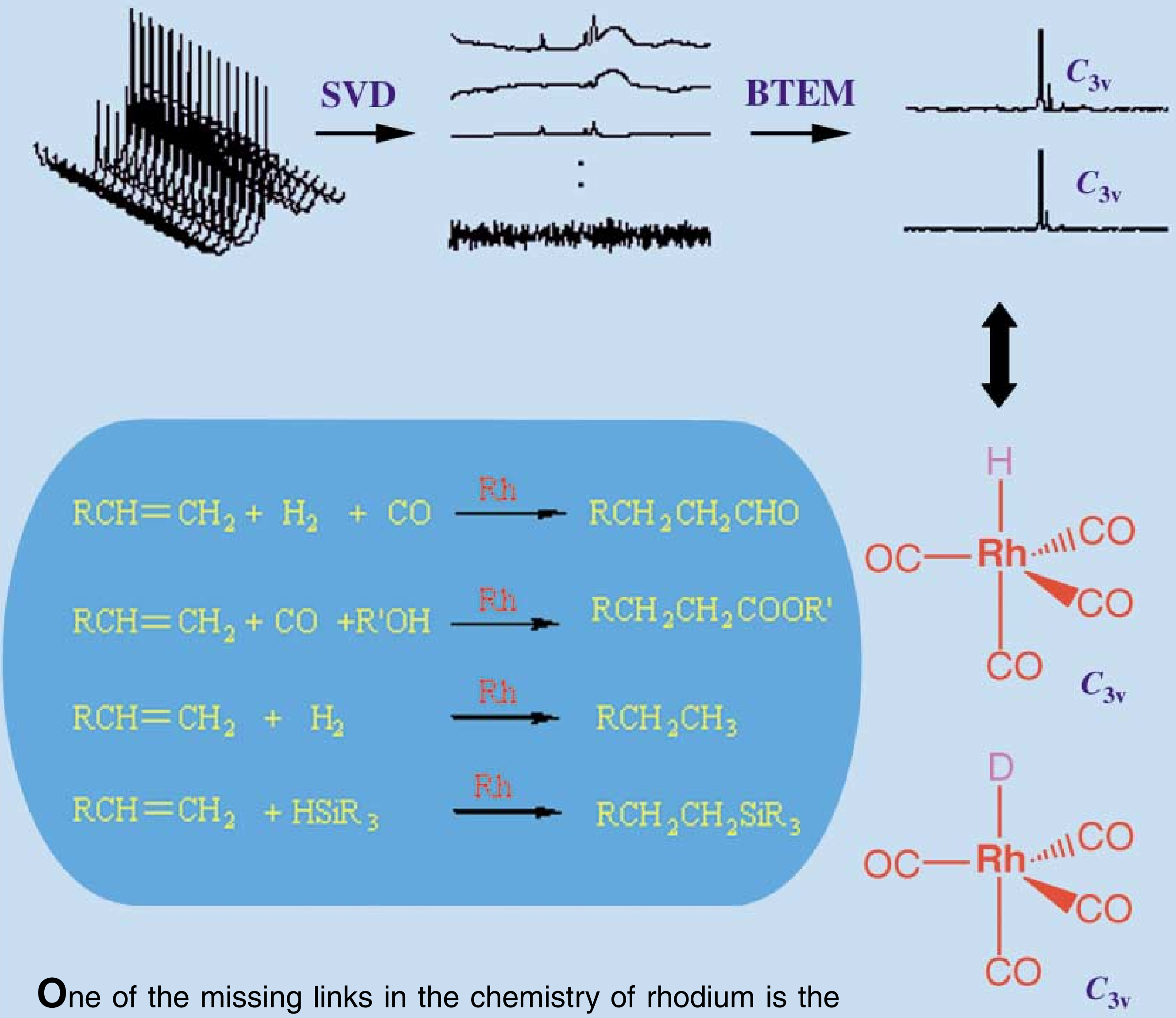
Rhodium Tetracarbonyl Hydride



One of the missing links in the chemistry of rhodium is the spectroscopic identification of the simple, unmodified rhodium carbonyl hydride [$HRh(CO)_4$]. Pure-component spectra of this compound and its deuterium analogue, [$DRh(CO)_4$], were obtained by investigating solutions of [$Rh_4(CO)_{12}$] in *n*-hexane upon exposure to varying partial pressures of H_2/CO and D_2/CO. The in situ high-pressure FTIR spectra were measured and subjected to band-target entropy minimization (BTEM), an advanced signal-processing technique (SVD = single-value decomposition). For more information see the following pages.

Rhodium Tetracarbonyl Hydride: The Elusive Metal Carbonyl Hydride**

Chuanzhao Li, Effendi Widjaja, Wee Chew, and Marc Garland*

Rhodium exhibits considerable activity in a wide range of heterogeneously and homogeneously catalyzed reactions.[1] Accordingly, many large-scale industrial plants, such as those for the synthesis of acetic acid and hydroformylation, have a total inventory of only a few kilograms of rhodium; hydroformylation is one of the five most important homogeneously catalyzed processes worldwide and responsible for about 10^7 t of organic products per year.[2] The activity of rhodium is certainly one of the primary reasons for the enormous number of rhodium complexes developed to date. This activity and industrial utility, together with the rarity of rhodium, are the main reasons for its position as the most expensive precious metal. Undoubtedly, the most well-known rhodium organometallic complexes are the Wilkinson complexes $[RhCl(PPh_3)_3]$ and $[HRh(CO)(PPh_3)_3]$,[3] which are extensively used in many homogeneously catalyzed reactions, in particular the hydroformylation of alkenes in the presence of molecular hydrogen and carbon monoxide to give aldehydes. One of the primary missing links in the industrial chemistry of rhodium is the identification of the simple, unmodified rhodium carbonyl hydride $[HRh(CO)_4]$. Here we report the spectroscopic identification, thermodynamics, and deuterium substitution of this compound.

In spite of the considerable synthetic effort invested in rhodium organometallic chemistry and the significant historical role played by metal carbonyl chemistry in the chemical process industry, the known chemistry of unmodified rhodium carbonyl complexes is very limited. Notable developments include the synthesis of the clusters $[Rh_4(CO)_{12}]$[4] and $[Rh_6(CO)_{16}]$[5] by Chini and co-workers, and the observation of $[Rh_2(CO)_8]$ under considerable CO partial pressures.[6] Ozin and Hanlan were able to spectroscopically identify [RhCO], $[Rh(CO)_2]$, $[Rh(CO)_3]$, and $[Rh(CO)_4]$; however, these were in low-temperature argon matrices.[7] The geometry of the latter species is a distorted tetrahedron, and the infrared spectra accordingly contain two terminal carbonyl vibrations at 2012 and 2019 cm^{-1}. In terms of simply substituted rhodium carbonyl compounds, only the mononuclear acyl complex $[RCORh(CO)_4]$ has been reproducibly observed.[8] Some 17 acyl complexes having aliphatic substituents for R have been characterized under hydroformylation conditions.[9]

In terms of rhodium carbonyl chemistry and homogeneous catalysis, the key species is the mononuclear hydride $[HRh(CO)_4]$. It represents the starting point for the catalytic hydrogenation of alkenes to alkanes and aldehydes to alcohols,[10] the catalytic hydroformylation of alkenes to aldehydes,[11] the hydrocarbonylation of alkenes with alcohols to form esters,[12] the hydrosilation of alkenes,[13] and many other reactions. Metal hydrides hold a special place in organometallic chemistry,[14] and they play a key role in homogeneous catalysis.[15] From a mechanistic perspective, the coordination of unsaturated ligands and subsequent insertion into the metal–hydride bond is the starting point for a wide variety of important and complex transformations.

Given its importance, numerous attempts to synthesize $[HRh(CO)_4]$ have been documented. Hieber and Lagally described the isolation of a yellow solid, assigned the tentative formula $[HRh(CO)_4]$, at cryogenic temperatures upon reduction of rhodium chloride with molecular hydrogen.[16] Chini and Martinengo made numerous unsuccessful attempts to protonate $[HRh(CO)_4]^-$.[17] Finally, Vidal and Walker reported the treatment of $[Rh_4(CO)_{12}]$ with 1300 bar of hydrogen and carbon monoxide and the in situ observation of an infrared spectrum with bands at 2008 (w), 2039 (vs), and 2070 (m) cm^{-1}, which they assigned to $[HRh(CO)_4]$, although four bands should be observed in the mid-infrared region.[18] It is important to note that the primary laboratories or groups involved with in situ spectroscopic studies of rhodium carbonyl chemistry and catalysis, namely Whyman at ICI, Pino and Bor in Zürich, and Markó at Veszprém,[19] never reported a successful attempt.

Recently, we introduced band-target entropy minimization (BTEM),[20] an advanced and model-free deconvolution technique based on a Shannon entropy criterion.[21] Tests of this novel algorithm with real in situ catalytic spectroscopic data have indicated that it is typically possible to account for more than 99 % of the experimental spectroscopic data. Even more striking is the ability to retrieve extremely weak spectra of pure components, for example, corresponding to species with less than 0.07 % of the integral intensity of the entire spectroscopic data set. With this tool, we have reinvestigated the $[Rh_4(CO)_{12}]/H_2/CO$ system in an aliphatic hydrocarbon solvent.

Experiments were conducted in *n*-hexane in a high-pressure batch reactor system with in situ FT-IR capability. The experiments typically lasted 24 h, and the spectra were taken at 5–10 min intervals in the range between 1000 and 2500 cm^{-1}. Details of the equipment and typical experimental procedures used as well as methods of purification and safety issues can be found elsewhere.[22] The experimental design typically involved 300 mL of solvent and other conditions in the following ranges: $T = 285–303$ K, $P_{H_2} = 1.0–5.0$ MPa (or $P_{D_2} = 0.5–2.0$ MPa), $P_{CO} = 1.0–5.0$ MPa, initial concentration of $[Rh_4(CO)_{12}] = 58–315$ mg, and $P_T = 2.0–8.0$ MPa. Each experiment was conducted in the semi-batch mode, whereby multiple perturbations in the variables hexane, H_2 or D_2, CO, and $[Rh_4(CO)_{12}]$ could be achieved in any 24-h run. Upon each perturbation of the reactive system, very small changes could be observed in the mid-infrared spectra during the subsequent few minutes. In total, 475 spectra were taken for

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reactions involving only molecular hydrogen, and about 200 spectra were recorded with molecular deuterium alone or with deuterium and hydrogen.

A singular value decomposition was performed on the data sets. Figure 1 shows some of the right singular vectors from the semi-batch experiments involving only molecular hydrogen. The numbers in Figure 1 indicate prominent spectral features in the vectors which were subsequently targeted in the BTEM algorithm. Details of the mathematical constructs and implementation of BTEM can be found in the literature.[20a,b] The first few vectors represent the primary contributions to signal variance, while the subsequent vectors have increasing contributions from white noise.

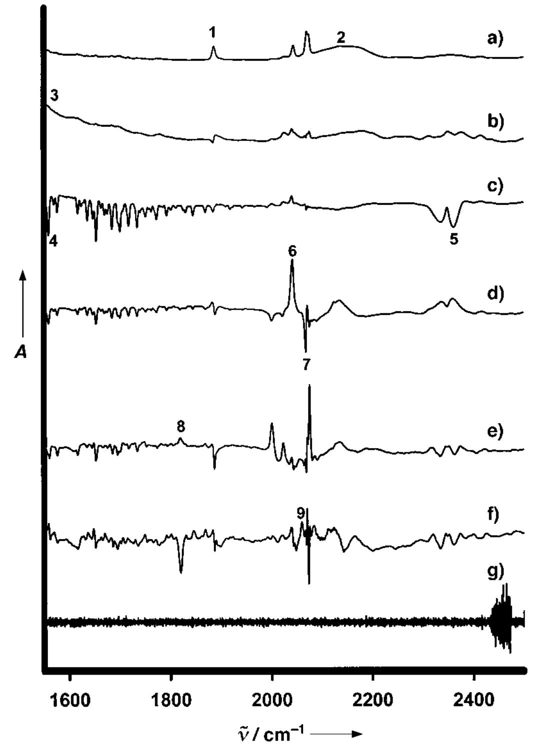


Figure 1. Several right singular vectors from the singular value decomposition: a) 1st vector, b) 4nd vector, c) 5th vector, d) 6th vector, e) 13th vector, f) 17th vector, g) 475th vector.

Figure 2 presents the reconstructed pure-component spectra of the “major” species present. These spectra were obtained by targeting the features 2 (CO), 3 (hexane), 4 (vapor-phase moisture), and 5 (vapor-phase carbon dioxide) indicated in Figure 1. Figure 3 shows the reconstructed pure-component spectra of the “minor” components, that is, the rhodium organometallic species. These spectra were obtained by targeting the features 1 ($[Rh_4(\sigma\text{-}CO)_9(\mu\text{-}CO)_3]$, maxima at 1885.8, 2043.8, 2070.2, 2073.8 cm^{-1}), 9 ($[Rh_2(\sigma\text{-}CO)_6(\mu\text{-}CO)_2]$, maxima at 1845.6, 1861.6, 2060.2, 2084.2 cm^{-1}), 7 ($[Rh_4(\sigma\text{-}CO)_{12}]$, maxima at 2068.0, 2076.0 cm^{-1}),[20b] and 8 ($[Rh_6(CO)_{16}]$, maxima at 1819.2, 2075.4 cm^{-1}). The concentration of $[Rh_6(CO)_{16}]$ was typically on the order of ppm or less, and its presence could be detected by unaided visual inspection only in a few experimental spectra.

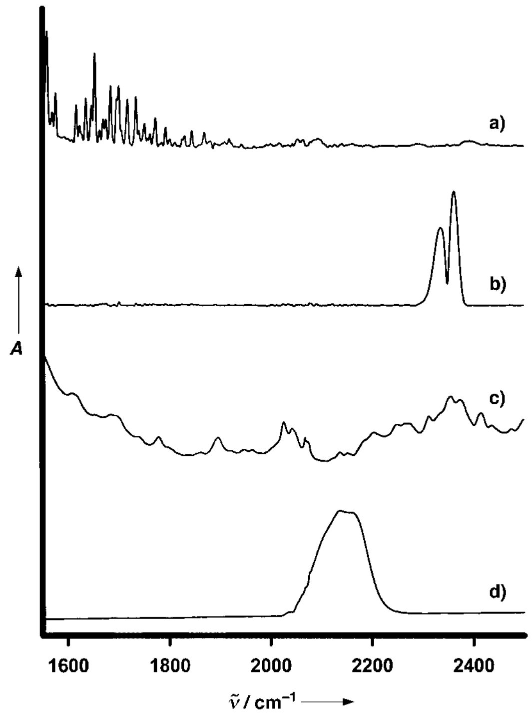


Figure 2. The reconstructed pure-component spectra of the major components: a) vapor-phase moisture, b) vapor-phase CO_2, c) *n*-hexane, d) dissolved CO.

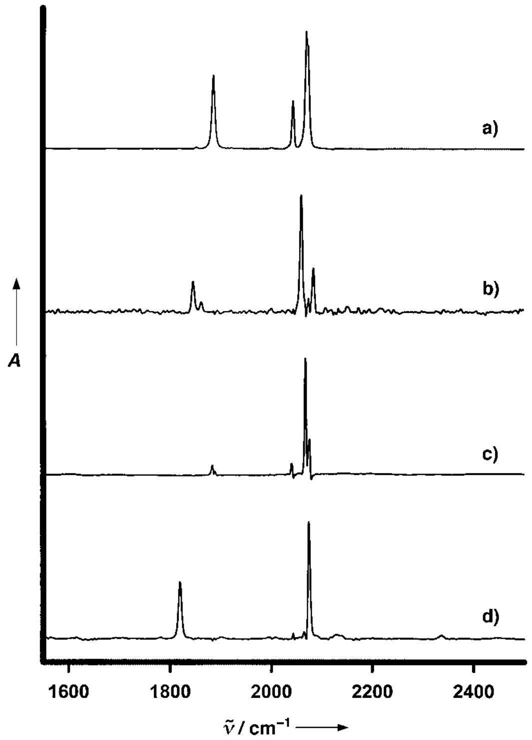


Figure 3. The reconstructed pure-component spectra of the minor organometallic components: a) $[Rh_4(\sigma\text{-}CO)_9(\mu\text{-}CO)_3]$, b) $[Rh_2(\sigma\text{-}CO)_6(\mu\text{-}CO)_2]$, c) $[Rh_4(\sigma\text{-}CO)_{12}]$, d) $[Rh_6(CO)_{16}]$.

Most importantly, BTEM was able to reconstruct two new and previously unknown mid-infrared pure-component spectra. One spectrum arose exclusively in the experiments with molecular hydrogen (spectral feature 6 in Figure 1) and the other arose exclusively in the experiments with molecular deuterium. These pure-component spectra correspond to only about 0.15% of the signals in the respective data sets. In the interest of completeness, it must be mentioned that BTEM also was able to reconstruct only one additional spectrum belonging to [Fe(CO)$_5$] with bands at 1964.8 (w), 2001.0 (vs), 2023.6 (m) cm^{-1}. The presence of [Fe(CO)$_5$] could be detected in some but not all experiments. It is an omnipresent trace impurity in commercial CO stored in stainless steel cylinders.

Figure 4 reports the entire mid-infrared region from 1550 to 2500 cm^{-1}, where either M–H or M–CO vibrations are expected to occur. Shown are a spectrum of [HCo(CO)$_4$] obtained in our laboratory as well as the new spectra recorded upon the use of molecular hydrogen and deuterium. [HCo(CO)$_4$] is known to have a trigonal-bipyramidal geometry with the hydrogen ligand in an axial position.[23] Accordingly, the symmetry of the molecule corresponds to the point group C_{3v}.[24] Three metal–carbonyl vibrations are expected and indeed observed at 2029.6 (vs), 2052.2 (m), and 2115.6 (w) cm^{-1} and the metal–hydrogen vibration appears at 1993.0 (w) cm^{-1}. In comparison, the literature values (with relative intensities) in *n*-heptane are 2029.8 (10), 2052.3 (3.2), 2116.1 (0.2), and 1993.0 (0.2) cm^{-1}.[25] The new spectrum observed under molecular hydrogen alone also has four vibrations in the mid-infrared range, and these occur in the same pattern, namely, a band of minor intensity at 2002.8 (w) cm^{-1} and three more intense bands at 2041.6 (vs), 2071.8 (m), and 2123.6 (w) cm^{-1}. The new spectrum observed under molecular deuterium has only three vibrations in the mid-infrared region at 2041.6 (vs), 2063.6 (m), and 2119.6 (w) cm^{-1}.

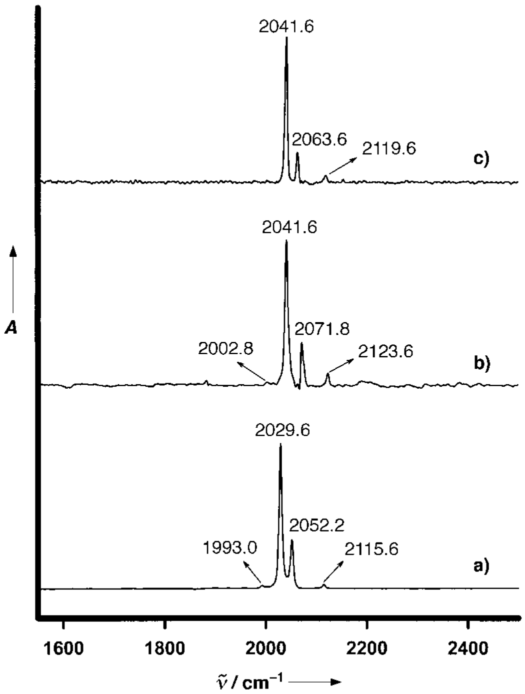
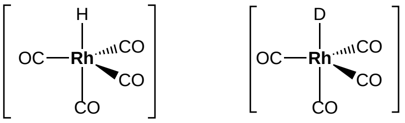


Figure 4. The reconstructed pure-component spectra of the organometallic carbonyl hydrides: a) [HCo(CO)$_4$], b) [HRh(CO)$_4$], c) [DRh(CO)$_4$].

The new spectra clearly correspond to [HRh(CO)$_4$] and [DRh(CO)$_4$]. These molecules have the expected trigonal-bipyramidal geometries with the protium or deuterium ligand in an axial position (Scheme 1). The vibrations at the very high wavenumbers 2123.6 and 2119.6 cm^{-1} correspond to the totally symmetric mode and are conclusive evidence that the molecules have very high symmetry and are mononuclear.[26]



Scheme 1. Schematic representation of the trigonal-bipyramidal structures of [HRh(CO)$_4$] and [DRh(CO)$_4$].

Furthermore, the shift in metal–carbonyl vibrations and the loss of the metal–hydrogen vibration upon substitution with deuterium is highly analogous to the case of cobalt tetracarbonyl hydride. Edgell and co-workers reported band at 2043, 2062, 2121, and 1934 cm^{-1} for [HCo(CO)$_4$] and at 2043, 2058, 2120, and 1396 cm^{-1} for [DCo(CO)$_4$].[27] The vibration at 2041.6 cm^{-1} for [HRh(CO)$_4$]/[DRh(CO)$_4$] belongs to the *e* mode and is insensitive to substitution, whereas the other two carbonyl vibrations belong to the a_1 mode and are moderately sensitive to substitution with deuterium. The D–Rh vibration could not be directly observed since the spectral window 1350–1500 cm^{-1} is opaque due to strong solvent absorption.

The equilibrium thermodynamics were also measured. The concentrations of all reactants were considered in mole fraction units, and the equilibrium was modeled as either a two-parameter expression in enthalpy and entropy of reaction or as a three-parameter expression in enthalpy, entropy, and volume of reaction. The equilibrium constant K_{eq} is given by Equation (1).

$$K_{eq} = [\mathrm{HRh(CO)_4}]^4/[\mathrm{Rh_4(CO)_{12}}]^1[\mathrm{CO}]^4[\mathrm{H_2}]^2 \qquad (1)$$

Since the overall reaction can be written as [Rh$_4$(μ-CO)$_3$(σ-CO)$_9$] + 2H$_2$ + 4CO$\leftrightarrow$4[HRh(σ-CO)$_4$], at least 19 bonds are broken and formed: six Rh–Rh bonds broken, three μ-CO bonds converted into three σ-CO bonds, two H–H bonds broken, four new Rh–H bonds formed, and four new Rh–CO bonds formed. The two-parameter model provided the thermodynamic parameters $\Delta_r H = -69.7 \pm 19.8$ kJ mol^{-1} and $\Delta_r S = -0.38 \pm 0.07$ kJ mol^{-1} K^{-1}. The exothermic nature of the reaction is consistent with the known thermochemistry of rhodium, namely, the low heat of formation of Rh–Rh and bridging Rh–CO bonds and the high heat of formation of Rh–H and Rh–CO bonds. Accordingly, higher conversions into [HRh(CO)$_4$] are achieved at lower temperatures. Also the negative entropy of reaction is consistent with the reaction of seven molecules to give only four molecules as products. The three-parameter model provided the thermodynamic parameters $\Delta_r H = -82.4 \pm 16.2$ kJ mol^{-1}, $\Delta_r S = -0.44 \pm 0.06$ kJ mol^{-1} K^{-1}, and $\Delta_r V = -1131 \pm 313$ mL mol^{-1}. The negative sign for the volume of reaction is consistent with the loss of the unusually large partial molar volumes of dissolved molecular hydrogen and carbon monoxide of about 60 mL mol^{-1} upon reaction.[28] However, a value on the order of -250 mL mol^{-1} rather than -1100 mL mol^{-1} is expected.[29]

These results indicate the severe limitation of the atypically small total pressure interval of ca. 5 MPa used in this study versus pressure intervals of ca. 100 MPa used in traditional reaction volume studies.[30]

The intrinsic reaction kinetics were too rapid to be captured with the present experimental setup. Indeed, characteristic times for gas–liquid mass transfer as well as liquid-phase mixing were on the order of a few minutes. Therefore, transport-controlled rather than intrinsic kinetics were observed.

Nevertheless, an informed assumption about the mechanism(s) can be proposed. After each perturbation, hydrogen activation on [$Rh_2(CO)_8$] (or equilibrated and unsaturated [$Rh_2(CO)_7$]) probably occurs very rapidly. After depletion of the dinuclear carbonyl species, the fragmentation of [$Rh_4(CO)_{12}$] (or possibly the equilibrated, open polyhedron structure [$Rh_4(CO)_{14}$])[31] is likely to be the rate-limiting step. Hence, the kinetics can be anticipated to involved contributions from a number of parallel pathways.

Finally, the BTEM analysis of data from previous and ongoing hydroformylation studies was performed. In these catalytic studies involving [$Rh_4(CO)_{14}$] as catalyst precursor in *n*-hexane with less reactive alkene substrates (i.e., cyclooctene and α-methylstyrene) it was possible to recover again the pure-component spectrum of [$HRh(CO)_4$]. The assignment of the fundamental vibrations at 2002.8 (w), 2041.6 (vs), 2071.8 (m) and 2123.6 (w) cm^{-1} is entirely reproducible. In some of these reconstructions, the rhodium–hydrogen vibration at 2002.8 cm^{-1} is better resolved or more pronounced.

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Spontaneous Deposition of Water-Soluble Substances into Microcapsules: Phenomenon, Mechanism, and Application**

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Novel hollow microcapsules with sizes ranging from 60 nm to 10 μm have recently been produced by the layer-by-layer (LBL) assembly of oppositely charged polyelectrolytes onto colloidal templates, followed by removal of the template cores.[1] Great progress has been made towards optimizing the fabrication conditions for capsules templated onto melamine formaldehyde (MF) particles, with an integrity of 90 % having

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