ELECTRONIC SUPPLEMENTARY INFORMATION

Adsorption and transformations of ethene on hydrogenated rhodium clusters in faujasite-type zeolite. A computational study

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1. Thermodynamic model

We used the relative Gibbs free energies of the $C_2H_x/H_{k-x}Rh_n$ complexes under study to construct a thermodynamic model for the hydrogen coverage as function of the temperature and the H₂ pressure. The relative Gibbs free energy, $\Delta G(C_2H_x/H_{k-x}Rh_n)$, of a structure $C_2H_x/H_{k-x}Rh_n$ (n = 3, 4) is defined via its formal formation from the system with adsorbed ethene and lowest hydrogen coverage, C_2H_4/HRh_n supported in the zeolite, after adsorption of (k-5)/2 H₂ molecules from the gas phase:

 $C_2H_4/HRh_n + (k-5)/2 H_2 \rightarrow C_2H_x/H_{k-x}Rh_n$

 $\Delta G(C_2H_x/H_{k-x}Rh_n) = \Delta H(C_2H_x/H_{k-x}Rh_n) - T\Delta S(C_2H_x/H_{k-x}Rh_n)$

Here $\Delta H(C_2H_x/H_{k-x}Rh_n)$ is the corresponding change in enthalpy (including the electronic energy and the zero-point energy correction), and $\Delta S(C_2H_x/H_{k-x}Rh_n)$ is the change in entropy, determined in standard fashion from the partition functions q of the corresponding clusters and the appropriate number of H₂ molecules in the gas phase.¹ The free rotation and the free translation were taken into account only for the H₂ molecules, but not for the systems $C_2H_x/H_{k-x}Rh_n$ and C_2H_4/HRh_n . When calculating the vibrational entropy we included the vibrational modes only of the adsorption complexes $C_2H_x/H_{k-x}Rh_n$ and the atoms of the three four-member rings where these complexes are adsorbed.

The mole fractions, α_m , of all adsorption complexes at specific temperature and hydrogen pressure, P(H₂), were determined by the equilibrium constant, K(C₂H_x/H_{k-x}Rh_n), which on the other hand were obtained from the relative Gibbs free energy of the species:

 $K(C_2H_x/H_{k-x}Rh_n) = exp[-\Delta G(C_2H_x/H_{k-x}Rh_n)/RT] = [\alpha_k (RT)^{(k-5)/2}] / [\alpha_0 P^{(k-5)/2}(H_2)]$ To define the molar fractions for complexes with various amounts of hydrogen, we used the following expressions:

$$\alpha_{0} = \left\{ 1 + \sum_{k \text{ odd}}^{k_{\text{max}}} \left[\left[P(H_{2}) / RT \right]^{(k-5)/2} K(C_{2}H_{x} / H_{k-x}Rh_{n}) \right] \right\}^{-1}$$

$$\alpha_{k} = \alpha_{0} \left[P(H_{2}) / RT \right]^{(k-5)/2} K(C_{2}H_{x} / H_{k-x}Rh_{n})$$

Here k_{max} is 13 for Rh₄ and 11 for Rh₃ species. Note that these expressions account only the species with odd values of k, which corresponds to interpolating the Gibbs free energy values for the species with even value of k, similar to the approach that we reported earlier for hydrogenated iridium clusters in a zeolite.²

2. Comments on the structure and the binding of the organic species

Rh₃. *Ethene.* For the cluster HRh₃ we modeled two coordination modes of ethene, di- σ - and π -bonded (Fig. S1). In the first case, there are two Rh-C contacts, from each C atom to a different Rh atom. One of the Rh-C distances is ~204 pm and the other one is somewhat longer, in the range 205–211 pm, depending on the amount of hydrogen ligands on the cluster. The C-C bond is ~149 pm for all hydrogen coverages, by about 3 pm shorter than the single bond in an isolated ethane molecule, 152 pm. The two C atoms of π -bonded ethene interact with a single Rh center and the Rh-C distances are longer than those for the di- σ -bonded species, increasing the number of hydrogen ligands of the metal moiety, from 211 pm for π -C₂H₄/HRh₃ and 213 pm for π -C₂H₄/H₃Rh₃ to 218 pm for π -C₂H₄/H₅Rh₃ and 228 pm for π -C₂H₄/H₇Rh₃. As expected, the C-C bond is shorter than that of di- σ -bonded ethene, decreasing with hydrogen loading from 142 pm for π -C₂H₄/HRh₃ and π -C₂H₄/H₃Rh₃ to 138 pm for π -C₂H₄/H₇Rh₃, approaching the value calculated for an isolated ethene molecule, 133 pm. This change of the C-C distance indicates the expected weakening the ethene-rhodium interaction due to bond competition when the hydrogen coverage increases.

*Rh*₃. *Ethyl*. On-top coordination of the ethyl intermediate at a Rh center was determined most favorable, irrespective of the H loading of the Rh₃ cluster. The one Rh-C contact varies from 202 pm to 206 pm, and the C-C bond varies in the range 151-153 pm, typical for single C-C bond.

Rh₃. Ethylidene and Ethylidyne. Ethylidene prefers to coordinate in a bridging fashion as the C atom from the CH fragment interacts with two Rh centers (Fig. S2). The C-C bond is 150 pm and the Rh-C distances vary from 197 pm to 206 pm, depending on the H loading. The ethylidyne intermediate coordinates in three-fold fashion to all centers of Rh₃ (Fig. S1). The C-C bond is 149 pm and the three Rh-C distances are in the range 191–204 pm (195 pm on average).

*Rh*₃. *Vinyl*. Vinyl coordinates to one of the Rh-Rh bonds of the cluster where the carbon center of the CH moiety binds to two Rh atoms with Rh-C distances of 194–216 pm and the CH₂ moiety forms one slightly longer Rh-C bond, 214–219 pm. The C-C bond is 142 pm, corresponding to an activated C-C double bond. This coordination of vinyl differs from that determined on a Rh(111) surface³ or on small transition metal clusters⁴ where the intermediate interacts with three metal centers and the C-C bond is parallel to the surface defined by those centers. In our model system of zeolite-supported Rh₃ cluster, the latter coordination mode was calculated to be less stable, likely due to the small size of the metal species.

Rh₃. Vinylidene. We will discuss only the structure CH₂C/H₃Rh₃ with lowest number of H adsorbed on the cluster because, for increasing H loading, the Rh-Rh distances increase

strongly to more than 300 pm, resulting in the destruction of the Rh₃ cluster. The C atom of vinylidene coordinates in three-fold fashion to all Rh centers of the cluster with Rh-C distances of 191 pm, 194 pm, and 200 pm. The remaining CH₂ fragment forms only one longer Rh-C bond, at 215 pm. The C-C bond of this intermediate was calculated to 142 pm.

Rh₄. Ethene. For the Rh₄ cluster, we also modeled the π - and the di- σ -bonded coordination modes of ethene (Figs. S3, S4). The two Rh-C bonds in each of the complexes of di- σ -bonded ethene have essentially the same length, in contrast to the Rh₃ cluster where the two bonds differ by 2–6 pm for the various complexes. The Rh-C bonds of the Rh₄ cluster models elongate with increasing H loading of the cluster, from 203 pm in di- σ -C₂H₄/HRh₄ to 215 pm in di- σ -C₂H₄/HgRh₄. The C-C distance, ~147 pm, is slightly shorter, by 2 pm, than calculated for di- σ -ethene on Rh₃, and by 5 pm shorter than calculated for a free ethane molecule. The C-C distance of π -bonded ethene, ~142 pm, is independent of the hydrogen loading, at variance from the trend for Rh₃ cluster. This indicates that the (additional) apical Rh atom, where ethene is coordinated, experiences a minor influence by hydrogen ligands. The two Rh-C contacts of π -bonded are in the range 211–216 pm, by 1–8 pm shorter than those calculated for the Rh₃ cluster.

Rh₄. Ethyl. The C₂H₅ intermediate on Rh₄ is discussed in detail in the main text.

*Rh*₄. *Ethylidene and Ethylidyne*. The coordination modes of ethylidene and ethylidyne intermediates on the Rh₄ cluster are similar to those determined for the Rh₃ cluster. The Rh-C and C-C distances in the ethylidene complex, 195-205 pm and 150-152 pm, respectively, fall in similar ranges as in the complexes involving Rh₃ clusters. Ethylidyne interacts with three Rh centers. In complexes with more than one H ligand (from the gas phase), this coordination induces a change of the tetrahedral shape of the cluster as one of the Rh-Rh bond breaks (involving a Rh atom interacting with the organic ligand); the corresponding distance is longer than 300 pm.

*Rh*₄. *Vinyl and Vinylidene*. These two intermediates coordinate to Rh₄ in essentially the same way as to Rh₃. For complexes of vinyl, the Rh-C distances of the CH₂ fragment were calculated by 1–18 pm longer than in the analogous structures with Rh₃. The C-C bond is 139 pm for CH₂CH/H₂Rh₄ complex and 142 pm for higher H loading of the cluster. Similar to the complexes with Rh₃, the adsorption of vinylidene leads to a distortion of the Rh₄ cluster for high amounts of H ligands. For structures with $k \ge 9$ (with 6, 8, and 10 H ligands on the Rh cluster) two of the Rh-Rh distances are longer than 300 pm.



Figure S1. Optimized structures of Rh₃ complexes of π -ethene, di- σ -ethene and ethylidyne (columns from left to right) for all numbers k of total H atoms modeled.



CH₃CH/HRh₃



CH₂CH/H₂Rh₃



CH₂C/H₃Rh₃



CH₃CH₂/Rh₃



CH₃CH/H₃Rh₃

CH₂CH/H₄Rh₃







CH₃CH/H₂Rh₃



CH₃CH/H₅Rh₃















CH₃CH/H₇Rh₃

CH₂CH/H₈Rh₃

CH₂C/H₉Rh₃

CH₃CH₂/H₆Rh₃

Figure S2. Optimized structures of Rh₃ complexes of ethylidene, vinyl, vinylidene and ethyl (columns from left to right) for all numbers k of total H atoms modeled.





 π -C₂H₄/HRh₄





 π -C₂H₄/H₃Rh₄

di- σ -C₂H₄/H₃Rh₄

CH₃C/H₄Rh₄





di-σ-C₂H₄/H₅Rh₄



CH₃C/H₆Rh₄



 π -C₂H₄/H₅Rh₄

 π -C₂H₄/H₇Rh₄



 π -C₂H₄/H₉Rh₄



 $di\text{-}\sigma\text{-}C_2H_4/H_7Rh_4$







CH₃C/H₈Rh₄





Figure S4. Optimized structures of Rh_4 complexes of ethylidene, vinyl, vinylidene and ethyl intermediates (columns from left to right) for all numbers k of total H atoms modeled.



Figure S5. Location of the complexes modeled in the faujasite channel, shown on the example of the complex C_2H_5/H_8Rh_4 .

3. Comments on the electron density distribution

The atomic charges of the modeled $C_2H_x/H_{k-x}Rh_n$ complexes were calculated using a Badertype analysis.⁵ The change of the total charges of the $C_2H_x/H_{k-x}Rh_n$ complexes with increasing k, i.e., the total amount of H atoms in the system, is shown in Figure S6 for the Rh₃ and Rh₄ complexes; the calculated values also are provided in Tables S1 and S2. The results for the vinylidene complexes on Rh₃ are omitted because this ligand induces a break-up of the metal cluster for k > 5.

The total positive charge of the complexes on Rh₃ varies in the range 0.66–0.77 e. These values are by only 0.05–0.07 e larger than the corresponding H_mRh₃ complexes without organic species, determined previously,⁶ as the total charge of all modeled complexes varies only within 0.11 e. This minor variation of the total charge of the complexes is likely due to the restricted ability of the charge counterbalancing zeolite framework to exchange electron density with the guest species. Stronger variations, within 0.43 e, are observed for the charge of the metal moiety due to exchange of electron density with the organic and hydrogen ligands. In the various complexes the Rh centers that interact with O atoms of the zeolite framework and with C atoms of the ligands show the highest charge, 0.35–0.48 e. Thus, the Rh moiety carries slightly higher positive charge in the complexes with ethylidyne, vinyl and vinylidene intermediates where three or four Rh-C bond are formed, 0.97-1.18 e, compared to the metal moiety in the complexes with ethyl species (0.75-0.90 e) or ethene species (0.87-0.90 e)1.04) with one or two Rh-C contacts, respectively (Table 1). On the other hand, terminal H ligands coordinated in the form of activated H₂ molecules (see the structures with the highest hydrogen loading in Figs. S1 and S2) leads to a lower total positive charge of the complexes. These hydrogen species typically have small positive charges, 0.01–0.09 e.

Both the variation of the total charge of the complex, 0.15 e, and of the metal moiety, 0.63 e, for Rh₄ complexes are somewhat larger than the corresponding values for the Rh₃ cluster (Table S2), likely due to the additional charge of the forth metal center. For Rh₄ complexes, the positive total charge in general decreases with increasing the H content (Fig. S6B). The highest total charge, 0.77 e, was calculated for the η -CH₃CH₂/Rh₄ complex, without any hydrogen ligands adsorbed on the metal moiety. The lowest total charge, 0.62 e, was calculated for the complex π -C₂H₄/H₉Rh₄. In this structure the organic ligand is bonded to a Rh atom far from the Al center of the zeolite framework. Similarly to Rh₃ complexes, the metal moiety in the complexes with ethylidyne, vinyl and vinylidene, 0.94–1.33 e, has slightly higher positive charge than the complexes with pseudo-ethyl or ethene ligands, 0.70–1.24 e (Table S2).

An earlier charge analysis of the metal moiety in hydrogenated transition metal clusters showed that the metal moiety is oxidized by H spillover form the bridging OH group of the zeolite^{6,7,8} This transfer accounts for 0.80 e of the positive charge of the clusters Rh₃ and Rh₄ when supported on a zeolite lattice. Considering the charge of the metal moiety in the complexes with lowest hydrogen loading, the adsorption of ethene is estimated to increase the degree of oxidation of the metal moiety, by 0.07 e for Rh₃ and 0.08 e for Rh₄, while for ethylidyne, vinyl and vinylidene as ligands the increase is by 0.17-0.36 e for Rh₃ and 0.14-0.37 e for Rh₄. On the other hand, for the complexes with ethyl intermediates without any H ligands adsorbed on the metal moiety, CH₃CH₂/Rh_n, the charge of the metal moiety is reduced to 0.75 e for Rh₃ and 0.70 e for Rh₄. Comparing the variations of the cluster charge with changes in the structure of the metal moiety, one may suggest a rough trend, namely that the increase of the charge of the metal moiety correlates with the breaking of one or more Rh-Rh bonds. The most noticeable examples are the complexes with vinylidene (with typically three or four Rh-C bonds), where the charge of the Rh_n moiety varies in the range 1.16–1.32 e (either for Rh₃ or Rh₄ cluster; Tables S1, S2) and in most cases some metal-metal bonds are broken (Figs. S2. S4).



Figure S6. Change of the total charge for modeled complexes of $C_2H_x/H_{k-x}Rh_3$ (A) and $C_2H_x/H_{k-x}Rh_4$ (B) with increasing the total number k of H atoms adsorbed. π -bonded ethene – dark blue squares, di- σ -bonded ethene – dark red rhombs, ethyl (or pseudo ethyl) – magenta triangles, ethylidyne – cyan circles, ethylidene – orange crosses, vinyl – grey stars. The vinylidene species are omitted in these graphs.

		Charge of	Total charge of	Charge of the
		Rh ₃ cluster	$C_2H_x/H_{k-x}Rh_3$ complex	organic ligand
di-σ-Ethene	di-o-C2H4/HRh3	0.87	0.72	-0.06
	$di-\sigma-C_2H_4/H_3Rh_3$	1.00	0.72	-0.10
	$di-\sigma-C_2H_4/H_5Rh_3$	1.04	0.70	-0.08
	$di\text{-}\sigma\text{-}C_2H_4/H_7Rh_3$	0.95	0.71	-0.04
π -Ethene	π -C ₂ H ₄ /HRh ₃	0.87	0.70	-0.04
	π -C ₂ H ₄ /H ₃ Rh ₃	0.94	0.70	-0.05
	π -C ₂ H ₄ /H ₅ Rh ₃	0.97	0.75	0.04
	π -C ₂ H ₄ /H ₇ Rh ₃	1.02	0.68	0.05
Ethyl	C ₂ H ₅ /HRh ₃	0.75	0.69	-0.06
	C_2H_5/H_2Rh_3	0.84	0.70	0.03
	C_2H_5/H_4Rh_3	0.90	0.70	-0.11
	C_2H_5/H_6Rh_3	0.88	0.69	0.07
Ethylidene	CH ₃ CH/HRh ₃	0.83	0.70	-0.05
	CH ₃ CH/H ₃ Rh ₃	0.92	0.72	-0.06
	CH ₃ CH/H ₅ Rh ₃	1.10	0.70	-0.06
	CH ₃ CH/H ₇ Rh ₃	0.87	0.77	-0.06
Vinyl	CH ₂ CH/H ₂ Rh ₃	0.98	0.72	-0.09
-	CH ₂ CH/H ₄ Rh ₃	0.98	0.67	-0.07
	CH ₂ CH/H ₆ Rh ₃	1.13	0.66	-0.04
	CH ₂ CH/H ₈ Rh ₃	1.04	0.69	-0.16
Ethylidyne	CH ₃ C/H ₂ Rh ₃	0.97	0.72	-0.07
	CH ₃ C/H ₄ Rh ₃	1.07	0.72	-0.04
	CH ₃ C/H ₆ Rh ₃	1.09	0.73	-0.07
	CH ₃ C/H ₈ Rh ₃	1.18	0.75	-0.06
Vinylidene	CH ₂ C/H ₃ Rh ₃	1.16	0.66	-0.22

Table S1. Calculated partial charges of the $C_2H_x/H_{k-x}Rh_3$ complexes.

		Charge of	Total abarga of	Charge of the
		Rh_4 cluster	$C_{2}H_{k}/H_{k}$ Rh ₄ complex	organic ligand
di-σ-Ethene	di-σ-C ₂ H ₄ /HRh ₄	0.88	0.70	-0.06
	di- σ -C ₂ H ₄ /H ₃ Rh ₄	1.14	0.67	-0.16
	di-σ-C ₂ H ₄ /H ₅ Rh ₄	1.24	0.66	-0.08
	di-σ-C ₂ H ₄ /H ₇ Rh ₄	1.17	0.67	-0.09
	di-σ-C ₂ H ₄ /H ₉ Rh ₄	1.09	0.67	-0.10
π -Ethene	π -C ₂ H ₄ /HRh ₄	0.89	0.67	-0.07
	π -C ₂ H ₄ /H ₃ Rh ₄	1.01	0.66	-0.11
	π -C ₂ H ₄ /H ₅ Rh ₄	1.05	0.66	-0.05
	π -C ₂ H ₄ /H ₇ Rh ₄	1.03	0.65	-0.08
	π -C ₂ H ₄ /H ₉ Rh ₄	1.17	0.62	-0.04
Ethyl	η-CH ₃ CH ₂ /Rh ₄	0.70	0.77	0.07
	η -CH ₃ CH ₂ /H ₂ Rh ₄	0.96	0.68	-0.03
	η-CH ₃ CH ₂ /H ₄ Rh ₄	1.03	0.69	0.00
	η-CH ₃ CH ₂ /H ₆ Rh ₄	1.14	0.68	0.01
	$\eta\text{-}CH_3CH_2/H_8Rh_4$	1.13	0.65	0.04
Ethylidene	CH ₃ CH/HRh ₄	0.91	0.73	-0.09
	CH ₃ CH/H ₃ Rh ₄	1.08	0.69	-0.06
	CH ₃ CH/H ₅ Rh ₄	1.18	0.67	-0.04
	CH ₃ CH/H ₇ Rh ₄	1.32	0.64	-0.06
	CH ₃ CH/H ₉ Rh ₄	0.96	0.71	-0.01
Vinyl	CH ₂ CH/H ₂ Rh ₄	0.94	0.67	-0.13
	CH ₂ CH/H ₄ Rh ₄	1.18	0.66	-0.11
	CH ₂ CH/H ₆ Rh ₄	1.13	0.68	-0.09
	CH ₂ CH/H ₈ Rh ₄	1.27	0.70	-0.10
	$CH_2CH/H_{10}Rh_4$	1.20	0.66	-0.11
Ethylidyne	CH ₃ C/H ₂ Rh ₄	0.98	0.74	-0.08
	CH ₃ C/H ₄ Rh ₄	1.21	0.70	-0.04
	CH ₃ C/H ₆ Rh ₄	1.12	0.69	0.00
	CH ₃ C/H ₈ Rh ₄	1.33	0.64	-0.06
	CH ₃ C/H ₁₀ Rh ₄	1.27	0.66	-0.06
Vinylidene	CH ₂ C/H ₃ Rh ₄	1.17	0.72	-0.13
	CH ₂ C/H ₅ Rh ₄	1.32	0.71	-0.15
	CH ₂ C/H ₇ Rh ₄	1.20	0.70	-0.15

Table S2. Calculated partial charges of the $C_2H_x/H_{k-x}Rh_4$ complexes.

4. Vibrational frequencies of the C₂H_x/H_{k-x}Rh_n complexes

The calculated harmonic frequencies of the characteristic vibrational modes of the organic moieties in the modeled complexes are presented in Tables S3 and S4. Here we discuss the frequencies of those organic species that were calculated to be dominant according to the thermodynamic model presented in Subsection 3.2.2 of the main text. These are the structures with π -bonded ethene, pseudo-ethyl, and ethylidyne.

For complexes of Rh₃ with π -bonded ethene the calculated anti-symmetric modes of the CH₂ groups vary with hydrogen loading in the range 3110–3172 cm⁻¹ and the symmetric in the range 3022–3072 cm⁻¹. Slightly narrower ranges were calculated for complexes with Rh₄ cluster, 3114–3150 cm⁻¹ for the anti-symmetric modes and 3028–3056 cm⁻¹ for the symmetric modes. As expected, due to the missing anharmonic corrections the calculated values are notably higher than the experimental frequencies of π -bonded ethene on rhodium. For example, experimental frequencies at 3021 cm⁻¹ and 3051 cm⁻¹ for Rh₆ clusters supported on MgO from IR spectroscopy were assigned to π -bonded ethene on Rh(111) surface.¹⁰

Ethylidyne intermediates were proposed to occur under reaction conditions of ethene hydrogenation.¹¹ For the CH₃C/H₂Rh₃, the asymmetric CH₃ stretching modes were calculated at 3018 cm⁻¹ and 3027 cm⁻¹ and the symmetric mode at 2938 cm⁻¹. For the complex CH₃C/H₈Rh₃ on the Rh₃ cluster with highest number of adsorbed H atoms, that was the dominant species according to our thermodynamic model (Fig. 5) under the experimental conditions (300 K and 10⁴ Pa pressure of H₂). The corresponding vibrational frequencies of the CH₃ fragment are calculated slightly red-shifted. The calculated asymmetric modes are 3022 cm⁻¹ and 3045 cm⁻¹ and the symmetric mode is 2947 cm⁻¹. For ethylidyne on a Rh₆ cluster, supported on MgO, a frequency was measured 2948 cm⁻¹ and the measured frequencies assigned to ethylidyne adsorbed on Rh particles supported on Al₂O₃ are 2886 cm⁻¹ and 2944 cm⁻¹.¹²

The C-H symmetric and anti-symmetric stretching frequencies of the free CH₃ group of on-top coordinated ethyl species on a supported Rh₃ cluster were calculated in the range 2880–3080 cm⁻¹ (Table S3). An experimental frequency assigned to ethyl on a supported Rh₆/MgO cluster is 2876 cm⁻¹. For the C-H modes of the methyl fragment of a pseudo-ethyl species on a Rh₄ cluster, a different behavior was determined. Most of the C-H stretching vibrational frequencies of the pseudo-ethyl species on the Rh₄ fall in the interval 2993–3106 cm⁻¹. Only the C-H stretching mode that involves the H atom from the CH₃ fragment bonded to a center of Rh₄ was calculated in the region 1946–2430 cm⁻¹ for complexes with different k values. The corresponding Rh-H vibrations involving the same H center are between 1468 and 1658 cm⁻¹ (Table S4). The latter frequencies fall in the interval of symmetric Rh-H stretching modes of bridge coordinated ligands 1468–1812 cm⁻¹ calculated in our previous study on hydrogenated zeolite-supported small Rh clusters.⁶

The calculated frequencies presented do not reveal any clear dependence on the amount of H atoms adsorbed on the cluster.

	C-C Str.	C-H _{sym}	C-H _{asym}	C-H _{str}
di- <i>o-Ethene</i>				
di-o-C2H4/HRh3	1035	2965, 2971	3038, 3059	
di- σ -C ₂ H ₄ /H ₃ Rh ₃	1030	2919, 2936	3006, 3029	
di- σ -C ₂ H ₄ /H ₅ Rh ₃	1046	2918, 2948	2918, 2948 3022, 3047	
di- σ -C ₂ H ₄ /H ₇ Rh ₃	1010	2950, 2986	3052, 3077	
π -Ethene				
π -C ₂ H ₄ /HRh ₃	1194	3028, 3049	3113, 3156	
π -C ₂ H ₄ /H ₃ Rh ₃	1219	3022, 3034	3110, 3136	
π -C ₂ H ₄ /H ₅ Rh ₃	1238	3052, 3060	3138, 3160	
π -C ₂ H ₄ /H ₇ Rh ₃	1283	3063, 3072	3149, 3172	
Ethyl				
C ₂ H ₅ /HRh ₃	967	2920, 2935	2975, 3038, 3062	
C_2H_5/H_2Rh_3	1016	2917, 2958	2978, 3033, 3083	
C_2H_5/H_4Rh_3	982	2879, 2959	2951, 3040, 3055	
C_2H_5/H_6Rh_3	1016	2924, 2952	3018, 3037, 3068	
Ethylidene				
CH ₃ CH/HRh ₃	1061	2917	2971, 3068	2965
CH ₃ CH/H ₃ Rh ₃	1052	2925	2985, 3055	2974
CH ₃ CH/H ₃ Rh ₃	1062	2917	2973, 3059	2948
CH ₃ CH/H ₅ Rh ₃	H ₅ Rh ₃ 1065 2926 2982, 3056		3012	
CH ₃ CH/H ₇ Rh ₃	1066	2926	2981, 3054	2922
Vinyl				
CH ₂ CH/H ₂ Rh ₃	1233	3021	3114	3073
CH ₂ CH/H ₄ Rh ₃	1279	3017	3137	3072
CH ₂ CH/H ₆ Rh ₃	1282	3037	3122	3077
CH ₂ CH/H ₈ Rh ₃	1278	3031 ^a	3140	3019 ^a
Ethylidyne				
CH ₃ C/H ₂ Rh ₃	1146	2938	3018, 3027	
CH ₃ C/H ₄ Rh ₃	1147	2946	3020, 3041	
CH ₃ C/H ₆ Rh ₃	1125	2950	3026, 3040	
CH ₃ C /H ₈ Rh ₃	1116	2947	3022, 3045	
Vinylidene				
CH ₂ C/H ₃ Rh ₃	1270	3018	3118	

Table S3. Calculated harmonic frequencies (cm^{-1}) of the characteristic vibrational modes of the organic ligands in $C_2H_x/H_{k-x}Rh_3$ complexes.

^a Modes that include also vibrations of H ligands of Rh atoms of the cluster.

	C-C str.	C-H _{sym}	C-H _{asym}	C-H _{str}	Rh-H(CH ₃)
di- <i>o-Ethene</i>					
di-o-C2H4/HRh4	1053	2873, 2937	2955, 3031		
di-o-C2H4/H3Rh4	1031	2919, 2938	3040, 3065		
di- σ -C ₂ H ₄ /H ₅ Rh ₄	1058	2913, 2993	3046, 3086		
di-o-C2H4/H7Rh4	1072	2940, 3003	3032, 3096		
di-o-C2H4/H9Rh4	1047	2933, 3005	3014, 3078		
π -Ethene					
π -C ₂ H ₄ /HRh ₄	1225 ^a	3020, 3032	3143, 3161		
π -C ₂ H ₄ /H ₃ Rh ₄	1186	3028, 3040	3114, 3137		
π -C ₂ H ₄ /H ₅ Rh ₄	1202	3038, 3050	3120, 3141		
π -C ₂ H ₄ /H ₇ Rh ₄	1195	3040, 3050	3120, 3141		
π -C ₂ H ₄ /H ₉ Rh ₄	1199	3047, 3056	3129, 3150		
Ethyl					
η -CH ₃ CH ₂ /Rh ₄	1010	2999 ^b , 3004	3074, 3089	2430 ^b	1468
η -CH ₃ CH ₂ /H ₂ Rh ₄	1053	2993 ^b , 3013	3074, 3098	1968 ^b	1655
η -CH ₃ CH ₂ /H ₄ Rh ₄	1059	2996 ^b , 3012	3068, 3098	2014 ^b	1632
η -CH ₃ CH ₂ /H ₆ Rh ₄	1063	2995 ^b , 3024	3071, 3103	1946 ^b	1644
η -CH ₃ CH ₂ /H ₈ Rh ₄	1064	3004 ^b , 3025	3077, 3106	1967 ^b	1658
Ethylidene					
CH ₃ CH/HRh ₄	989	2918	2972, 3022	2910	
CH ₃ CH/H ₃ Rh ₄	1001	2904	2964, 3041	2874	
CH ₃ CH/H ₅ Rh ₄	1066	2979	2979, 3064	2883	
CH ₃ CH/H ₇ Rh ₄	1048	2935	2991, 3056	2887	
CH ₃ CH/H ₉ Rh ₄	988	2929	2997, 3015	2966	
Vinyl					
CH ₂ CH/H ₂ Rh ₄	1275	3045	3153	2968	
CH ₂ CH/H ₄ Rh ₄	1221	3023	3128	2991	
CH ₂ CH/H ₆ Rh ₄	1242	3038	3132	2979	
CH ₂ CH/H ₈ Rh ₄	1273	3049	3141	2936	
CH2CH/H10Rh4	1296	3043	3131	2972	
Ethylidyne					
CH ₃ C/H ₂ Rh ₄	1060	2926	3005, 3026		
CH ₃ C/H ₄ Rh ₄	1062 ^a	2936	3017, 3028		
CH ₃ C/H ₆ Rh ₄	1070	2943	3016, 3063		
CH ₃ C/H ₈ Rh ₄	1086	2930	3017, 3019		
CH ₃ C/H ₁₀ Rh ₄	1092	2938	3021, 3025		
Vinylidene					
CH_2C/H_3Rh_4	1211	3004	3104		
CH ₂ C/H ₅ Rh ₄	1183	3031	3122		
CH ₂ C/H ₇ Rh ₄	1259	3026	3113		

Table S4. Calculated harmonic frequencies (cm⁻¹) of the characteristic vibrational modes of the organic ligands in $C_2H_x/H_{k-x}Rh_4$ complexes.

^a Modes that include also vibrations of H ligands or Rh atoms of the cluster.

^b Modes that include vibrations of the atoms of the CH₃ fragment, interacting with Rh center.



Figure S7. Variation of the average $\langle Rh-Rh \rangle$ distance in complexes of Rh₃ (dashed lines) and Rh₄ (solid lines) with adsorbed π -bonded ethene (dark blue squares) or di- σ -bonded ethene (dark red rhombs) vs. the total number k of H atoms in the system. The number of H ligands coordinated to the Rh cluster is k–4.



Figure S8. Phase diagram of the dominant total number k of H atoms on the modeled complexes of (A) Rh_3 and (B) Rh_4 clusters as function of temperature T and hydrogen pressure $P(H_2)$.

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