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Stabilization of Hexarhodiumhexadecacarbonyl by Attachment to Chemically Modified Silica Surfaces

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The behaviour of several inorganic supports for the attachment of $Rh_6(CO)_{16}$ has been studied by infrared spectroscopy. It is found that chemically modified silicas, namely silicas bearing phosphine, mono- and diamine ligands, bind the rhodium cluster with retention of its structural integrity. These materials are thermally relatively stable versus *aggregation and can be partially decarbonylated reversibly. The nature of the substituent ligand sensitively determines the bonding onto the support and the susceptibility to ligand dissociation. The increased lability of CO ligands in the attached clusters creates vacant coordination sites, to which reactants such as olefins or acetylenes may be coordinated. Catalytic activity for gas phase hydrogenation of olefins and acetylenes below 370 K has been detected. The possibility of catalyst tayloring with attached clusters is suggested.*

Introduction

A wide variety of well characterized transition metal clusters have been synthesized in recent years [1–3]. These polynuclear complexes catalyze several classes of reactions in solution such as isomerization and hydrogenation of olefins [4–6], acetylene hydrogenation [7–10], oxidation reactions [11], hydroformylation of olefins [12, 13], cyclization and polymerization reactions [7, 9, 10, 14], dehydrogenation of cyclic dienes [4, 15], selective hydrogenation of α,β-unsaturated carbonyl and nitrile compounds [16], and reduction of aldehydes to alcohols [17]. Some cluster catalysts, namely $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$, show the unique ability to catalyze the reduction of CO to CH_4 [18]. This reaction usually requires solid metal catalysts and no mononuclear complex is known yet, that would catalyze the CO reduction. $[Rh_{12}(CO)_{30}]^{2-}$ has been shown to be present in solutions during catalytic conversion of synthesis gas CO + H_2 into a mixture of ethylene glycol, propylene glycol, methanol, and other products [19]. These observations suggest that the existence of metal–metal bonds in the polynuclear clusters and the occurrence of certain geometric arrangements of the metal atoms (preferentially triangular units) may be responsible for their catalytic properties. Analogous structural units occur on metal surfaces, the triangular one on close-packed (111)-faces in particular. Certain similarities between the interaction of ligands and metal cluster units and the chemisorption on metal surfaces may be encountered [20–22, 41]. Discrete metal clusters have therefore been suggested as attractive models of metal surfaces for chemisorption and catalysis [20, 21, 23–25, 46].

Although their detailed electronic structure will be different, discrete metal clusters may also be considered as idealized models for small metal particles. Such metal particles form the active phase in supported metal catalysts. The use of discrete metal clusters as model systems is particularly attractive since *e.g.* carbonyl cluster compounds undergo several ligand displacement reactions with molecules such as hydrogen, olefins and acetylenes. The structures of the resulting entities have been reported for a variety of transition metal clusters [20, 23, 26]. Such systems may serve as models for chemisorbed species on single crystal faces and on small supported metal particles. It is therefore an interesting question, whether discrete metal clusters can also be stabilized with retention of cluster integrity on support surfaces. $Rh_6(CO)_{16}$ [27–30] and $Ir_4(CO)_{12}$ [31] have in fact been bound successfully to phosphinated polystyrene matrices. There are only two reported attempts to attach transition metal clusters onto inorganic supports; Smith *et al.* [32] claim that $Rh_6(CO)_{16}$ could be stabilized by adsorption on Al_2O_3 surfaces, while $Rh_4(CO)_{12}$ was readily converted into $Rh_6(CO)_{16}$. Conrad *et al.* [22] adsorbed $Rh_6(CO)_{16}$ on a silica surface. IR spectroscopic results indicated the probable retention of cluster integrity.

In the present research we have attempted to test a series of unmodified and chemically modified oxide surfaces with respect to their ability to stabilize

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transition metal clusters. The behaviour as support materials of MgO and SiO_2, and of SiO_2 surfaces chemically modified by the introduction of phosphine, mono- and diamine functional groups has been studied. $Rh_6(CO)_{16}$ was chosen as a representative metal cluster, since it is one of the most thoroughly characterized clusters [3, 33, 34] and since it is thermally and air stable. IR spectroscopy has been used for the characterization of the attached rhodium clusters*; thermal stability, reversibility of decarbonylation/carbonylation reactions and ligand exchange with ethylene are reported in this paper.

Experimental

Solid Oxide Supports

MgO was prepared from $Mg(OH)_2$, which was precipitated from a $Mg(NO_3)_2$ solution by concentrated ammonia. The hydroxide was then transformed to the MgO by thermal treatment *in vacuo* ($\leqslant 10^{-1}$ Nm^{-2}) at 570 K.

The SiO_2 used was Aerosil 380 from DEGUSSA, Hanau, BRD. This material consists of nonporous spherical particles with diameters between 5 and 15 nm. It has a BET-surface area of 340 m^2/g.

Modification of SiO_2

The SiO_2 support was chemically modified by reaction with freshly distilled (2-aminoethyl)-aminopropyltrimethoxysilane (GF 91 from Wacker-Chemie GmbH., Burghausen, BRD) and Cyclohexyl-aminopropyl-trimethoxysilane (GF 92 from Wacker-Chemie) and with diphenylphosphinopropyl-trimethoxysilane. The latter reactant was synthesized as follows: A solution of potassium diphenylphosphine was prepared according to Isleib and Tzschach [42]. This solution was added to a dioxane solution of chloropropyltrimethoxysilane under nitrogen. This mixture was refluxed for 3 hours and the precipitated KCl filtered off. The diphenyl-phosphine-trimethoxysilane solution in dioxane was then directly used for the modification of the SiO_2 surface.

The SiO_2 was treated in O_2 at 570 K and subsequently *in vacuo* ($\leqslant 10^{-1}$ Nm^{-2}) prior to the modification. The pretreated material was then exposed to a dry and O_2-free nitrogen atmosphere and suspended in either methanol or benzene.

For the modification with the amino-silanes, a SiO_2 suspension in methanol was refluxed for 1 hour, the amino-silanes were then added and refluxed for another 2 hours. The resulting suspension was kept for 24 hours at room temperature, the liquid phase was decanted, the modified silica washed with methanol and dried. The two amino-silicas are designated SIL-$(CH_2)_3NH(CH_2)_2NH_2$ and SIL-$(CH_2)_3NH$ C_6H_{11}, respectively. Elemental analysis gave a value of 1.1 diamine- and monoamine groups per nm^2, respectively.

The modification of SiO_2 with diphenyl-phosphino-propyl-trimethoxysilane was carried out in benzene-dioxane solution by refluxing for 18 hours. The modified silica, designated SIL-$(CH_2)_3PPh_2$ was separated from the solution, washed with dioxane and methanol, and dried. Elemental analysis gave a value of 1.1 phosphine groups per nm^2.

Attachment of $Rh_6(CO)_{16}$ onto the Supports

The attachment of the cluster onto the supports was carried from a saturated solution of $Rh_6(CO)_{16}$ in $CHCl_3$. The unmodified oxides MgO and SiO_2 were contacted at 328 K for 10 to 20 minutes with the $CHCl_3$ solution. This procedure was repeated several times until the solution was not discoloured any more. The materials were then washed with $CHCl_3$ and dried.

The modified silicas were dried at 353 K in vacuo before attachment of the cluster. SIL-$(CH_2)_3PPh_2$ was then stirred in the saturated $Rh_6(CO)_{16}$ solution at 333 K for 1 hour. The solution was slowly discoloured under these conditions. The material was then washed with $CHCl_3$ and dried. The procedure with the other two modified silicas was analogous, the only difference being reaction temperature and time.

SIL-$(CH_2)_3NH(CH_2)_2NH_2$ was stirred in the cluster solution at room temperature for 2 hours, while SIL-$(CH_2)_3NHC_6H_{11}$ was kept in solution at room temperature for 12 hours. All the supported clusters were stored under argon. Table I gives some analytical details of the $Rh_6(CO)_{16}$ clusters attached to the modified silica supports.

TABLE I. Analytic Data of Hexarhodiumhexadecacarbonyl Attached to Chemically Modified Silicas.

Support	Number of Ligands per nm^2	Rh Content (%Wt)	Number of Clusters per nm^2	Ratio Ligands/Clusters
SIL-$(CH_2)_3PPh_2$	1.1	0.24	6.76×10^{-3}	162
SIL-$(CH_2)_3NHC_6H_{11}$	1.1	0.66	1.88×10^{-2}	58
SIL-$(CH_2)_3NH(CH_2)_2NH_2$	1.1	0.76	2.17×10^{-2}	51

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*Following a suggeston of Jarrell [38], the terms bound and attached will be used to indicate a distinct cluster stabilized on a surface, while the term supported designates a solid metal catalyst with a range of sizes and structures of metal entities.

Infrared Spectra

The IR spectra were recorded on a Perkin–Elmer Spectrophotometer type 225. An IR cell was used which allowed *in situ* treatment and heating of the samples. This cell has been described in detail previously [35]. The powders of the supported clusters were pressed into self-supporting wafers; applied pressures were 1.8×10^7 Nm^{-2} with the MgO bound system and 6×10^6 Nm^{-2} with the samples containing SiO_2 as basic support material. Due to the lattice absorptions which begin just below 2000 cm^{-1} with SiO_2 samples, compensation in the reference beam with an optically equivalent SiO_2 wafer (not containing attached clusters) was necessary. The globar was run at low power to reduce the heating of the sample wafer by the infrared beam. The spectral slit width was typically 1.7 cm^{-1} at 2000 cm^{-1}.

Results and Discussion

$Rh_6(CO)_{16}$ is an octahedral cluster which has four face-bridging CO ligands and 12 terminal CO ligands [33, 34]. This cluster (T_d symmetry) shows two infrared-active terminal C–O stretching frequencies at 2073 and 2026 cm^{-1}, and one infrared-active asymmetric bridge C–O stretching frequency at 1800 cm^{-1} (see Table II).

$MgO/Rh_6(CO)_{16}$

The $Rh_6(CO)_{16}$ cluster adsorbed on MgO gave an infrared spectrum with strong bands at 2095, 2020 and 2000 cm^{-1} as well as a shoulder at 2075 cm^{-1}. These bands are sharp and must be assigned as terminal C–O stretching frequencies. The characteristic band of the bridging CO ligands cannot be detected. The increased number of terminal C–O stretching bands is probably due to a reduced symmetry of the bound cluster, although the octahedral structure may still be retained in the freshly prepared material. Pumping leads to decarbonylation of the adsorbed cluster and the spectra show drastic changes on successive decarbonylation-carbonylation cycles at 410 K. The changes may be due to molecular transformations of the cluster into certain mono- or dinuclear complexes. Adsorbed water of surface OH groups may be involved in these reactions [45]. Finally, relatively broad bands appear between 2000 and 2100 cm^{-1} and near 1870 cm^{-1} which suggest the aggregation of the cluster to metal particles [36, 37].

$SiO_2/Rh_6(CO)_{16}$

This system had been studied previously [22]. It had been concluded that the rhodium-clusters form small, relatively well defined metal particles during mild heat treatments (<370 K). These conclusions were supported by the present results, which additionally demonstrated the aggregation of the rhodium clusters to larger ill-defined metal particles on more severe heat treatments (≤510 K).

Intermediate reactions such as on MgO may also occur on SiO_2.

MgO and SiO_2 do not appear to stabilize cluster integrity and have therefore not been studied in more detail.

SIL-$(CH_2)_3PPh_2/Rh_6(CO)_{16}$

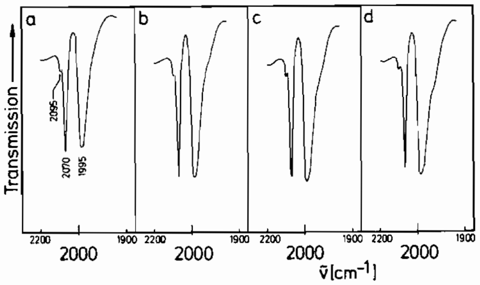

Figure 1. Thermal stability of SIL-$(CH_2)_3PPh_2/Rh_6(CO)_{16}$; carbonyl infrared spectra obtained in CO atmosphere of 2.7×10^3 Nm^{-2}: a) freshly prepared; (b) treated at 370 K for 2 hr; (c) treated at 420 K for 2 hr; (d) treated at 470 K for 2 hr.

Figure 1a shows a spectrum of the terminal C–O stretching range between 1900 and 2100 cm^{-1} of a freshly prepared SIL-$(CH_2)_3PPh_2/Rh_6(CO)_{16}$ sample in a CO-atmosphere of 2.7×10^3 Nm^{-2}. Two strong bands at 2070 and 1995 cm^{-1} and a weak band at 2095 cm^{-1} is observed. In no case were the characteristic bridge C–O stretching bands expected between 1800 and 1900 cm^{-1} observed. These bands were either not present or obscured by uncompensated absorptions of the SiO_2 support. The same result was obtained by Jarrell and Gates [30] with their $Rh_6(CO)_{16}$ attached to phosphinated polystyrene. The observed infrared bands are compared with reported carbonyl frequencies of comparable systems in Table II. The two strong bands at 2070 and 1995 cm^{-1} compare very nicely with the band pair observed by Iwatate *et al.* [28] for $Rh_6(CO)_{13}$-$(PPh)_3$ and with the bands at 2055 and 1985 cm^{-1} obtained for $Rh_6(CO)_{13}$TP by the same authors. $Rh_6(CO)_{16}$ attached to phosphinated polystyrene also gave spectra with two comparable strong bands near 2080 and 2000 cm^{-1} [28, 30]. It is therefore assumed that also in the present system the rhodium cluster has retained its integrity on attachment to SIL-$(CH_2)_3PPh_2$. Under this working hypothesis, it must be assumed that the cluster has undergone ligand exchange reactions by substitution of an unknown number of CO ligands for phosphine ligands. The spectra of $Rh_6(CO)_{16}$ can be interpreted with the assumption that the coupling between terminal groups attached to different rhodium atoms is

TABLE II. Carbonyl Stretching Frequencies for Hexarhodium-Carbonyl Species.

Sample	Solvent/Treatment or Atmosphere	Carbonyl Stretching Frequency (cm^{-1})		Reference
		Terminal	Bridging	
$Rh_6(CO)_{16}$		2073 2026	1800	Beck and Lottes [33]
				Corey *et al.* [34]
		2077(s), 2074(s), 2041(m), 2016(m)	1770(s)	Griffith, Wickham [43]
$Rh_6(CO)_{16}/Al_2O_3$	dried in air	2080(s) 2000(s)		Smith *et al.* [32]
	CO, 10^5 Nm^{-2}	2095(w), 2060(s) 2010(m)	1805(s)	Smith *et al.* [32]
$Rh_6(CO)_{16}/SiO_2$	CO, heat	2095(w), 2060(s) 2035(s)	1860	Conrad *et al.* [22]
$Rh_6(CO)_{13}(PPh)_3$	$CHCl_3$	2095(w), 2079(s), 2066(s), 2005(s)	1850(s), 1780(m)	Iwatate *et al.* [28]
$Rh_6(CO)_{10}(PPh)_6$	$CHCl_3$	1984(s), 1965(s), 1938(m)	1779(s)	Booth *et al.* [44]
$Rh_6(CO)_{13}TP^a$	nujol mull	2055(s), 2020(w), 1985(s)	1835(w), 1785(s)	Iwatate *et al.* [28]
$Rh_6(CO)_{16}/PPS^b$	CO, 10^5 Nm^{-2}	2080(s) 2000(s)	1855(s)	Iwatate *et al.* [28]
	CO, 10^5 Nm^{-2}	2078(s) 2008(s)	–	Jarrell and Gates [30]
$Rh_6(CO)_{16}/SIL\text{-}PPh_2$	CO, 2.7 × 10^3 Nm^{-2}	2095(w), 2070(s) 1995(s)		Present Work

[a] TP = tris-(2-diphenylphosphinoethyl)phosphine. [b] PPS = Phosphinated polystyrene.

negligible [34]. This assumption should also hold for the phosphine substituted clusters. The band at 2070 cm^{-1} may thus be assigned to an isolated $Rh(CO)_2$ group, while the band at 1995 cm^{-1} should be due to a singly phosphinated Rh atom, *i.e.* to a $Rh(CO)$-$(-PPh_2)$ group. The lower C–O stretching frequency of the latter group is due to the lower π-acidity of phosphine groups as compared to CO ligands. The assignment of the weak band at 2095 cm^{-1} is not quite clear. It may be due to a cluster bound by a lower number of phosphine ligands. However, its assignment to some mono- or dinuclear degradation products cannot completely be ruled out [3]. Although the number of phosphine groups by which the clusters are bound is not known and may vary in principle, the sharp infrared bands suggest that the majority of attached clusters is bound in the same way. The relative intensities of the bands at 2070 and 1995 cm^{-1} may vary slightly for different samples (see Figures 1 and 2), which should indicate somewhat different degrees of substitution. Due to the high ratio between the numbers of available phosphine groups and attached clusters (see Table I), one would expect relatively highly substituted clusters to occur, although the correspondence of the observed bands with those of $Rh_6(CO)_{13}(PPh)_3$ and Rh_6-$(CO)_{13}TP$ suggests a similar substitution of the attached cluster.

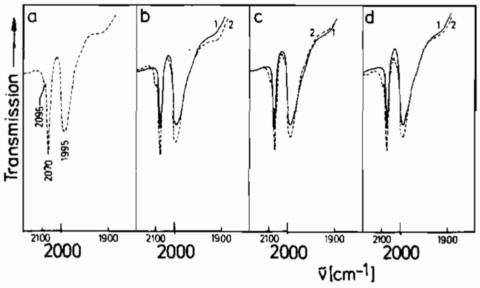

Figure 2. Decarbonylation of $SIL\text{-}(CH_2)_3PPh_2/Rh_6(CO)_{16}$ at 390 K. Spectra recorded after decarbonylation by evacuation for 2 hr (———) and after admission of CO at 2.7×10^3 Nm^{-2} (----). (a) Fresh sample; (b) first cycle; (c) second cycle; (d) third cycle.

The thermal stability of the $SIL\text{-}(CH_2)_3PPh_2/Rh_6$-$(CO)_{16}$ in a CO atmosphere of 2.7×10^3 Nm^{-2} has been tested. The spectra a–d in Fig. 1 show that no principle changes of the infrared bands occur up to 470 K. Band intensities are slightly higher in spectra b–d, indicating that the cluster in the freshly prepared sample was partially decarbonylated. The supported cluster is apparently thermally stable at temperatures below 470 K. At substantially higher temperatures aggregation to larger metal particles occurs even in a CO atmosphere.

The behaviour of the $Rh_6(CO)_{16}$ attached to phosphine groups on $SIL\text{-}(CH_2)_3PPh_2$ during successive decarbonylation–carbonylation cycles at 393 K is shown in Figure 2. As evidenced by the spectra, ligand dissociation occurs on pumping; the band at 2095 cm^{-1} vanishes completely, while the strong bands at 2070 and 1995 cm^{-1} are reduced to approximately 65 and 80%, respectively, of their original intensity. This process is completely reversible, since the original spectra are restored on exposure of the decarbonylated sample to 2.7×10^3 Nm^{-2} CO. The cycles can be repeated many times even at temperatures up to 470 K without any alteration of the spectra. Metal clusters are electron deficient [3] and are stabilized by the coordination of electron donor ligands, such as CO. The ability of the attached cluster to experience dissociation of a part of its CO ligands is thus a remarkable property, which is of importance for the catalytic activity of these systems. The cluster must offer one or more vacant coordination sites to coordinate the reactants. Jarrell and Gates [30] in their study of the $Rh_6(CO)_{16}$/PPS system, observed a complete decarbonylation under conditions of ethylene hydrogenation. The CO ligands could then be coordinated to the cluster again with a relatively low rate. It was therefore suggested, that the decarbonylated cluster was not completely bare, but interacted with the solvent-like polymer support, particularly the aromatic rings of the backbone. The $Rh_6(CO)_{16}$ attached to $SIL\text{-}(CH_2)_3PPh_2$ behaves somewhat differently. Firstly, carbonylation seems to occur readily, indicating that the vacant coordination sites are probably not occupied by other ligands. The type of solvent-like interactions as with PPS are not possible in the present system. Secondly, total decarbonylation does not occur. As suggested by Jarrell and Gates [30], the decreased π-acidity of phosphine ligands leaves a higher electron density on the metal cluster, which facilitates the dissociation of

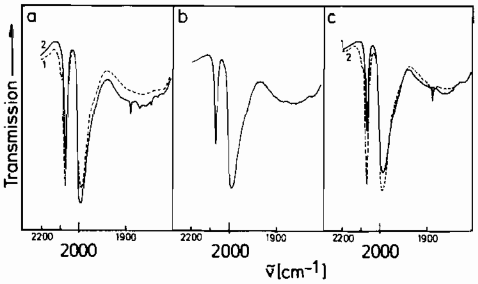

Figure 3. Carbonyl infrared spectra of $SIL\text{-}(CH_2)_3PPh_2/Rh_6$-$(CO)_{16}$ during interaction with ethylene. (a) Fresh sample at $2.7 \times 10^3 Nm^{-2}$ CO (spectrum 1) and after interaction with C_2H_4 at $1.33 \times 10^5 Nm^{-2}$ and 330 K for 15 hr (spectrum 2); (b) after interaction of sample with C_2H_4 at 1.33×10^5 Nm^{-2} and 390 K for 45 minutes and subsequent evacuation; (c) sample (b) after admission of $1.33 \times 10^5 Nm^{-2}$ C_2H_4 at room temperature (spectrum 1) and after subsequent recarbonylation in CO at 2.7×10^3 Nm^{-2} and room temperature (spectrum 2).

CO ligands. This dissociation may be assisted by the solvent-like interactions with the PPS backbone. The lack of this assistance in the SIL-$(CH_2)_3PPh_2$ system may account for the lower tendency towards total decarbonylation.

The admission of ethylene also leads to a reversible displacement of CO ligands. Figures 3a and b demonstrate that admission of 1.3×10^4 Nm^{-2} C_2H_4 and evacuation at 393 K leads to a preferential reduction of the band at 2070 cm^{-1} (to about 50% of its initial intensity), while the band at 1995 cm^{-1} is affected much less significantly. This suggests that C_2H_4 replaces CO ligands more easily from $Rh(CO)_2$ units than from $Rh(CO)(-PPh_2)$ units. The cluster can readily be recarbonylated as shown in Figure 3c. The nature of the coordinated C_2H_4 is still unknown since no characteristic infrared bands of this species could be detected, because of their low extinction coefficients and the low cluster density.

SIL-$(CH_2)_3NH$ $C_6H_{11}/Rh_6(CO)_{16}$ and SIL-$(CH_2)_3NH$-$(CH_2)_2NH_2/Rh_6(CO)_{16}$

The freshly prepared SIL-$(CH_2)_3NHC_6H_{11}/Rh_6$-$(CO)_{16}$ develops two sharp terminal C–O stretching bands at 2085 and 2005 cm^{-1} as shown in Figure 4a.

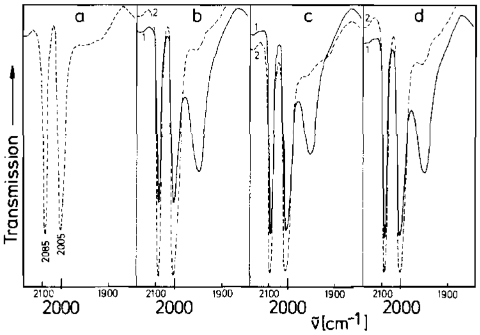

Figure 4. Carbonyl infrared spectra of SIL-$(CH_2)_3NHC_6H_{11}/$ $Rh_6(CO)_{16}$ during decarbonylation–carbonylation cycles at 368 K. Spectra recorded after decarbonylation by evacuation for 1 hr (——) and after admission of CO at 2.7×10^3 Nm^{-2} (---). (a) Fresh sample; (b)–(d) first to third cycle.

Again, the bridge C–O bands cannot be detected. These spectra remain unchanged in a CO atmosphere at temperatures up to 420 K, indicating thermal stability of the material at temperatures below this upper limit. At higher temperatures aggregation to metal particles occurs. Decarbonylation–carbonylation cycles are reversible at 368 K as demonstrated in Figure 4 b–d. The behaviour of the system on decarbonylation, however, differs significantly from that of SIL-$(CH_2)_3PPh_2$ where merely a decrease in the CO band intensities was observed. In contrast, decarbonylation of SIL-$(CH_2)_3NHC_6H_{11}/Rh_6(CO)_{16}$ produces a significant decrease of the terminal C–O stretching band intensities, but additionally a new very pronounced feature is developed at 1950 cm^{-1}. On carbonylation in a CO atmosphere of 2.7×10^3 Nm^{-2}, this band vanishes nearly quantitatively and the original intensity of the terminal C–O stretching bands is restored.

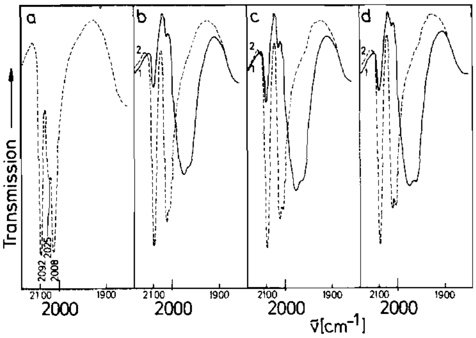

Figure 5. Carbonyl infrared spectra of SIL-$(CH_2)_3NH(CH_2)_2$-$NH_2/Rh_6(CO)_{16}$ during decarbonylation–carbonylation cycles at 368 K. Spectra recorded after decarbonylation by evacuation for 1 hr (——) and after admission of CO at 2.7 $\times$ 10^3Nm^{-2} (---). (a) Fresh sample; (b)–(d) first to third cycle.

The freshly prepared SIL-$(CH_2)_3NH(CH_2)_2NH_2/$ $Rh_6(CO)_{16}$ (Fig. 5a) shows sharp terminal C–O stretching bands at 2092(s), 2025(m) and 2008(s). Bridge C–O stretching bands cannot be detected. The system is thermally stable up to 420 K and aggregates to larger metal particles at higher temperatures even in a CO atmosphere. On decarbonylation (Figures 5 b–d) at 368 K the terminal C–O stretching bands decrease in intensity much more significantly than in the monoamine system; the initially strong band at 2008 cm^{-1} vanishes nearly completely, while a new pronounced doublet band appears at 1975/1960 cm^{-1}. Recarbonylation leads to some changes in the spectra in subsequent cycles. Particularly, the medium strong band at 2025 cm^{-1} is greatly intensified; its intensity finally compares with that of the band at 2008 cm^{-1}.

The interpretation of these data is by far not as certain as that for the SIL-$(CH_2)_3PPh_2/Rh_6(CO)_{16}$ system since infrared spectra of comparable systems are not available in the literature. Chini *et al.* [39] reported the formation of $[RNH_3]^+[Rh_6(CO)_{15}$-$(CONHR)]^-$ on reaction of $Rh_6(CO)_{16}$ with primary amines. This reaction apparently has not occurred on the modified silicas since the reported C–O stretching frequencies of the amide substituted cluster are much lower than those found in the present study. As a tentative interpretation we suggest that the rhodium cluster has retained its structural integrity also when bound to the amine modified silicas. The positions of the terminal C–O stretching frequencies should then be determined by the (unknown) degree of substitution and the chemical nature of the ligands, namely the electron donating properties and the vanishing π-acidity of the amine ligands. The bands around 1950 to 1975 cm^{-1}, which appear on decarbonylation still fall into the spectral range where usually terminal C–O stretching frequencies are expected [3, 40]. One may therefore assign these bands as terminal C–O stretching bands which are shifted to lower frequencies due to an increased substitution by amine groups and due to the corresponding increased negative charge density in the cluster entity. The increased substitution is obviously caused by a replacement of C–O ligands by amine groups during the decarbonylation. This process is entirely reversible in the monoamine system, while some irreversible changes occur with the diamine ligands. The introduction of electron donating ligands again indicates an increased tendency of the cluster towards CO ligand dissociation, whereby the cluster integrity appears to be retained.

Conclusions

The present study demonstrates that $Rh_6(CO)_{16}$ can be stabilized with retention of its structural integrity by attachment onto functional groups (phosphine and amine) of chemically modified silicas. Electron donation from these ligands into the cluster facilitates CO ligand dissociation (the effect seems to be more pronounced with amine than with phosphine groups) and thus provides the vacant coordination sites necessary for binding and activation of reactant molecules. In fact, some catalytic tests have shown that $Rh_6(CO)_{16}$ attached to modified silicas bearing phosphine or amine groups is an active catalyst for ethylene hydrogenation*, butene and 3-hexyne hydrogenation below 370 K in the gas phase. Kinetic studies of these reactions are presently underway in our laboratory as well as in Prof. Gates' laboratory at University of Delaware. The electronic and steric nature of ligands can be modified in principle, so that a catalyst tayloring might be possible with this class of catalytic materials in the future.

Acknowledgements

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