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Surface Organometallic Chemistry on Metals. Evidence for a Surface-Stabilized Germylene, $Rh_s[Ge(Ad)(H)]_y/SiO_2$ (Ad = Adamantyl) Obtained by a Controlled Reaction between Rh/SiO_2 and $(Ad)GeH_3$

M. Taoufik, C. C. Santini,* J.-P. Candy, A. de Mallmann, and J. M. Basset*

Contribution from the Laboratoire COMS, UMR 9986 CNRS-CPE-Lyon,
43 Boulevard du 11 Novembre 1918, 69616 Villeurbanne Cedex, France

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Abstract: Selective reaction of $(Ad)GeH_3$ (Ad = adamantyl) with a Rh/SiO_2 surface has been carried out at 50 °C. The surface reaction and the characterization of the surface organogermanium complex have been followed by infrared spectroscopy, surface microanalysis, analysis of the gases evolved during the surface reaction, thermal decomposition of the surface organometallic complex, and use of CO as a molecular probe. In the absence of metallic rhodium, $(Ad)GeH_3$ does not react significantly with the silica surface at room temperature. It is only reversibly adsorbed, and the molecular interaction responsible for this adsorption process is a hydrogen-bonding interaction between either the C−*H* or Ge−*H* atoms and the surface silanols. In the presence of metallic Rh, a chemical reaction occurs exclusively on the metallic particles. $(Ad)GeH_3$ initially physisorbed onto the support migrates to the Rh surface between 25 and 50 °C, where it quickly loses one molecule of hydrogen. The grafted species still contains one hydride ligand since the reaction between $(Ad)GeD_3$ and the rhodium catalyst gives rise to a ν(Ge−D) vibration at the expected frequency. Formulation of the grafted entity as Ge(Ad)(H) (major species) is deduced from surface microanalysis and from its thermal decomposition, which produces adamantane by a reductive elimination process (concomitant disappearance of the ν(C−H) and ν(Ge−H) vibration bands). The organogermane complex is very likely grafted onto rhodium for the following reasons: (i) $(Ad)GeH_3$ does not react with the silanols of the support. (ii) The amount of grafted germanium is close to (but lower than) the number of surface rhodium atoms. (iii) The amount of rhodium accessible to carbon monoxide drops by a factor of 80% after the grafting reaction takes place, indicating that the metallic surface has been covered by the Ge(Ad)(H) fragment, results that are in agreement with the elemental analysis ($Ge/Rh_s = 0.8$). (iv) The infrared results indicate a strong electronic interaction between carbon monoxide adsorbed on the remaining rhodium sites and the Ge−H bond. The major species which is present on the surface after grafting is supposed to be a kind of germylene(II) surface species stabilized by coordination to a surface rhodium atom.

1. Introduction

Surface organometallic chemistry (SOMC) is a relatively new field of chemistry devoted to the study of the reactivity of organometallic complexes with surfaces.[1] The complexes may be those of main group elements, transition metals, lanthanides, or actinides.[2−4] The surfaces may be those of highly divided inorganic oxides[5,6] or those of zerovalent metallic particles.[7−10] In the latter case, the field is defined as surface organometallic chemistry on metals (SOMC/metals). The nature of the metallic surface may be that of a highly dispersed metallic particle, supported or unsupported, or eventually that of a single crystal. The reaction of an organometallic complex with the surface of a metal leads, in certain cases, to new catalytic materials which exhibit much higher activities and/or selectivities than conventionally prepared catalysts. For example, the presence of Bu−Sn fragments on the surface of Rh completely reverses the chemoselectivity of this metal in the hydrogenation of α,β-unsaturated aldehydes.[11,12] It is therefore expected that changing the nature of the alkyl group of the organometallic fragment should result in a possible influence on the chemo-, regio-, or stereoselectivity of a variety of reactions catalyzed by metallic surfaces.

In order to achieve this goal, we have previously studied[13] the reaction of hydrogenolysis of $R'_{4-x}SnR_x$ with a metallic surface of rhodium:

$$Rh/SiO_2 + R'_{4-x}SnR_x + H_2 \rightarrow Rh(Sn\,R'_uR_v)/SiO_2 + (4-x-u)R'H + (x-v)RH \quad (1)$$

$$R', R = Bu, tBu, Np\ (CH_2CMe_3), cyclohexyl$$

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* Authors to whom correspondence should be addressed.

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The obtained results support the fact that the regioselectivity of this hydrogenolysis is weak; but in several cases a unique final surface species could be obtained from different organotin precursors and formulated as Rh[Sn(R)]. In order to obtain selectively this kind of surface organometallic species, it is necessary to choose an organometallic precursor RMX_3 in which the M−X bond is very labile; X = H could be a good choice, but $RSnH_3$ derivatives are rare[14] and the Sn−H bond is known to react also with the hydroxyl group of the silica surface.[15] In addition, $RGeH_3$ can be more easily synthesized and the Ge−H bond is much less sensitive to the reaction of protolysis than the Sn−H bond.[14]

This article reports results which demonstrate, for the first time, that it is possible to graft organogermane fragments, namely, "Ge(Ad)(H)", onto the surface of Rh particles supported on silica. These organometallic fragments are obtained by selective reaction of $(Ad)GeH_3$ on metallic Rh and are thermally stable on the particle up to a temperature of ca. 200 °C.

2. Experimental Section

Adamantyltrihydridogermane $(Ad)GeH_3$ has been synthesized as described in the literature.[16] The same experimental procedure using $LiAlD_4$ instead of $LiAlH_4$ has been used to obtained $(Ad)GeD_3$.

The preparation of the monometallic catalyst has been described elsewhere.[17] The silica support (Aerosil 200 $m^2\ g^{-1}$) was purchased from Degussa. The Rh was grafted onto silica by cationic exchange between $[RhCl(NH_3)_5]^{2+}$ ions and surface $[\equiv SiO]^-[NH_4]^+$ groups. The surface complex obtained was decomposed by calcination at 400 °C in a flowing nitrogen/oxygen mixture (5/1), reduced in flowing H_2 at 400 °C, and then "passivated" at 25 °C under dry air. The Rh and Cl loadings were 1.1% and 0.06% (wt), respectively. The particle size distribution of Rh/SiO_2 catalyst has been determined by conventional transmission electron microscopic (CTEM) analysis. The average value for the detectable particles is 1.4 nm. Assuming that the particles have a cuboctahedral shape,[18] the dispersion (D = surface rhodium atoms/total rhodium atoms) is close to 0.75.

The chemisorption measurements were carried out using conventional static volumetric equipment already described.[17] The vacuum was achieved by means of a pump, and the equilibrium pressure was measured with a Schlumberger gauge (pressure range 0−1000 mbar, accuracy 0.1 mbar). The gas phase was extracted from the vessel and then analyzed by gas chromatography (GC).

The temperature-programmed reaction (TPR) between $(Ad)GeH_3$ and reduced Rh particles (Rh_s-SiO_2) was performed in the same apparatus as described before.[17] A given amount of the monometallic Rh/SiO_2 catalyst was loaded in the reactor, reduced at 623 K under H_2, and then stabilized at room temperature under vacuum. This catalyst is described as Rh^0 catalyst from here on. The desired amount of $AdGeH_3$ was then carefully introduced in the reactor without any contact with air. The reaction was performed at 50 °C. The gas evolved during the reaction was trapped at liquid nitrogen temperature in another part of the apparatus, to avoid possible feedback of the gas on the catalytic surface and further hydrogenolysis. After each step, the gas phase was analyzed by GC and volumetric measurements.

Infrared spectra were obtained with a Nicolet 10 MX Fourier transform instrument. The samples were placed on a sample holder which could move inside a closed reactor from the treatment position (located in an oven) to the analysis position (located in between two CaF_2 windows in the infrared beam). The reactor could be evacuated or filled with a known pressure of gas (e.g., CO). The adsorption bands were recorded as the difference between the IR spectra of bare and CO-covered samples.

3. Results and Discussion

3.1. Interaction between $(Ad)GeH_3$ and $SiO_{2(350)}$ in the Absence of Metallic Rh. The reaction of $AdGeH_3$ with $SiO_{2(350)}$, at 50 °C under vacuum, was monitored by infrared spectroscopy. Bands due to ν(C−H) (2930 and 2903 and 2848 cm^{-1}) and $\delta(CH_2)$ vibrations (1451 and 1344 cm^{-1}) of the adamantyl group and ν(Ge−H) vibrations (2055 cm^{-1}) of the hydride ligands are immediately observed. The sharp band at 3747 cm^{-1} attributed to ν(OH) vibrations of linear silanol groups decreases in intensity, and simultaneously, a broad band appears at 3691 cm^{-1}. The latter is attributed to hydrogen bonding between the silanol groups and either the C−*H* or Ge−*H* atoms of $(Ad)GeH_3$ which has been physisorbed onto the support (Figure 1a,b). No significant change occurs when the pellet is heated at 150 °C for 2 h (Figure 1c). This kind of interaction is now commonly observed when organometallic complexes with alkyl or hydride ligands are "physisorbed" on partially dehydroxylated silica.[15] No gas is evolved in the gas phase. At this stage, if the sample is kept under dynamic vacuum during 12 h at room temperature, all bands which were attributed to adsorbed $AdGeH_3$ disappear and the band due to free silanol at 3747 cm^{-1} is fully recovered (Figure 1d). These infrared and analytical results confirm that $(Ad)GeH_3$ is only reversibly adsorbed on the silica surface and that there is no significant reaction between the $(Ad)GeH_3$ and the silica support under our experimental conditions.

3.2. Interaction between $(Ad)GeH_3$ and $Rh_s/SiO_{2(350)}$. Infrared spectroscopy was the first technique used to follow the reaction of $(Ad)GeH_3$ with the catalyst $Rh_s/SiO_{2(350)}$ (Figure 2a). Room temperature adsorption of $(Ad)GeH_3$ onto the Rh_s/SiO_2 catalyst in the absence of molecular hydrogen strongly modifies the ν(OH) vibrations of the silica support, which are initially situated at 3747 cm^{-1} (Figure 2a,b). After adsorption of $(Ad)GeH_3$ at room temperature, the silanol band decreases in intensity and a new broad peak appears at ca. 3695 cm^{-1}. As already mentionned, the new broad peak is believed to be due to hydrogen bonding between the silanol groups and the compound $(Ad)GeH_3$ which has been adsorbed onto the support. The infrared bands corresponding to $(Ad)GeH_3$, mostly physisorbed on the silica, *vide supra*, are observed at respectively 2055 cm^{-1} (ν(Ge−H)), 2915 and 2854 cm^{-1} (ν(C−H)), and 1453 and 1344 cm^{-1} ($\delta(CH_2)$) (Figure 2a,b).

Treatment of the solid for 2 h at 50 °C and then under dynamic vacuum for 12 h at room temperature (same experimental conditions as with the silica surface) causes the frequency and intensity of the ν(OH) bands of the starting silica to be quite fully restored, whereas the broad peak at ca. 3695 cm^{-1} decreases to its initial intensity. But, in contrast to the behavior of the same complex on silica alone, the presumed ν(Ge−H) band at 2055 cm^{-1}, the ν(C−H) bands at 2915 and 2854 cm^{-1}, and the $\delta(CH_2)$ bands at 1453 and 1344 cm^{-1} corresponding to the adamantyl group are still observed (Figure 2c,d).

In conclusion, these infrared results support the conclusion that $(Ad)GeH_3$ is grafted onto the surface of the catalyst Rh_s/SiO_2. Since the ν(O−H) bands of silica are almost fully restored (Figure 2c,d) one can reasonably assume that most of the germanium complex is grafted onto the metallic rhodium particles.

In order to assign with certainty the band at 2055 cm^{-1}, the same work as above was repeated with $(Ad)GeD_3$. The infrared spectra of pure $(Ad)GeD_3$ and $(Ad)GeH_3$ are reported in Figure

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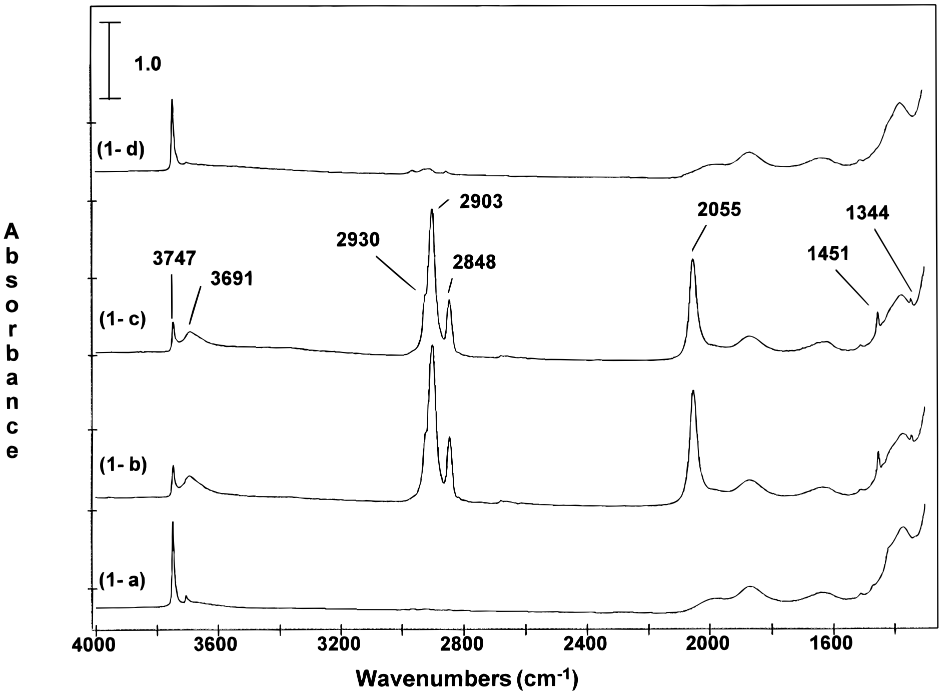

Figure 1. IR spectra of (Ad)GeH_3 physisorbed on silica: (a) $silica_{(350)}$; (b) after sublimation of (Ad)GeH_3 onto $silica_{(350)}$ and heating at 50 °C for 2 h; (c) sample b after heating at 150 °C for 2 h; (d) after evacuation for 12 h at room temperature.

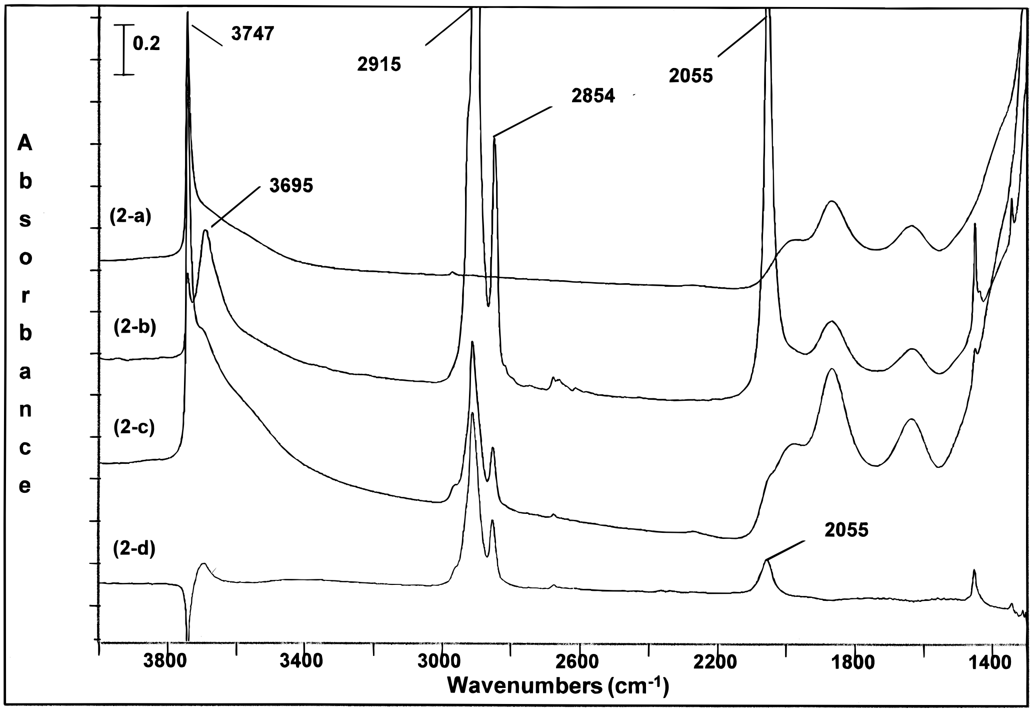

Figure 2. Infrared spectra corresponding to the interaction between (Ad)GeH_3 and $Rh_s/silica_{(500)}$: (a) $Rh_s/silica_{(350)}$; (b) after sublimation of (Ad)GeH_3 at room temperature; (c) after heating at 50 °C for 2 h, followed by evacuation for 12 h at ambient temperature; (d) difference spectrum of sample c obtained by subtracting the background spectrum of $Rh_s/silica_{(350)}$.

3. The ν(Ge−H) and ν(Ge−D) are respectively observed at 2055 and 1485 cm^{-1} at the expected frequency (observed ratio ν(Ge−H)/ν(Ge−D) = 1.41 instead of 1.38 (calculated)). After addition of (Ad)GeD_3 onto the pellet of Rh_s/SiO_2 and treatment for 2 h at 50 °C and then 12 h under dynamic vacuum at room temperature, the infrared spectra show ν(C−H) bands at 2915 and 2853 cm^{-1}, a $\delta(CH_2)$ band at 1451 cm^{-1} corresponding to the adamantyl group, and a ν(Ge−D) band at 1485 cm^{-1} (Figure 4a). This latter band can be replaced under molecular hydrogen by the ν(Ge−H) one previously observed at 2055 cm^{-1} (Figure4b).[32,33] One can conclude from these experiments that the grafted germanium species has retained both the adamantyl fragment and one or several hydrides.

In order to have an average formula for the grafted organometallic fragment, quantitative analysis of the gas phase was performed during the grafting reaction. For this particular experiment, the amount of (Ad)GeH_3 introduced was calculated so that the ratio of Ge introduced per surface Rh atom was fixed to *ca.* 0.8. This reaction was followed by qualitative and quantitative analysis of the gas evolved during the TPR study. After reaction at 50 °C during 2 h, 1 mol of hydrogen was evolved per mole of (Ad)GeH_3 introduced (Figure 5).

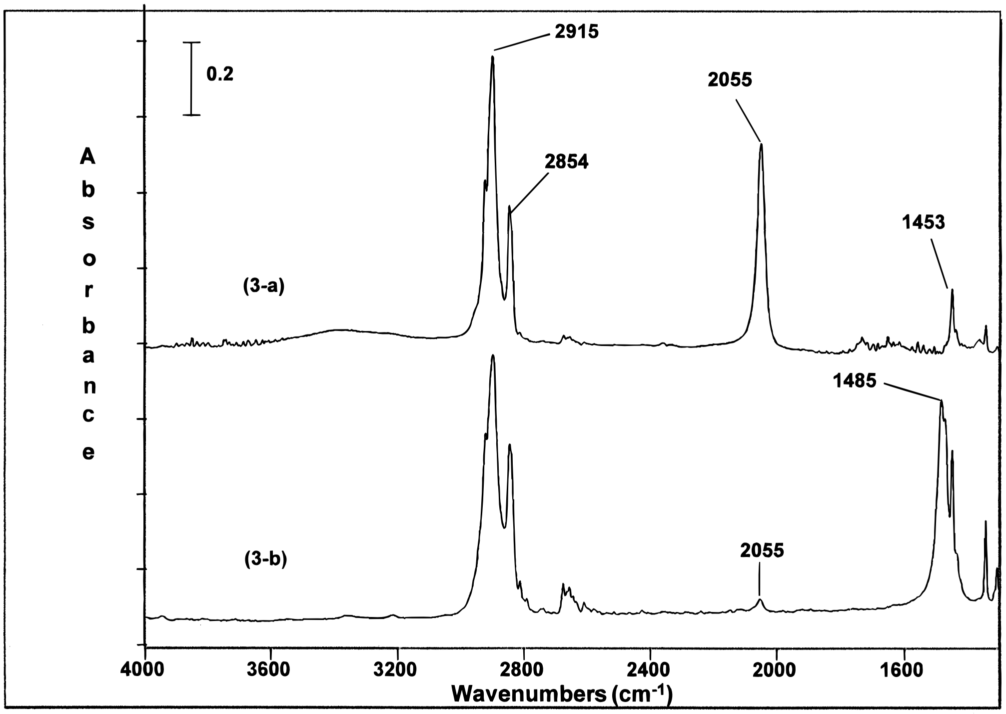

Figure 3. Infrared spectra of (a) pure (Ad)GeH$_3$ and (b) pure (Ad)GeD$_3$.

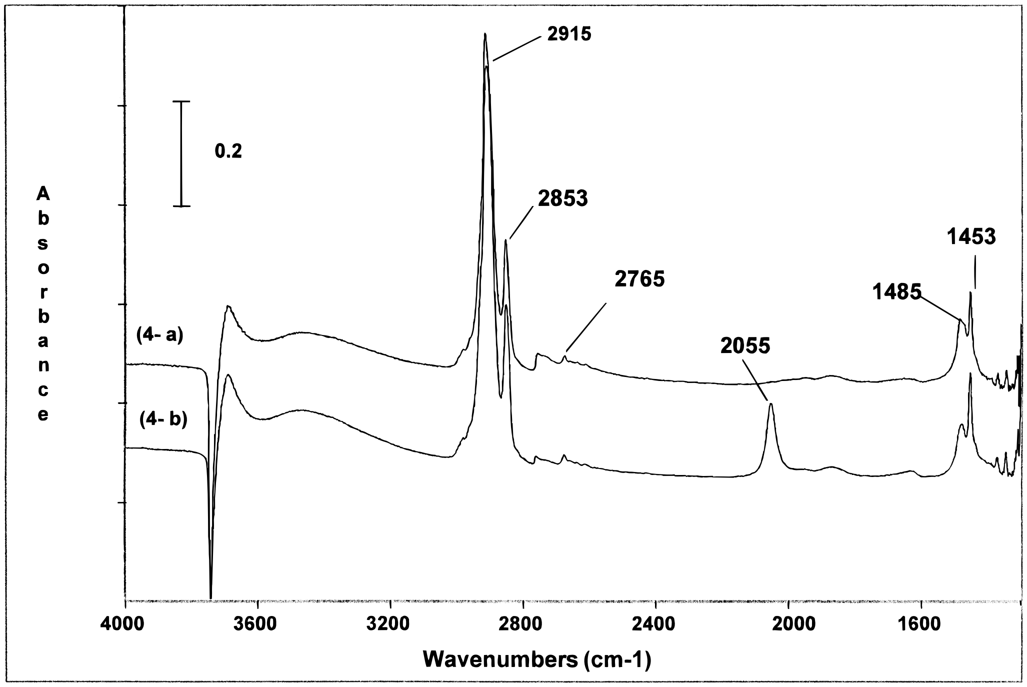

Figure 4. IR spectra corresponding to the interaction between (Ad)GeD$_3$ and Rh$_s$/silica$_{(350)}$ (the spectrum of Rh$_s$/SiO$_2$ was removed by subtraction): (a) after sublimation of (Ad)GeD$_3$ at ambient temperature and treatment at 50 °C for 2 h, followed by evacuation for 12 h at ambient temperature; (b) after 3 h of reaction with molecular hydrogen (30 Torr) at room temperature.

Chemical analysis of this sample gave a Ge/Rh$_s$ ratio equal to 0.76 (expected value 0.8), which shows that the germanium complex has almost fully reacted with the surface rhodium atoms. Additionally a C/Ge ratio of 8 was found, indicating that the Ad/Ge ratio is equal to 0.8. This value indicates that, for 20% of the (Ad)GeH$_3$ introduced, Ad−Ge bond cleavage had occurred with formation of adamantane. Effectively some white crystals of adamantane were found to be condensed on the cold part of the vessel. These data support the fact that the main reaction (80%) leads to a grafted [Ge(Ad)(H)] fragment and a side reaction (20%) leads to the cleavage of the Ge−adamantyl bond.

In order to confirm that this fragment is effectively located on the rhodium particle, chemisorption of carbon monoxide was carried out on the pure Rh/SiO$_2$ and on the presumed Rh$_s$[Ge-(Ad)(H)]$_y$/SiO$_2$ species. The isotherm of chemisorption of CO on Rh/SiO$_2$ was measured at 25 °C (Figure 6a). This isotherm shows a plateau, at an equilibrium pressure of 10 kPa of CO. The amount of adsorbed CO was corrected for the amount of gas adsorbed on the silica support. The accepted stoichiometry at the above mentioned equilibrium pressure is ca. 1 CO molecule per surface Rh atom.[18,19]

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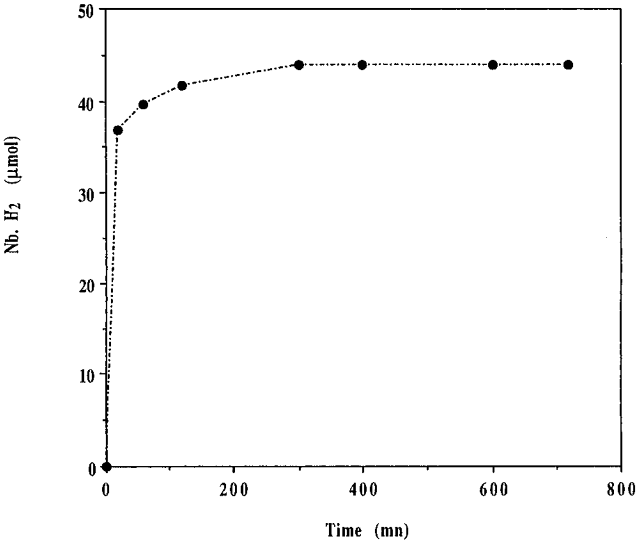

Figure 5. Volumetric determination of the amount of molecular hydrogen evolved during the reaction of (Ad)GeH_3 with Rh_s/silica$_{(350)}$.

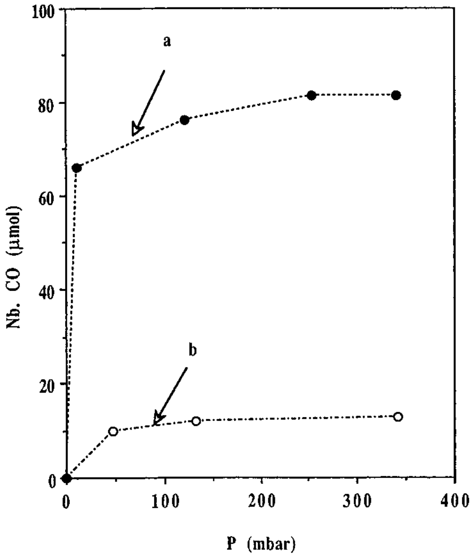

Figure 6. Volumetric determination of the amount of CO adsorbed on the catalyst described as (a) Rh_s/silica$_{(350)}$ and (b) [Rh_s/silica$_{(350)}$ + 0.8(Ad)GeH_3].

Volumetric adsorption of CO has also been used to quantify the number of Rh atoms still accessible to this probe molecule when the metallic surface is covered by the presumed $Rh_s[Ge(Ad)(H)]_y/SiO_2$ fragment. As indicated in Figure 6b, a sharp decrease of the amount of CO adsorbed is observed: approximately 20% of the Rh surface still remains accessible to the CO molecule. These results, when compared with the amount of grafted Ge (0.76/Rh_s), suggest that, on average, one germanium atom blocks one surface rhodium atom.

Thermal decomposition of the presumed $Rh_s[Ge(Ad)(H)]_y/SiO_2$ fragment was followed by infrared spectroscopy (quantitative disappearance of the ν(C−H) and ν(Ge−H) bands). Figures 7 and 8 indicate that the surface species begins to decompose at 50 °C and is almost fully decomposed at ca. 300 °C. Interestingly, the decrease of the intensity of the ν(C−H) and ν(Ge−H) vibrations is concomitant above ca. 125 °C. This can be interpreted as a reductive elimination to afford AdH and $Rh_s[Ge^0]$ which is nearly complete at 300 °C:

$$Rh_s[AdGeH] \xrightarrow[\Theta < 125\ ^\circ C]{\Delta,\ p = 10^{-6}\ Torr} Rh_s[Ge^0] + [AdH]_{ads} \xrightarrow[\Theta > 125\ ^\circ C]{\Delta,\ p = 10^{-6}\ Torr} Rh_s[Ge^0] + [AdH]$$

For temperatures below 125 °C, the discontinuity observed between the two curves of Figure 8 is probably due to the fact that adamantane formed at low temperature remains adsorded on the silica surface as we always observe for any alkane above C_8 (adamantane sublimes at 200 °C/760 Torr).

CO has been used as a "molecular probe" to characterize the metallic phase remaining accessible after grafting the Ge organometallic fragment. The volumetric experiments of adsorption of CO previously described suggest that only 20% of the rhodium surface is accessible to this probe molecule. IR experiments were carried out on a reduced Rh sample which was exposed to CO (1 atm) at room temperature. The resulting IR spectrum is typical of CO adsorbed on a fully reduced Rh particle, with two main bands at 2064 and 1875 cm^{-1}, in agreement with previous studies (Figure 9a).[19−27] The narrow peak at 2064 cm^{-1} has already been ascribed to the linear form of coordinated CO, while the broader band at 1875 cm^{-1} is usually attributed to the multiply-bonded (μ_{-2} or μ_{-3}) forms of CO coordinated to two or three Rh atoms ("bridging" CO).[20−27] The absence of any detectable bands at ca. 2080 and 2020 cm^{-1} which would correspond to the species $Rh^I(CO)_2$ confirms that the rhodium atoms are totally reduced and that there are no unreduced isolated Rh^I organometallic fragments on the silica support.[23,24]

Infrared spectroscopy was then used to study the mode of coordination of CO on the pellet of Rh_s/SiO_2 treated with (Ad)GeH_3, as described above, and for which a $Rh_s[Ge(Ad)(H)]$ surface fragment has been formed (Figure 10a). When this material is treated under CO at room temperature, the ν(Ge−H) band initially present at 2055 cm^{-1} is shifted immediately to 2032 cm^{-1} with approximately the same intensity. Simultaneously two weak and broad bands centered at 1975 and 1850 cm^{-1} are observed (Figure 10b). By treatment under oxygen for 72 h at room temperature, the starting ν(Ge−H) band initially present at 2055 cm^{-1} is fully restored in frequency and intensity whereas the other low-frequency ones are eliminated (Figure 10c).

The fact that there is a reversible shift under CO of the ν(Ge−H) band suggests that carbon monoxide is chemisorbed in the vicinity of the Ge(Ad)(H) fragment which is chemically modified by the probe molecule. The fact that the two weak bands at 1975 and 1850 cm^{-1} rapidly disappear after exposure to 10 Torr of dry oxygen at room temperature in 2 h with formation of CO_2 indicates that these low-frequency bands are due to carbon monoxide.[28]

These results are consistent with a coordination of carbon monoxide in the vicinity of the Ge(Ad)(H) fragment. This

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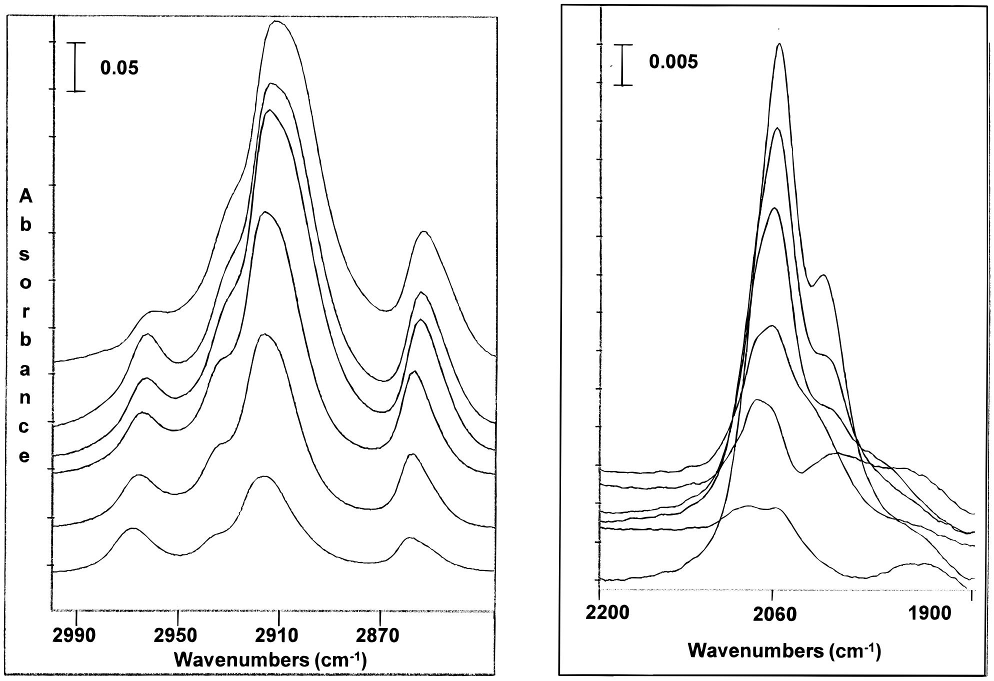


Figure 7. Infrared spectra in the (left) ν(C−H) and (right) ν(Ge−H) regions during the thermolysis of the surface species $[Rh_s[GeAd(H)]_y/SiO_2$.

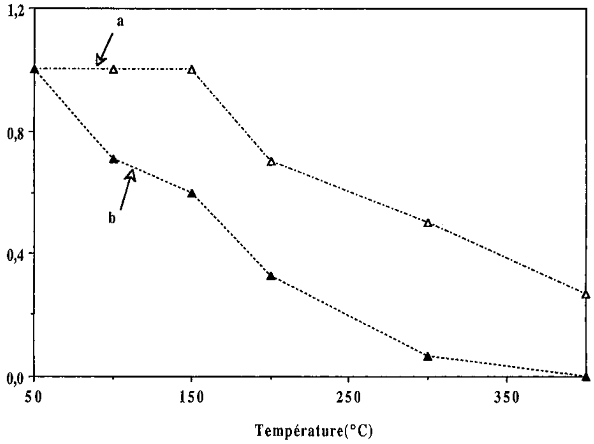
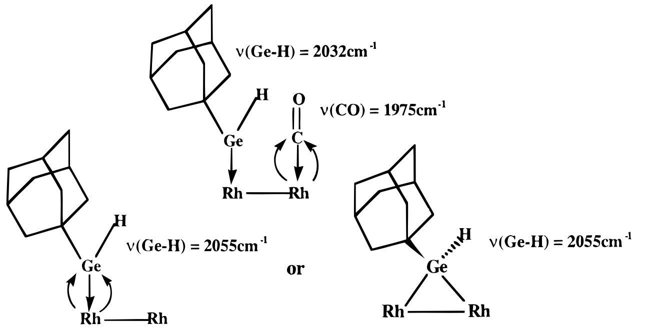


Figure 8. Variation of intensity of the ν(C−H) and ν(Ge−H) bands during the thermolysis of the surface species $[Rh_s[GeAd(H)]_y/SiO_2$.

electronic interaction between two adjacent ligands at the surface of a metallic particle has precedent in surface chemistry.[29]



4. Conclusion

In the course of this paper we have studied the selective reaction of (Ad)GeH_3 with a silica-supported Rh particle. (Ad)GeH_3 does not react significantly with the silica surface under the experimental conditions used in this work. It is only reversibly adsorbed, and the molecular interaction responsible for this adsorpion process is a hydrogen-bonding interaction between either the C−*H* or Ge−*H* atoms and the surface silanols. Such molecular interactions are known to occur when tin−alkyl or tin hydrides are physisorbed on the surface of silica.[31] This lack of chemical reaction between (Ad)GeH_3 and the surface silanols at room temperature is consistent with other studies carried out in our laboratory.[15] At room temperature and up to 100 °C, (Ad)GeH_3 is simply physisorbed.

In the presence of metallic Rh, a chemical reacion occurs exclusively on the metallic particles. (Ad)GeH_3 initially physisorbed onto the support migrates to the Rh surface between 25 and 50 °C, where it quickly loses one molecule of hydrogen. The grafted species still contains one hydride ligand since the reaction between (Ad)GeD_3 and the rhodium catalyst gives the grafted Ge−D at the expected frequency for a ν(Ge−D) surface species.

Formulation of the grafted entity as Ge(Ad)(H) (major species) may be deduced from surface microanalysis, which give a Ad/Ge ratio of 0.8 instead of unity. This discrepancy is not very significant considering the accuracy of the surface microanalytical methods and the fact that some adamantane is also formed during the reaction of the organometallic with the surface.

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(30) (a) Burgess, K.; Guerin, C.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985,** *295,* C3−C6. (b) Anema, S. G.; Mackay, K. M.; McLeod, L. C.; Nicholson, B. K.; Whitter, J. M. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 759. (c) Anema, S. G.; Audett, J. A.; Mackay, K. M.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1988**, 2629.

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(32) Note that during this reaction we observe the appearance of a sharp medium peak at 2766 cm^{-1}. This can be attributed to a ν(Si−OD) vibration. The formation of this band may be associated with an exchange between D_2 formed during the reaction of (Ad)GeD_3 onto the Rh/SiO_2 surface.

(33) The fact that the band at 2055 cm^{-1} is the same for $AdGeH_3$ and for RhsGe(H)(Ad) may appear surprising. However, the stretching vibration Ge−H is poorly dependent on the number of hydrido ligands coordinated to Ge. For example, the ν(Ge−H) vibrations for $(PhCH_2)_3Ge{-}H$ and $(PhCH_2)_2Ge{-}H_2$ are respectively situated at 2034 and 2037 cm^{-1}. Cross, R. J.; Gockling, F. *J. Organomet. Chem.* **1965**, *3,* 146−155.

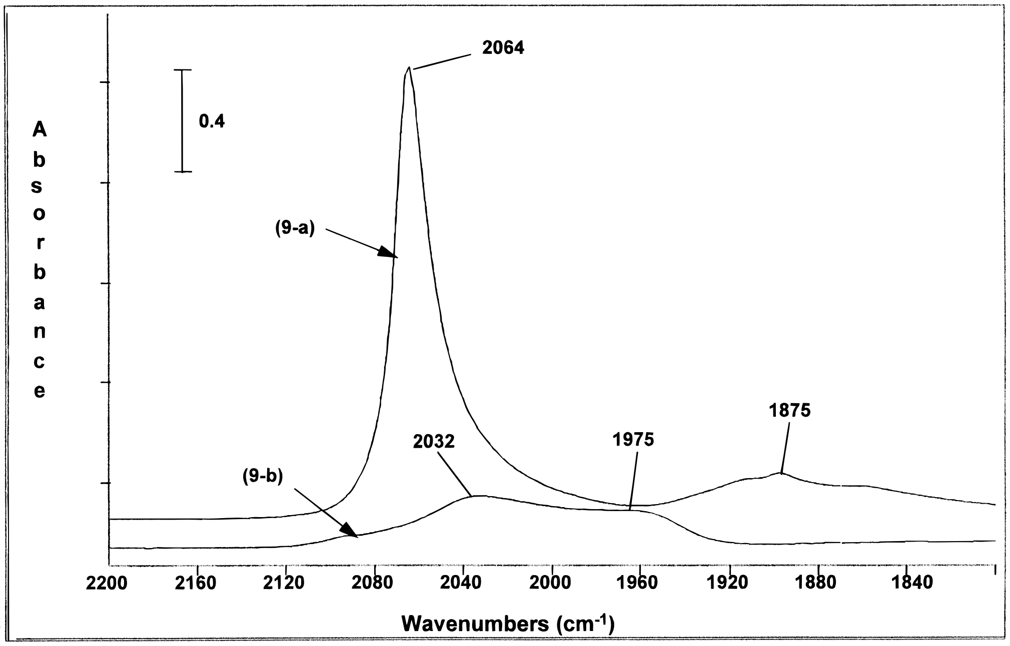


Figure 9. Infrared spectra in the ν(CO) region (the spectrum of Rh_s/SiO_2 was removed by subtraction): (a) Rh_s/silica$_{(350)}$ exposed to 10 Torr of CO at room temperature; (b) [Rh_s/SiO_2 + 0.8(Ad)GeH_3] treated at 50 °C for 2 h followed by evacuation for 12 h at room temperature and then exposed to 10 Torr of CO at room temperature.

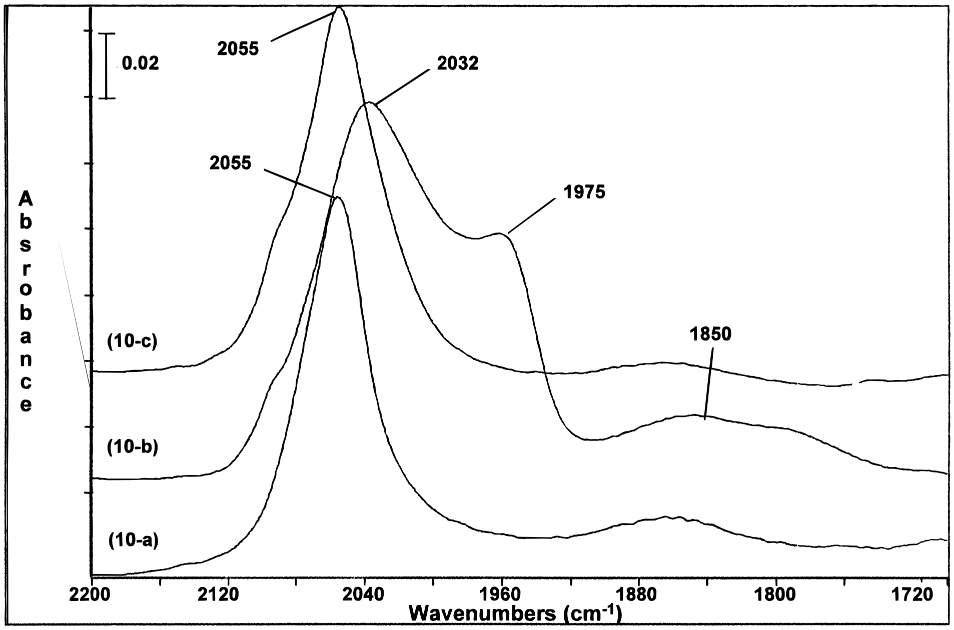
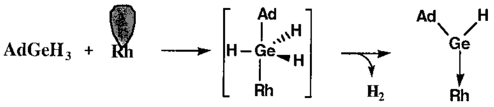


Figure 10. IR spectra in the ν(CO) region: (a) CO adsorbed on [Rh_s/silica$_{(350)}$ + 0.8(Ad)GeH_3] treated at 50 °C for 2 h followed by evacuation for 12 h at room temperature; (b) sample a exposed to CO (10 Torr) at room temperature; (c) spectrum obtained after 72 h of reaction with molecular oxygen (10 Torr) at room temperature.

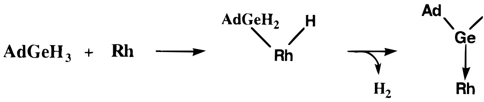
Formulation of the grafted entity as Ge(Ad)(H) may also be deduced from its thermal decomposition producing Ad−H with concomitant disappearance of the ν(C−H) and ν(Ge−H) vibration bands.

The organogermane complex is very likely grafted onto rhodium for the following reasons: (i) (Ad)GeH_3 does not react with the silanols of the support. (ii) The amount of grafted germanium is close to the number of surface rhodium atoms. (If one introduces a Ge/Rh_s ratio of 0.8, the micoanalysis after grafting indicates a value of 0.76). (iii) The amount of rhodium accessible to carbon monoxide drops by a factor of 80% after the grafting reaction takes place, indicating clearly that the metallic surface has been covered by the Ge(Ad)(H) fragment. (iv) The infrared results indicate a strong electronic interaction between the carbon monoxide adsorbed on the remaining rhodium sites and the ν(Ge−H) vibration demonstrating a kind of proximity effect between the CO and the germylene species.

In conclusion, the major species which is present on the surface after grafting is a kind of germylene surface species stabilized by coordination to a surface rhodium atom. The formation of a germylene(II) species suggests that the grafting has occurred by a reductive elimination of H−H from the Ge(Ad)H_3. The mechanism of this reductive elimination is not clear, but perhaps, as already suggested for tin−alkyl adsorption on rhodium surfaces, a pentacoordination of Ge could be a precursor state before reductive elimination of molecular hydrogen.[13]



Another possible mechanism could be the oxidative addition of a Ge−H fragment to the zerovalent rhodium, with formation of a Rh(H)(Ge(Ad)(H)$_2$ species. There are several examples of oxidative addition of a Ge−H bond to zerovalent metals.[30] This surface species Rh(H)(Ge(Ad)(H)$_2$ would then reductively eliminate hydrogen with formation of the surface germylene.



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