.

These catalysts were prepared by adsorbing from solution onto carbon (Monarch 880, a low-ash carbon, pretreated with H_2 at 1000°C, cooled in hydrogen atmosphere, and handled with an oxygen-exclusive technique) the indicated organometallic compounds, at appropriate loadings. The solvent was removed *in vacuo,* and the organic ligands were removed from the immobilized organometallic compound by treating a bed of the solvent-free powder with flowing H_2 at temperatures less than 200°C. Low- and high-loading catalysts were prepared by the same methods.

Among the requirements we recognized as necessary for success in achieving the objective of atomic (or diatomic) dispersion are: (1) The organometallic compound should be immobilized as isolated molecules, and (2) the ligand removal procedure should deposit on the nearby surface the metal component(s) of the organometallic precursor, under conditions which do not encourage atom mobility.

As will be seen below, the low-loading catalysts prepared by this method are stable below 200°C; at 300°C the low-loading preparations acquire the same properties as those with high loading.

REMOVAL OF LIGANDS FROM CATALYST PRECURSORS ON CARBON

Since the unique properties we describe were found with low-loading catalysts (<0.02% rhodium), it was important to show with those low-loading samples that the ligands are eliminated by the activation procedure. Allyl ligands from $Rh(allyl)_3$ on carbon were removed quantitatively as propane by reducing in H_2 at 125°C. Similarly, ethylene ligands were quantitatively removed as ethylene from $Cp^*Rh(C_2H_4)_2$ on carbon by treatment with H_2 at 125°C. The Cp* ligands (pentamethylcyclopentadienyl) could not be removed from the ethylene-free preparation by pumping at 200°C in the absence of hydrogen, but they were removed quantitatively as an isomeric mixture of pentamethylcyclopentanes in H_2 atmosphere at 200°C. After removal of ligands, four different monorhodium precursors produce catalysts with the same activity patterns (vide infra), consistent with the assumption that the removal of the ligands from each of them was complete.

From the dirhodium precursor, $Rh_2(\mu\text{-}CH_2)(CO)_2Cp_2$ on carbon, CO ligands were removed quantitatively as methanol and Cp ligand as cyclopentane, by reducing in H_2 at 200°C. From $Rh_2(COD)_2(\mu\text{-}Cl)_2$ on carbon, COD ligands were removed quantitatively as cyclooctane by reducing at 200°C in H_2. Similar catalytic properties of these catalysts and those from four additional dirhodium precursors (vide infra) indicate identical active sites, consistent with complete removal of ligands from each of the six precursors.

CATALYTIC BEHAVIOR AS A FUNCTION OF METAL LOADINGS; ACTIVE SITES *A* AND *B*

A set of identically prepared catalysts with loadings from 1.0 to 0.0008 wt% Rh/C was prepared using $Rh(allyl)_3$ as the precursor. Measured amounts of $Rh(allyl)_3$ in solution were adsorbed on carbon, the solvent removed, activated at 125°C in H_2, and then used as catalysts for the reactions of 1-butene with H_2 at 30°C (see Table 3 and Fig.

TABLE 3

Catalytic Behavior as a Function of Metal Loadings

Loadings Rh/C (wt%)	r_H[a]	r_t[b]	r_c[c]	r_T[d]	*I/H*[e]
1.00	2616.	876.	772.	4264.	0.6
0.35	1600.	876.	819.	3295.	1.0
0.080	706.	1099.	968.	2773.	2.9
0.020	231.	676.	628.	1535.	5.6
0.0068	231.	680.	611.	1522.	5.6
0.0040	216.	681.	592.	1490.	5.9
0.0020	108.	302.	275.	684.	5.4
0.00080	39.0	112.	101.	252.	5.5

Note. Precursor: Rh(Allyl)$_3$. Activation: 125°C, H_2. Catalysis at 30°C.

[a] Rate of hydrogenation (mol product)(mol Rh)$^{-1}$ h^{-1}.

[b] Rate of *trans*-butene formation (mol product) (mol Rh)$^{-1}$ h^{-1}.

[c] Rate of *cis*-butene formation (mol product) (mol Rh)$^{-1}$ h^{-1}.

[d] $r_H + r_t + r_c$.

[e] $(r_t + r_c)/r_H$.

TABLE 4

Catalytic Behavior as a Function of Metal Loadings

Loadings Rh/C (wt%)	r_H[a]	r_t[b]	r_c[c]	r_T[d]	*I/H*[e]
1.00	3540.	801.	616.	4959.	0.40
0.080	1370.	897.	748.	3015.	1.2
0.020	542.	709.	645.	1896.	2.5
0.0068	561.	737.	553.	1852.	2.3
0.0040	591.	676.	564.	1830.	2.1
0.0020	290.	399.	327.	1016.	2.5

Note. Precursor: Rh_2 Cp_2(COT)[*trans*]. Activation: 200°C, H_2. Catalysis at 30°C.

[a] Rate of hydrogenation (mol product)(mol Rh)$^{-1}$ h^{-1}.

[b] Rate of *trans*-butene formation (mol product) (mol Rh)$^{-1}$ h^{-1}.

[c] Rate of *cis*-butene formation (mol product) (mol Rh)$^{-1}$ h^{-1}.

[d] $r_H + r_t + r_c$.

[e] $(r_t + r_c)/r_H$.

1). The activity of these catalysts is loading dependent, reaching constant behavior below 0.02% metal loadings; there is a plateau of constant specific activity (r_T) and selectivity (ratio of isomerization to hydrogenation, *I/H*) below 0.02%. The selectivity remains constant for catalysts with loadings between 0.02 and 0.0008%, indicating a new monodispersed system, *A*. The product composition on the low-loading plateau is distinctly different from those obtained with high-loading catalysts. The high-loading catalysts are similar to the conventional rhodium-on-carbon catalysts (Fig. 3). Conventional rhodium catalysts and our high-loading catalysts mainly effect hydrogenation with this probe reaction; the low-loading catalysts mainly effect isomerization. Except for the two lowest loadings the specific activities are also constant. The loss of activity at 0.0020 and 0.0008% may be due to some low-concentration poisons present on carbon; these would affect a larger percentage of active sites at the lowest loadings.

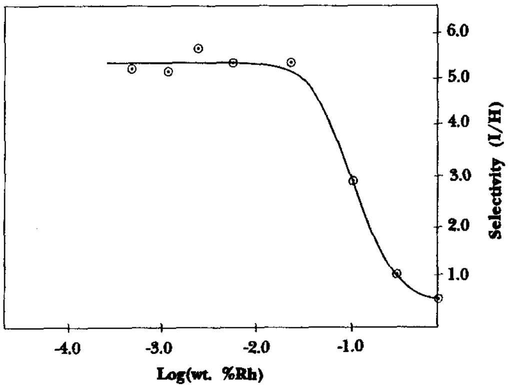

FIG. 1. Plot of selectivity (*I/H*) vs log (wt% Rh). The catalysts were prepared from Rh(allyl)$_3$ by activating at 125°C in H_2.

The same type of low-loading plateau response is obtained with the dirhodium precursor, $Rh_2Cp_2(COT)_2$[*trans*], but with a different low-loading plateau value (Table 4 and Fig. 2). At high loading all catalysts are the same as the conventional Rh/C catalyst. The low-loading plateau indicates a second new monodisperse system, *B*.

The plateaus with altered selectivities be-

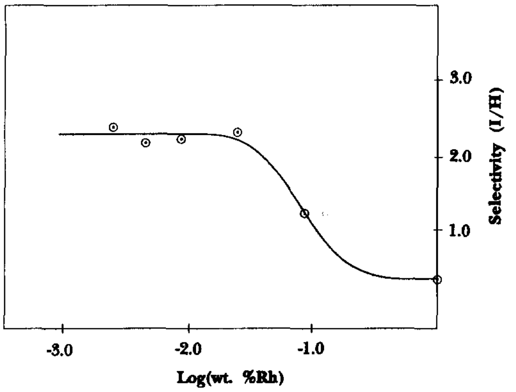

FIG. 2. Plot of selectivity (*I*/*H*) vs log (wt% Rh). The catalysts were prepared from $Rh_2Cp_2(COT)$(*trans*) by activating at 200°C in H_2.

low 0.02% loadings are highly significant findings, indicating the possibility that *A* and *B* sites are each monodisperse and different from one another as well as from those present in the corresponding high-loading catalysts. While these observations taken alone do not indicate that the sites be monoatomic or diatomic, etc., the high dilution required for their preparation and the findings that all monorhodium organometallics make the same catalysts at low loadings and that all dirhodiums make a different catalyst (vide infra) are readily rationalized by the assignment of monoatomic sites to *A* and diatomic sites to *B*.

The absorption of the organometallics at low concentration (<1 molecule/250 nm^2) is expected to result in immobilization of discrete, widely separated, organometal molecules on the carbon surface. The removal of solvent prior to activation should reduce their mobility. The mild conditions for conversion of ligands to saturated hydrocarbons and the possibility that the bare metal atoms might be complexed to the surface are parts of the overall rationalization which lead to the assignments of compositions of the active sites in the low-loading systems, the same as the nuclearity of the precursor molecules.

CATALYSTS FROM OTHER MONORHODIUM COMPOUNDS; FURTHER PRECURSORS FOR ACTIVE SITE *A*

Low-loading (0.0068%) catalysts were made from $Cp^*Rh(C_2H_4)_2$, $CpRh(C_2H_4)_2$ and $CpRh(CO)_2$. These were activated at 200°C in H_2, and catalysis was studied at 30°C in the differential microreactor as before. Results are shown graphically, along with the $Rh(allyl)_3$ results, in Fig. 3, indicating each of these precursors makes the same active sites *A*. A conventional 1.0% rhodium on carbon catalyst, from Alfa Chemical Co., was characterized following activation at 125°C in H_2, and results are also shown in Fig. 1 for comparison. The high-loading catalyst from trisallylrhodium and the commercial catalyst behave similarly. The minor difference between the two high-loading catalysts may be due to the fact that our catalysts were made on ash-free reduced carbon (Monarch 880) in moisture- and oxygen-free atmosphere, whereas the Alfa catalyst was made on activated carbon, most probably containing ash, oxygen, and moisture. However, the low-loading catalysts are different from these high-loading catalysts, forcing the conclusion that these low-loading catalysts have a distinctly different active site.

HYDROGENATION OF 1,3-BUTADIENE OVER *A*-TYPE CATALYSTS

Hydrogenation of 1,3-butadiene was used as an alternative probe reaction to distinguish *A*-type catalysts from conventional catalysts, examining the relative rates of formation of 1-butene, *cis*- and *trans*-2-butene, and butane.

Low-loading (0.0068% Rh/C) and high-loading (1.0%) catalysts from $Rh(allyl)_3$ were activated at 200°C, and catalysis was studied with 1,3-butadiene at 30°C as usual; results are shown in Fig. 4. Both the selectivity and specific activity of the low-loading catalyst are different from those of the high-loading catalyst. It is especially noteworthy that only *cis*-2-butene and 1-butene (negligi-

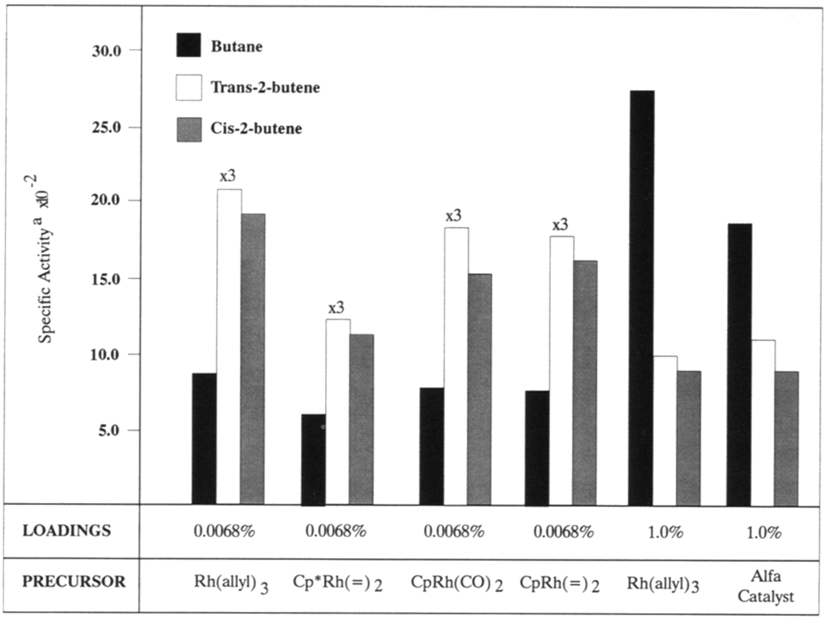

FIG. 3. Product distributions in the reaction of 1-butene with H_2 at 30°C on Rh/C. The catalysts were prepared from different monorhodium organometallics by activating at 200°C in H_2. [a] Mol product · (Mol Rh)$^{-1}$ · h^{-1}.

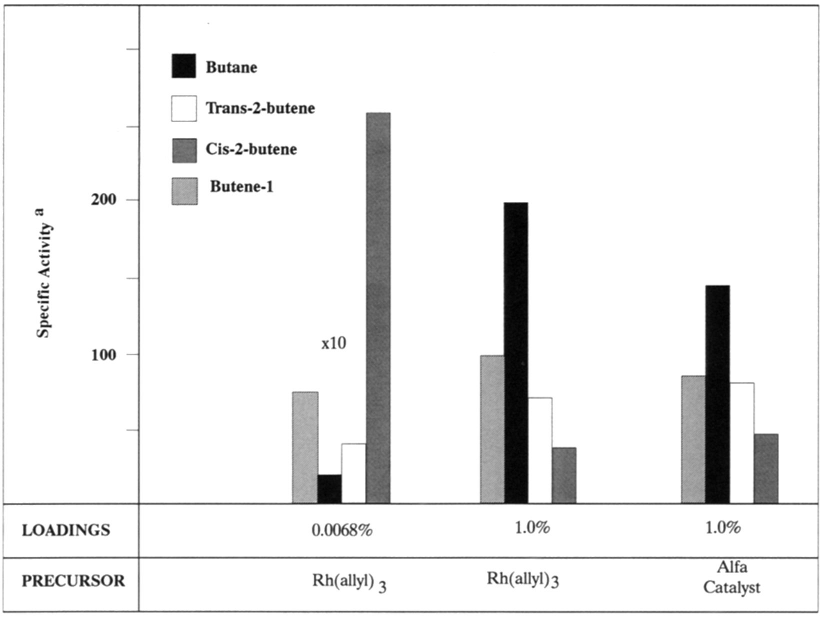

FIG. 4. Product distributions in the reaction of 1,3-butadiene with H_2 at 30°C on Rh/C. The catalysts were prepared by activating at 200°C in H_2. [a] Mol product · (Mol Rh)$^{-1}$ · h^{-1}.

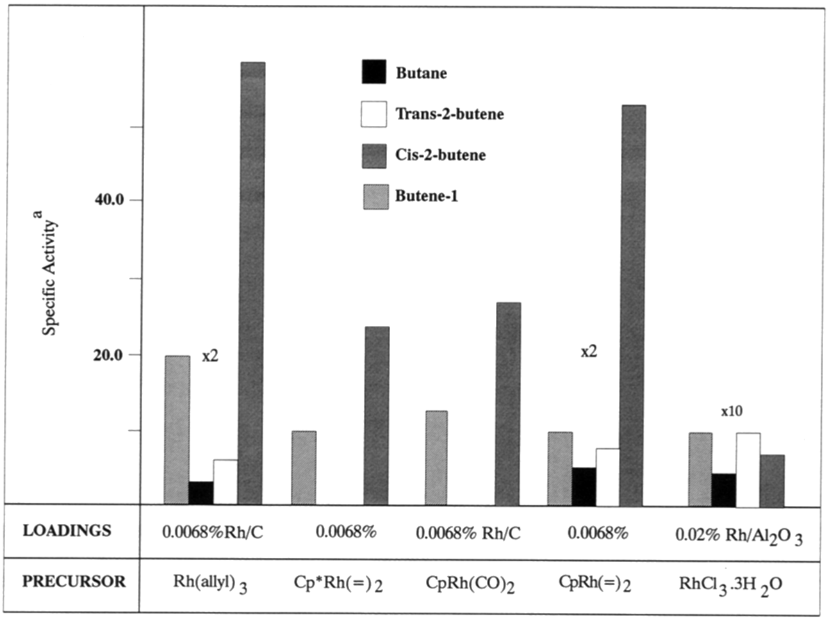

FIG. 5. Product distributions in the reaction of 1,3-butadiene with H_2 at 30°C on Rh catalysts. The catalysts were prepared from different monorhodium compounds by activating at 200°C in H_2. [a] Mol product · (Mol Rh)$^{-1}$ · h^{-1}.

ble amounts of *trans*-2-butene and butane) are formed with the low-loading catalyst (*17*), whereas with the high-loading catalyst, prepared from the same precursor compound, butane, 1-butene, *trans*-2-butene, and *cis*-2-butene are formed. The conventional 1.0% rhodium-over-carbon catalyst from Alfa, following activation with H_2 at 125°C, is the same as the high-loading catalyst from trisallylrhodium (and the binuclear precursor, vide infra). Here is a second clear indication that the low-loading catalyst with *A* sites is distinctly differentiated from the high-loading catalysts.

Low-loading (0.0068%) catalysts from the other monorhodium organometallic precursors were also characterized with the butadiene/hydrogen reaction at 30°C (see Fig. 5). All the low-loading monorhodium catalysts behave similarly, showing *A*-site behavior, consistent with the conclusion that *all the monorhodium organometallics make, at low loadings, the same A site, irrespective of the organic ligands of the precursor.*

A low-loading (0.02%) Rh/Al_2O_3 catalyst was examined with the butadiene test reaction. The product ratios (Fig. 5) are very low, and distinctly different from those of the low-loading monorhodium catalysts on carbon. This observation indicates that *A*-type sites are not produced on alumina support at loadings down to 0.02%.

ACTIVE SITE *B*; CATALYSTS FROM BINUCLEAR ORGANOMETALLICS

Low-loading (0.0068%) catalysts were made from $Rh_2(\mu\text{-}CH_2)(CO)_2Cp_2$, $Rh_2(\mu\text{-}CO)(CO)_2Cp_2$, $Rh_2(COD)_2(\mu\text{-}Cl)_2$, $Rh_2(allyl)_4(\mu\text{-}Cl)_2$, $Rh_2Cp_2(\mu\text{-}COT)$(*cis*), and $Rh_2Cp_2(\mu\text{-}COT)$(*trans*); a high-loading (1.0%) catalyst was made from $Rh_2(\mu\text{-}CH_2)(CO)_2Cp_2$. These were activated at 200°C in H_2, and catalysis was examined at 30°C. Figures 6 and 7 show graphically the results in the reaction of H_2 with 1-butene and 1,3-butadiene, respectively. The low-loading catalysts are distinctly different from the high-loading

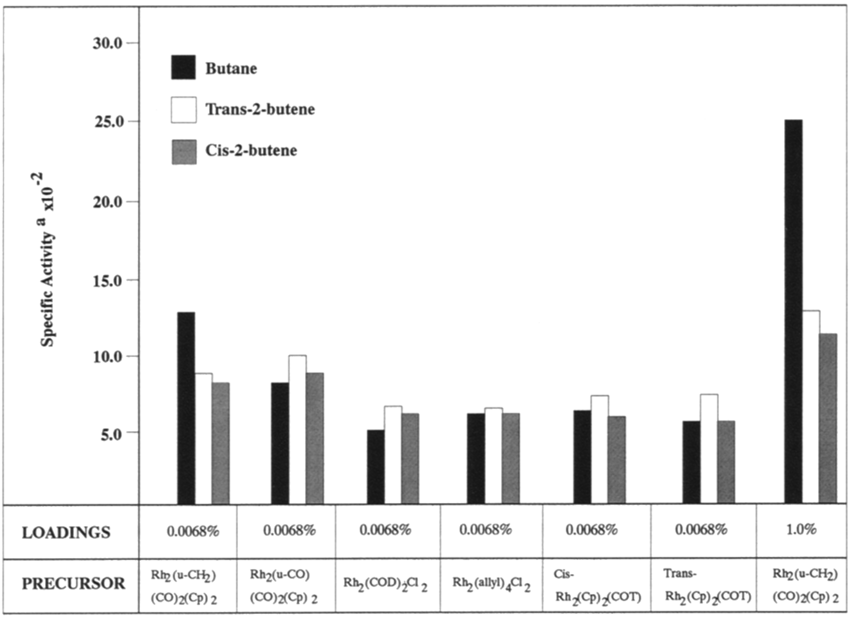

FIG. 6. Product distributions in the reaction of 1-butene with H_2 at 30°C on Rh/C. The catalysts were prepared from different dirhodium organometallics by activating at 200°C in H_2. ^{a} Mol product · (Mol Rh)$^{-1}$ · h^{-1}.

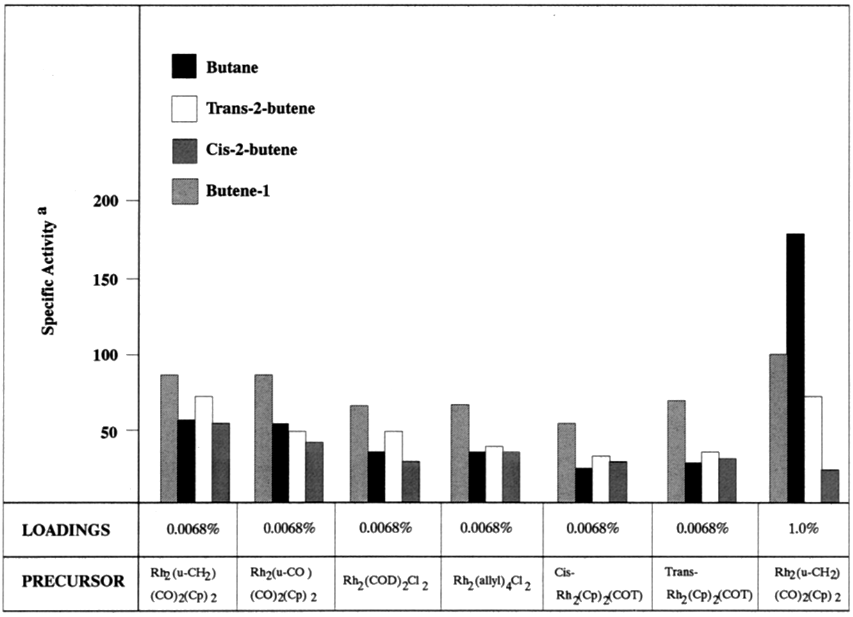

FIG. 7. Product distributions in the reaction of 1,3-butadiene with H_2 at 30°C on Rh/C. The catalysts were prepared from different dirhodium organometallics by activating at 200°C in H_2. ^{a} Mol product · (Mol Rh)$^{-1}$ · h^{-1}.

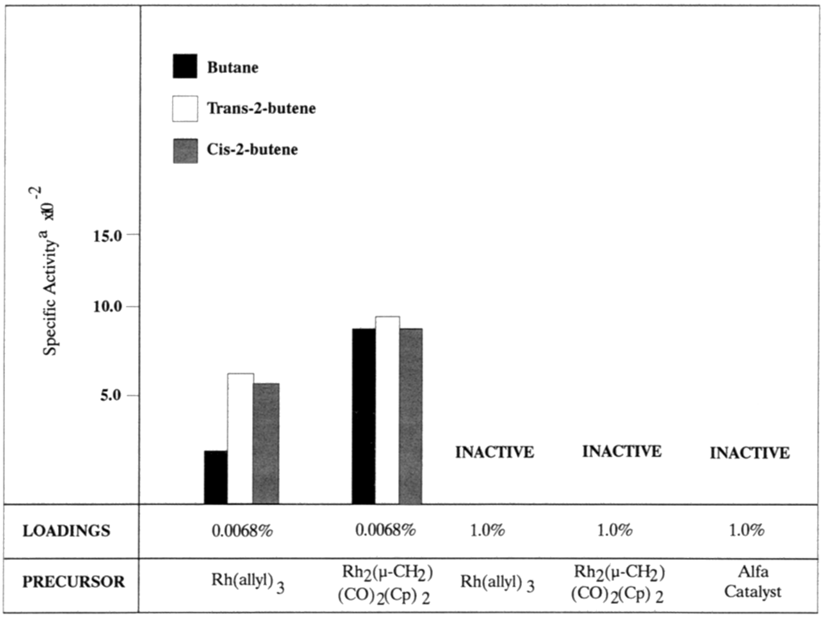

FIG. 8. Product distributions in the reaction of 1-butene with H_2 at 30°C on Rh/C. The catalysts were (1) prepared by reduction in H_2 at 200°C, (2) treated with trimethylphosphine at RT, (3) re-reduced at 125°C with H_2 and 1-butene. ^{a} Mol product · (Mol Rh)$^{-1}$ · h^{-1}.

catalysts. This difference between high- and low-loading catalysts leads to the conclusion that the low-loading active sites are different from metallic active sites of high-loading catalysts. Again, the low-loading catalysts from different dirhodium organometallics behave similarly, indicating the same active sites from the six dirhodium precursors. This active site is the same as that recognized by the low-loading plateau (Table 4), designated *B*.

These low-loading catalysts differ from the low-loading monorhodium catalysts (Figs. 3 and 4), leading to the conclusion that *A* and *B* sites are different. The difference in hydrogenation of 1,3-butadiene is especially noteworthy: Catalyst *A* produces almost exclusively 1- and *cis*-2-butenes, while *B* has a higher overall but nonselective activity, making butane and three butenes. Catalyst *A* is remarkably effective in producing *cis*-2-butene.

DIFFERENCE IN POISONING WITH TRIMETHYLPHOSPHINE AND REACTIVATION OF *A*, *B*, AND HIGH-LOADING SITES

Low-loading (0.0068%) catalysts *A* and *B*, prepared respectively from Rh(allyl)$_3$ and $Rh_2(\mu\text{-}CH_2)(CO)_2Cp_2$, were compared with high-loading catalysts (1% Rh) after treatment to saturation with $(CH_3)_3P$ gas at room temperature: All catalysts became inactive. The low-loading deactivated catalysts regained their complete activity and characteristic *A* and *B* selectivities on treatment at 125°C with H_2 and 1-butene (see Fig. 8). The high-loading catalysts from Rh(allyl)$_3$, $Rh_2(\mu\text{-}CH_2)(CO)_2Cp_2$, or commercial Alfa catalyst, on treatment with $(CH_3)_3P$ at room temperature, could not be reactivated; they remained inactive after treatment with H_2 at 200°C, or after prolonged treatment at 125°C with H_2 and 1-butene. These observations again show a distinct difference between low- and high-loading catalysts, from which trimethylphosphine is readily displaced from *A* and *B* sites with 1-butene, but not from the sites of aggregated metal surfaces. These experiments strongly indicate that aggregated sites are not present in *A* or *B* catalysts, and that high-loading catalysts do not have *A* or *B* sites.

REACTION OF *A* SITES WITH ETHYLENE AND PROPYLENE

If an *A*-site catalyst is treated first with ethylene and then with trimethylphosphine, the preparation remains catalytically inactive after subsequent treatment with H_2 at 125°C. It can be brought to full original activity by treatment with 1-butene and H_2 at 125°C. This behavior is the same as that observed if the ethylene treatment is omitted and in both instances is attributed to a rhodium atom, saturatedly liganded with $(CH_3)_3P$.

However, propylene behaves differently when used in the same sequence. An *A* catalyst, treated first with propylene and then with trimethylphosphine, is subsequently reactivated by H_2 alone at 125°C, but makes, under these conditions, a new catalyst (not *A* selectivity). This new non-*A* catalyst is alternatively made by treating Rh(allyl)$_3$-on-carbon with trimethylphosphine, followed by activation with hydrogen at 125°C. This trimethylphosphine-modified catalyst can be brought to full original activity by treatment with 1-butene and H_2 at 125°C. Thus, *A* sites react with propylene to make supported trisallylrhodium or some other rhodium–propylene compound with identical behavior toward trimethylphosphine. The treatment of *A* sites with ethylene produces no recognizable alteration of the site.

High-loading catalysts put through similar sequences with ethylene or propylene, followed by treatment with trimethylphosphine, cannot be activated under any conditions. Clearly, high-loading catalyst behavior toward trimethylphosphine is not modified by prior treatment with propylene, thereby providing another indication that *A* sites are not present in high-loading catalysts.

MIGRATION AND AGGREGATION OF RHODIUM ATOMS ON CARBON

When a low-loading (0.0068% Rh) *A* catalyst, prepared from trisallylrhodium, was heated in the presence of hydrogen at temperatures between 125 and 200°C, there was no alteration of catalytic properties (studied at 30°C). However, treatment with H_2 at 300°C affects a distinct change in specific activity and selectivity (Fig. 9), the catalytic properties approaching that of a high-loading catalyst. This result was duplicated with the precursor, $CpRh(C_2H_4)_2$ (Fig. 9). We suggest that these results identify the conditions for migration and clustering of rhodium atoms in *A* catalyst.

RECONSTRUCTION OF ACTIVE SITES IN HIGH-LOADING CATALYSTS

During hydrogenation of 1,3-butadiene over high-loading catalysts (from any precursor) at 30°C, in the early stages the activity of the catalysts increases with time; subsequently there is a gradual decrease in activity (Fig. 10). However, with low-loading catalysts, *A* or *B*, from any precursor, percentage conversion decreases with time; there is no initial increase in activity (see Fig. 11, illustrating for catalyst A). These observations can be rationalized as follows: when 1,3-butadiene interacts with the metal surface, the surface morphology is altered (sites reoriented) for better interaction with butadiene, with a consequent increase in percentage conversion during the early use of the catalyst; after reorientation is finished, catalyst activity suffers the customary deterioration. However, for mono- or diatom sites, reorientation with respect to neighbor metal atoms would be irrelevant, and thus one would not expect, as observed, an initial increase in efficiency as found with high-loading catalysts.

Reconstruction to platinum particles of higher activity was reported by Burwell and

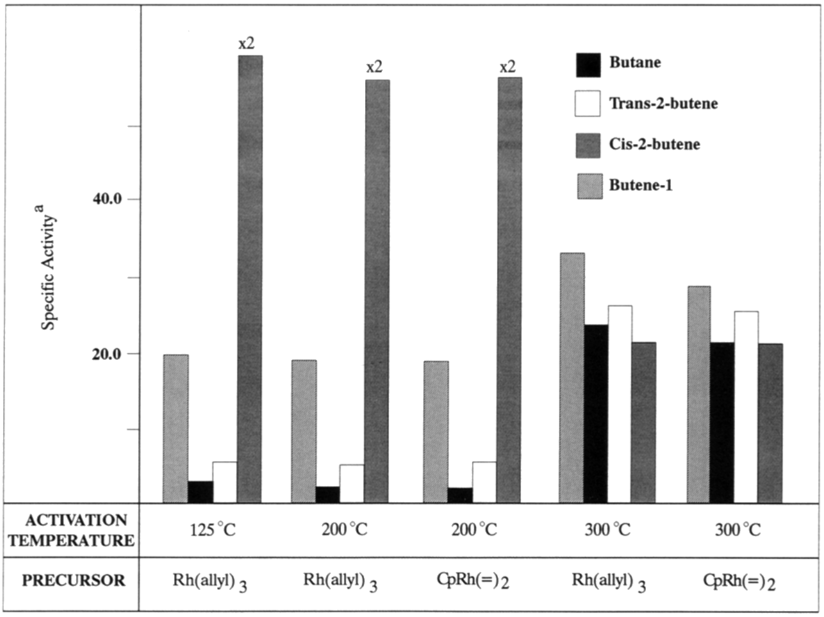

FIG. 9. Product distributions in the reaction of 1,3-butadiene with H_2 on 0.0068% Rh/C at 30°C as a function of activating temperature. The catalysts were prepared from different monorhodium organometallics by activating with H_2 at different temperatures. [a] Mol product · (Mol Rh)$^{-1}$ · h^{-1}.

co-workers (*18*) for the hydrogenation of alkynes.

DISCUSSION

The loadings of less than 1 atom/250 nm^2 required for *A* and *B* catalysts are apparently too low for the physical methods currently employed to describe surface morphologies. However, these low-loading catalysts have been clearly differentiated from high-loading catalysts by examining a number of inde-

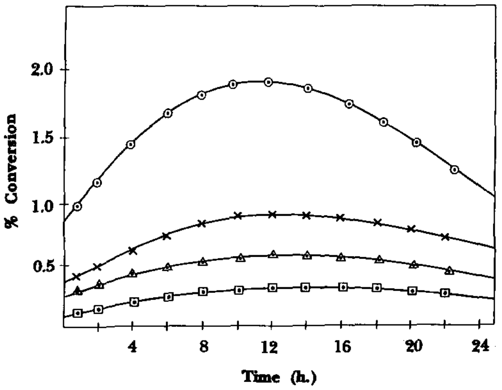

FIG. 10. Course of the hydrogenation of 1,3-butadiene at 30°C on 1.0% Rh/C. The catalyst was prepared from a Rh(allyl)$_3$ precursor by activating at 125°C.

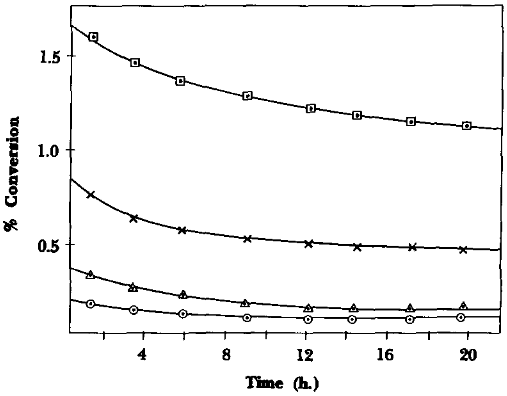

FIG. 11. Course of the hydrogenation of 1,3-butadiene at 30°C on 0.0068% Rh/C. The catalyst was prepared from a Rh(allyl)$_3$ precursor by activating at 125°C in H_2.

pendent chemical properties: the trimethylphosphine-selective poisonings indicate the absence of aggregated sites in *A* and *B* catalysts (full activity recovered) and, conversely, the absence of these sites in high-loading catalysts (no activity recovered). It is apparent that this alteration of characteristics is not a monotonic function of loading, but instead follows an *S*-function over a factor of 10 in loadings, with different plateaus in the high- and low-loading regions. Each of the plateaus is indicative of a region of uniformity of active site, independent of loading. Further, the low-loading regions must be uniform in dispersion, since there is no site or selectivity dependency on loading. Considering that these catalysts required for their preparations that precursor be distributed <1 molecule/250 nm^2, it is reasonable to conclude that each of the low-loading plateaus requires a different unique monodisperse site description for *A* and *B*.

It seems reasonable that for small clusters (perhaps one to six atoms) the chemical (and catalytic) properties will differ notably, but beyond those numbers the distinction from large aggregates will be negligible (note that it has been demonstrated that rafts of 8–12 atoms and bulk metal show the same selectivities on alumina). Thus, a model to explain the differences in *A*, *B*, and high-loading behavior *which rejects* the proposal that *A* and *B* have mono- and diatom sites, respectively, must assign a value (or values) of 3–6 for one of these catalysts and a different set for the other; if some combination of these values is specified, it must be invariant with dilution. Clearly, it requires a high degree of special pleading for a diffusion model, starting with mononuclear or binuclear precursors immobilized at loadings <1 molecule/250 nm^2 to make, during activations, single-size particles of three, four, five, or six atoms, or an invariant ratio of these, regardless of loading! It puts a strain on credulity to attribute *A* and *B* behavior to two distinctly different degrees of aggregation, other than 1 and 2, which are unaltered by alterations of precursor loadings from 1 molecule/250 nm^2 down to 1 molecule/6250 nm^2.

Although no single one of the experimental approaches (summarized below) requires the conclusion that *A* and *B* sites are mono- and diatomic, respectively, *each of the sets of observations is consistent with that assignment,* with no special pleading.

1. On alumina support 8–12 atom rafts and bulk metal, low- and high-loading, rhodium catalysts have the same selectivity.
2. On Monarch 880 carbon support, high-loading rhodium catalysts obtained from both mononuclear and binuclear organorhodium precursors are identical.
3. On this same carbon support, at low loadings, four mononuclear organorhodium precursors make catalyst *A*, and six binuclear organorhodiums make catalyst *B*. *A* and *B* are distinctly different from one another, and from the high-loading catalyst. Catalyst *A* is strikingly unique in the hydrogenation of 1,3-butadiene, making *cis*-2-butene uncontaminated by *trans*.
4. Catalyst *A* is stable below 200°C; at 300°C *A* is converted to a catalyst with the same properties as the high-loading catalyst.
5. The high-loading catalyst is completely and *irreversibly* deactivated by trimethylphosphine; *A* and *B* are also made inactive by trimethylphosphine, but can be reversed to full original activities and selectivities with hydrogen and 1-butene at 125°C, conditions which have no effect on the deactivated high-loading catalyst.
6. Catalyst *A* reacts with propylene to make a product indistinguishable from trisallylrhodium-on-carbon in its reaction with trimethylphosphine, making a new ligand-modified *A* catalyst; this modified *A* is converted to *A* with hydrogen and 1-butene at 125°C. This same modified *A* catalyst can be made by treating trisallylrhodium-on-carbon with trimethylphosphine. Rodium in high-loading does not undergo these reactions; intervention by propylene to preserve

activity does not occur. This distinction is the same as that observed for free atoms and bulk metal.

7. A number of ligand-modified catalysts related to *A* or *B* will be described elsewhere. They are interrelated by way of conversions within the *A* or *B* system, without crossover. With high loading these same ligands do not modify the catalysis properties.

8. High-loading rhodium-on-carbon reconstructs at 30°C in hydrogen/1,3-butadiene atmosphere to improve its efficiency in the early stages of the reaction. The low-loading catalysts, *A* and *B*, show no increase in efficiency.

9. Less than monolayer adsorption of precursors on Monarch 880 carbon (<1 molecule/250 nm^2) is required to make *A* or *B*.

It is reasonable to ask whether the support sites which immobilize the Rh_1 or Rh_2 in *A*- or *B*-type catalysts are the major one recognized for carbon surfaces. The requirement that precursors be present at <1 molecule/250 nm^2 to achieve *A* or *B* plateaus gives a strong indication that some highly unusual feature on the Monarch 880 carbon surfaces is being used to immobilize the precursors, and possibly, but not necessarily, the ligand-free atoms or diatoms. If the plateau phenomena are attributed to saturation of these sites, then they are present approximately one per 10,000 carbon surface atoms. It is hoped that further work will help to characterize this surface feature.

SUMMARY

1. Two new rhodium-on-carbon catalysts have been made from organometallic precursors, starting with loadings less than 1 molecule/250 nm^2. These ligand-free catalyst sites are assigned compositions Rh_1 and Rh_2, the same as the nuclearity of the precursor. The properties of each of these catalysts is distinctly different; also they differ from the high-loading catalysts.

2. These catalysts are stable at temperatures below 200°C; above 200°C, the Rh_1 catalyst sinters, altering to the high-loading type.

3. Rhodium metal surface reconstructs in a hydrogen/1,3-butadiene atmosphere at room temperature.

OVERVIEW

The application of these catalyst preparation methods to appropriate precursors with other metals should make them accessible in analogous dispersions. The chemical properties of these species may resemble those of the free species, although some alteration should be anticipated as a consequence of bonding to the carbon surface. The preparation of electrodes with these forms of dispersed metals may prove to be a useful innovation.

EXPERIMENTAL

Catalyst precursor compounds. Several compounds were used as catalyst precursors. $Rh(C_3H_5)_3$ (*19*), $Rh_2(C_3H_5)_4(\mu\text{-}Cl)_2$ (*19*), and $CpRh(C_2H_4)_2$ (*20*) were prepared and purified according to published procedures. $RhCl_3 \cdot 3H_2O$ and $Rh_2(COD)_2(\mu\text{-}Cl)_2$ were purchased from Alfa Chemical Co. $Cp^*Rh(C_2H_4)_2$, $CpRh(CO)_2$, $[Rh_2(\mu\text{-}CH_2)(CO)_2Cp_2]$ and were gifts from Professor W. A. Herrmann, TU-Munchen. $[Rh_2Cp_2(\mu\text{-}COT)]$(*cis*) and $[Rh_2Cp_2(\mu\text{-}COT)]$(*trans*) were gifts from Dr. A. Salzer, U. Zurich.

Solvents. All solvents used were distilled over Na/K alloy under N_2 atmosphere, and then degassed prior to use. The water used was doubly distilled and was degassed. Benzene was found to be the most suitable solvent for all organometallic compounds used.

Supports. The carbon support used was an acid-washed Monarch 880, 300 m^2/g carbon black from Cabot Corp. It was then further purified by reducing in H_2 (100 ml/min) at 1000°C for 24 h to remove oxygen and sulfur impurities. The alumina support used was a 200 m^2/gm γ-alumina from Degussa Corp. It was degassed under vacuum at 300°C for 24 h before use inside the glovebox.

Gases. Ultrahigh-purity hydrogen (Linde) and helium (Linde) used for catalyst runs were further purified by passing through oxy-traps (Alltech Associates) and molecular sieve traps. 1-Butene (Philips, research grade) and 1,3-butadiene (MG Industries, instrument grade) were dried over molecular sieves (Linde 4A), distilled *in vacuo* into heavy-walled glass storage tubes, and degassed before use.

Catalyst precursor preparation. All catalyst manipulations were carried out in an oxygen-free atmosphere using standard Schlenk and glovebox techniques. In a typical catalyst preparation, a solution of an organometallic compound was added with stirring to a slurry of carbon (~1–2 g) in benzene. After stirring for about half an hour, the solvent was slowly removed by pumping, and the dry sample was then stored in the inert glovebox.

Catalyst preparation and evaluation. The apparatus used for kinetic evaluation of the catalysts included a gas manifold for mixing gases in appropriate ratios, a small glass-fitted U-shaped catalyst bed which could be mounted on the catalyst line using two Cajon fitted two-way ball valves, and a catalyst bed interface which provides access to the gas manifold, vacuum line, and gas chromatography detection system.

In a typical catalyst evaluation the catalyst bed was loaded with the desired amount of an organometal-on-carbon (usually 0.3 to 0.4 g) in the glovebox. The sealed catalyst bed was then attached to the manifold and reduced at the desired temperature (usually 200°C) for 3 h in H_2 (100 ml/min). After reduction, the catalyst bed was purged with helium (89 ml/min) as the bed gradually cooled to room temperature. The temperature was maintained at 30°C with a stirred oil bath using a thermistor-controlled temperature regulator. A mixture of 1-butene or 1,3-butadiene/H_2/He (1/10/89) was passed through the catalyst bed at a total flow of 100 ml/min. Mass flow controllers (±1% calibrated Brooks Model 5850) were used to meter reactive gases. The effluent from the catalyst bed was sampled without interrupting flow, sending the sample directly to the FID gas chromatograph (30 ft × $\frac{1}{4}$ in.) 30% propylene carbonate on Gaschrom R), output monitored with a Hewlett–Packard 3390A integrator.

The total conversion of products was maintained below 10% (differential mode) in order to minimize concentration gradients. In the event total conversions exceeded 10%, the catalyst sample was dry-diluted in the glovebox with an appropriate amount of support. Rates were calculated with Eq. [1].

$$r = \frac{Fdx}{w} \qquad [1]$$

where r is the ratio of moles product/mole metal/h; F is the feed rate of 1-butene or 1,3-butadiene; dx is the differential conversion; and w is the number of moles of metal.

The catalyst activity was generally monitored for 20–24 h. All rates were reported as initial rates. These were determined by plotting the percentage conversion as a function of time and then extrapolating the linear portion to zero time. This was found to be reproducible (±5%).

COLLECTION OF LIGANDS OBTAINED BY REDUCING CATALYSTS

A. *From Rh(allyl)$_3$ on Carbon*

Typically 3.0 gm of 0.02% Rh/C, in the form of Rh(allyl)$_3$-on-carbon was taken in a catalytic U-tube and reduced at 125°C in H_2 (20 ml/min). The effluent gases were passed through a −196°C trap for 5 h, and then by pumping. The amount of propane collected (16.0×10^{-3} mmol) was determined by chromatographing the trap contents. This is 90.5% of the theoretical yield, based on 3 mol C_3H_8 per $Rh(C_3H_5)_3$. Insignificant further amounts of propane were obtained, when the above catalyst was re-reduced at either 200 or 300°C, indicating complete removal of ligands at 125°C.

B. From $Cp^*Rh(C_2H_4)_2$ on Carbon

The procedure was identical to that described above, using $Cp^*Rh(C_2H_4)_2$. In this case, 2.8 g of 0.02% Rh/C material was reduced. The effluent gases were first passed through a −78°C trap, and then through −196°C. When the catalyst was reduced at 125°C in H_2, 10.4×10^{-3} mmol of ethylene (94.9% yield) was collected at the −196°C trap. When the above catalyst was re-reduced at 200°C, contents at the −78°C trap were analyzed by GC and GC/MS. An isomeric mixture of pentamethylcyclopentane (4.1×10^{-3} mmol, 74.8% yield) and tetramethylcyclopentane (2.7×10^{-4} mmol, 4.9% yield) was obtained. Yields were determined by calibrating with pentamethylcyclopentadiene. No more ethylene or cyclopentane derivatives were obtained when the catalyst was further reduced at 300°C.

C. From $Rh_2(\mu\text{-}CH_2)(CO)_2Cp_2$ on Carbon

Three grams of 0.0068% Rh/C catalyst precursor was reduced in H_2 at 200°C and the effluent gases were passed through a −78°C trap. The contents at the −78°C trap were analyzed by GC and GC/MS. Methanol (1.55×10^{-3} mmol, 78.2% yield) and cyclopentane (1.59×10^{-3} mmol, 80.2% yield) were obtained. Yields were determined by calibrating with an authentic sample.

D. From $Rh_2(COD)_2(\mu\text{-}Cl)_2$ on Carbon

The procedure was identical to that described above. In this case, contents at the −78°C trap were analyzed by GC and GC/MS and found to be mostly cyclooctane (1.69×10^{-3} mmol, 85.2% yield), along with a small amount of cyclooctene (9.9×10^{-5} mmol, 5.0% yield); no chloride was found. When the reduced catalyst was washed with distilled water, the washing gave a positive test for chloride with silver nitrate solution.

E. Poisoning of Catalysts with Trimethylphosphine

Typically 0.3 g of a catalyst was taken in the catalyst bed, and an excess of trimethylphosphine gas was injected to the catalyst by a gas-tight syringe, in inert atmosphere. After about half an hour, the catalyst tube was connected to the catalyst line and excess trimethylphosphine was removed either by pumping or by flushing with helium for 5 h. In all cases, phosphine-treated catalyst was inactive at 30°C (H_2 + 1-butene). Subsequent treatments are described in text.

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REFERENCES

1. Klabunde, K. J., "Chemistry of Free Atoms and Particles." Academic Press, New York, 1980.
2. Yates, D. J. C., Murrel, L. L., and Prestridge, E. B., *J. Catal.* **57,** 41 (1979).
3. Yates, D. J. C., Murrel, L. L., and Prestridge, E. B., *in* "Growth and Properties of Metal Clusters" (J. Bourdon, Ed.), p. 137. Elsevier, New York, 1980.
4. Graydon, W. F., and Langan, M. D., *J. Catal.* **69,** 180 (1981).
5. Yates, J. T., Jr., Duncan, T. M., Worley, S. D., and Vaughn, R. W., *J. Chem. Phys.* **70,** 1219 (1979).
6. Rice, C. A., Worley, S. D., Curtis, C. W., Guin, J. A., and Tarrer, A. R., *J. Chem. Phys.* **74,** 6487 (1981).
7. Cavanagh, R. R., and Yates, J. T., Jr., *J. Chem. Phys.* **74,** 4150 (1981).
8. Yates, J. T., Jr., Duncan, T. M., Worley, S. D., and Vaughn, R. W., *J. Chem. Phys.* **70,** 1225 (1979).
9. Van't Bilk, H. F. J., Van Zon, J. B. A. D., Hulzinga, T., Vis, J. C., Koningsberger, D. C., and Prins, R., *J. Phys. Chem.* **87,** 2264 (1983).
10. Via, G. H., Meitzner, G., Lytle, F. W., and Sinfelt, J. H., *J. Chem. Phys.* **79,** 1527 (1983).
11. Ward, M. D., and Schwartz, *J. Mol. Catal.* **11,** 397 (1981).
12. Foley, H. C., DeCanio, S. J., Tau, K. D., Chao, K. J., Onuferko, J. H., Dybowski, C., and Gates, B. C., *J. Amer. Chem. Soc.* **105,** 3074 (1983).
13. Daza, L., Ayuso, T. G., Mendioroz, S., and Pajares, J. A., *Appl. Catal.* **13,** 295 (1985).
14. Boudart, M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 20, p. 153. Academic Press, San Diego, 1969.
15. Baetzold, R. C., *Surf. Sci.* **36,** 123 (1972).
16. The decrease of specific activity with decreasing metal loadings can be explained as follows: It is reasonable to expect an increasing percentage of smaller aggregate, or monoatomic sites, with pro-

gressively lower metal loadings; since there is no indication of altered selectivity, apparently these lower aggregated sites are not active; the progressive loss of activity suggests that with lesser aggregation (perhaps monoatoms) the active sites are lost, possibly by reaction with the support to make a catalytically inactive rhodium aluminate. Rafts of 8–12 atoms appear to be the smallest viable active sites on alumina.

17. It *may* be significant that hydrogenation of butadiene with homogeneous mononuclear catalysts produce *cis*-2 and 1-butene, in approximately the same ratio as that obtained with the *A* catalyst. On aggregated metal surfaces butadiene can coordinate both double bonds in the *s-trans* configuration and thus reasonably *trans*-2-butene and butane would be products, in addition to the others. However, in order to coordinate both double bonds with a metal atom, butadiene must be in the *s-cis* form, thus favoring *cis*-2-butene formation by 1,4-addition of hydrogen. See Raythatha, R., and Pennavalia, T. J., *J. Organometal. Chem.* **218,** 115 (1981).
18. Kung, H. H., Pellet, R. J., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **98,** 5603 (1976).
19. Powell, J., and Shaw, B. L., *J. Chem. Soc. A*, 583 (1968).
20. King, R. B., *Inorg. Chem.* **2,** 528 (1963).