

# Liquid-Phase Reaction of Monosubstituted and Disubstituted Alkynes with Tetrarhodium Dodecacarbonyl under CO and CO/H<sub>2</sub> Mixtures. In-Situ IR Spectroscopic Characterization of 20 New Alkyne–Rhodium Complexes<sup>†</sup>

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It is well-known that the liquid-phase homogeneous unmodified rhodium-catalyzed hydroformylation of alkenes is irreversibly poisoned by the presence of trace quantities of alkynes. In the present contribution, we examined the reaction of four series of monosubstituted and disubstituted alkynes (20 compounds) with Rh<sub>4</sub>(CO)<sub>12</sub> in *n*-hexane solvent at 293 K under both (A) 2.0 MPa CO and (B) 2.0 MPa CO and 2.0 MPa H<sub>2</sub>. The analytic method used was in-situ high-pressure infrared spectroscopy. It was observed that (I) all alkynes used in this study reacted quantitative with Rh<sub>4</sub>(CO)<sub>12</sub> in a matter of hours, (II) the final spectra were not influenced by the presence of hydrogen, (III) the monosubstituted alkynes consistently gave a final product involving six terminal  $\nu_{\text{CO}}$  vibrations in the region 2036–2121 cm<sup>-1</sup> and two vibrations at ca. 1668 and 1689 cm<sup>-1</sup>, and (IV) the disubstituted alkynes consistently gave a final spectrum consistent with the superposition of the spectra obtained in III plus a spectrum involving five terminal  $\nu_{\text{CO}}$  vibrations in the region 2030–2100 cm<sup>-1</sup> and one vibration at ca. 1630 cm<sup>-1</sup>. These results are consistent with the existence of two primary types of observable species in the final products. Due to the band positions and absorptivities, we tentatively propose that these species are substituted dirhodium carbonyl species, specifically Rh<sub>2</sub>(CO)<sub>6</sub>{ $\mu$ - $\eta$ <sup>1</sup>-(CO–HC<sub>2</sub>R)} for terminal alkynes and Rh<sub>2</sub>(CO)<sub>6</sub>{ $\mu$ - $\eta$ <sup>1</sup>-(CO–R<sup>1</sup>C<sub>2</sub>R<sup>2</sup>)} and Rh<sub>2</sub>(CO)<sub>6</sub>{ $\mu$ - $\eta$ <sup>2</sup>-(R<sup>1</sup>C<sub>2</sub>R<sup>2</sup>)} in the case of disubstituted alkynes. These complexes are the rhodium analogues of well-known dicobalt carbonyl alkyne complexes. It appears that, in the case of terminal alkynes, the dirhodium–alkyne complexes undergo rapid CO insertion under 2.0 MPa CO. In the case of disubstituted alkynes, CO insertion seems more difficult to obtain, and an observable equilibrium is established between the bridged alkyne species and the insertion product. In both cases the final alkyne complexes are stable under CO even in the presence of molecular hydrogen. This is probably the primary reason that trace quantities of alkynes are able to poison the catalytic alkene hydroformylation reaction.

## Introduction

Rhodium complexes have been used in the liquid-phase homogeneous catalytic hydroformylation reaction for approximately 50 years. Although the hydroformylation of alkenes was initially performed with unmodified rhodium complexes,<sup>1</sup> phosphine-modified rhodium complexes are now responsible for much of the ca. 10<sup>7</sup> tonnes per annum of alkene hydroformylation products. The low activity of the unmodified systems compared to modified systems under mild reaction conditions,<sup>2</sup> as

well as their sensitivity to trace impurities of dienes and alkynes,<sup>3</sup> is largely responsible for the infrequent use of unmodified rhodium carbonyl complexes on an industrial scale today. In contrast, not only are many rhodium phosphine complexes relatively insensitive to the trace presence of dienes and alkynes, but such complexes can actually hydroformylate such substrates. Examples include the hydroformylation of 1-hexyne to heptanal, 1-butyne to pentanal, and 2-butyne to 2-methylbutanal using HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>, and the hydroformylation of acetylene, 1-butyne, and 2-butyne using mixtures of Rh<sub>2</sub>O<sub>3</sub> and phosphines.<sup>4</sup>

<sup>†</sup> Experimental research performed at ETH-Zurich, 1992–1995. Analysis performed at NUS, 1998.

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Over the past decade our group has focused on detailed in-situ infrared spectroscopic and kinetic studies of the unmodified rhodium hydroformylation using numerous alkenes as substrates. These studies have concentrated on (A) the first identification of acyl rhodium tetracarbonyl as the only observable intermediate in  $\text{Rh}_4(\text{CO})_{12}$  hydroformylations of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal at 293 K,<sup>5</sup> (B) the identification of acyl rhodium tetracarbonyl as the only observable intermediate in  $\text{CoRh}(\text{CO})_7$  and  $\text{CoRh}(\text{CO})_8$  hydroformylations of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal at 293 K, as well as the associated kinetics of the induction period, product formation, and deactivation,<sup>6</sup> (C) the detailed kinetics of the hydroformylations of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal using  $\text{Rh}_4(\text{CO})_{12}$  as precursor,<sup>7</sup> (D) the detailed kinetics of the hydroformylation of cyclohexene to cyclohexane carboxaldehyde using  $\text{Rh}_4(\text{CO})_{12}$  as precursor where the phenomenon of equilibrium precursor conversion was observed,<sup>8</sup> (E) the kinetics of the hydroformylation of 3,3-dimethylbut-1-ene to 4,4-dimethylpentanal at 293 K using a variety of phosphine-free rhodium complexes,<sup>9</sup> (F) the experimental, numerical, and statistical aspects of evaluating hydroformylation turnover frequencies,<sup>10</sup> (G) the detailed regioselective kinetics of the hydroformylation of styrene to ( $\pm$ )-2-phenylpropanal and 3-phenylpropanal using  $\text{Rh}_4(\text{CO})_{12}$  as precursor,<sup>11</sup> (H) the search for a catalytic binuclear elimination reaction mechanism at very high  $\text{Rh}_4(\text{CO})_{12}$  concentrations during the hydroformylation of cyclohexene,<sup>12</sup> and (I) the characterization of ca. 20 new acyl rhodium tetracarbonyls during hydroformylations with  $\text{Rh}_4(\text{CO})_{12}$  as precursor.<sup>13</sup> However, until now, we have not investigated the chemistry of the deactivation phenomenon initiated by either dienes nor alkynes.

In the present contribution we investigate the reactivity of four series of alkynes (20 compounds) toward  $\text{Rh}_4(\text{CO})_{12}$  in *n*-hexane as solvent at 293 K in the presence 2.0 MPa CO and 2.0 MPa CO/2.0 MPa  $\text{H}_2$ . The alkynes are conveniently classified as (a) a homologous series of terminal unsymmetric alkynes from 1-pentyne to 1-hexadecyne, (b) a homologous series of symmetric alkynes from 2-butyne to 6-dodecyne, (c) a homologous series of increasingly symmetric alkynes from 1-decyne to 5-decyne, and (d) a miscellaneous collection of other monosubstituted and disubstituted alkynes. The objective of the study was to identify the predominate rhodium alkyne complex(es) present under hydroformylation conditions, and hence the probable reason that rhodium is unavailable for alkene hydroformylation in alkene hydroformylations tainted by the presence of trace alkynes.

## Experimental Section

**General Information.** All solution preparations were carried out under argon (99.999% Pan Gas AG, Luzern, Switzerland) using standard Schlenk techniques.<sup>14</sup> The argon was further purified prior to use by passage through a column containing 100 g of reduced BTS-catalyst (Fluka AG Buchs, Switzerland) and 100 g of 4 Å molecular sieves to adsorb trace oxygen and water, respectively. All reactions were carried out under carbon monoxide (99.997% Messner Griesheim GmbH, Germany) and hydrogen (99.999% Pan Gas AG, Luzern, Switzerland) after further purification through deoxy and zeolite columns.

The precious metal complex  $\text{Rh}_4(\text{CO})_{12}$ , with stated purity of 98% min, was obtained from Strem Chemicals SA (Bischheim, France) and was used without further purification, although trace quantities of the high-nuclearity cluster  $\text{Rh}_6(\text{CO})_{16}$  is virtually always present. The complex  $\text{Rh}_4(\text{CO})_{12}$  is known to be oxygen, water, and light sensitive.<sup>15</sup> The *n*-hexane solvent (stated purity >99.6%, Fluka AG) was refluxed over sodium potassium alloy under argon. Weights were measured with a precision of  $\pm 0.1$  mg. Volumes were measured with a precision of  $\pm 0.045$  mL. Further microanalytic techniques were not employed.<sup>16</sup> All alkynes used in this study were of the highest quality commercially obtainable, usually 99.0+% (Wiley Organic Chemicals or Lancaster Chemicals, U.K.). Concerning further purification, the alkynes were simply degassed before use.

**Equipment.** In-situ spectroscopic studies were performed in a 1.5 L stainless steel (SS316) autoclave (Büchi-Uster, Switzerland), which was connected to a high-pressure infrared cell. The autoclave ( $P_{\text{max}} = 22.5$  MPa) was equipped with a packed magnetic stirrer with six-bladed turbines in both the gas and liquid phases (Autoclave Engineers, Erie, PA) and was constructed with a heating/cooling mantle. A high-pressure membrane pump (Model DMK 30, Orlita AG, Geissen, Germany), with a maximum rating of 32.5 MPa and a 3 L/h flow rate, was used to circulate the *n*-hexane solutions from the autoclave to the high-pressure IR cell and back to the autoclave via jacketed 1/8 in. (SS316) high-pressure tubing (Autoclave Engineers). The entire system, autoclave, transfer lines, and infrared cell, was cooled using a Lauda cryostat Model RX20 and could be maintained isothermal ( $\Delta T \leq 0.5$  °C) at 298–313 °C. Temperature measurements were made at the cryostat, autoclave, and IR cell with PT-100 thermoresistors. The necessary connections to vacuum and gases were made with 1/4 in. (SS316) high-pressure tubing (Autoclave Engineers), and 1.0, 5.0, and 10.0 piezocrystals were used for pressure measurements (Keller AG Winterthur, Switzerland). The entire system was gastight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

The high-pressure infrared cell was constructed at the ETH-Zürich of SS316 steel and could be heated and cooled. The  $\text{CaF}_2$  single-crystal windows (Korth Monokristalle, Kiel, Germany) had dimensions of 40 mm diameter by 15 mm thickness. Two sets of Viton and silicone gaskets provided sealing, and Teflon spacers were used between the windows. The construction of the flow-through cell<sup>17</sup> is a variation on a design due to Noack<sup>18</sup> and differs in some respects from other high-pressure infrared cells described in the literature (for a review, see Whyman<sup>19</sup>).

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The high-pressure cell was situated in a Perkin-Elmer 983 infrared spectrometer. The resolution was set to  $4\text{ cm}^{-1}$  for all spectroscopic measurements. A schematic diagram of the experimental setup can be found in ref 11.

**In-Situ Spectroscopic Studies.** All experiments were performed in a similar manner. First, single-beam background spectra of the IR sample chamber were recorded. Then 1–10 mL of alkyne was dissolved in 150 mL of *n*-hexane, and this solution was transferred under argon to the autoclave. Under 0.2 MPa CO pressure, infrared spectra of the alkyne solution in the high-pressure cell were recorded. The total system pressure was raised to 2.0 MPa CO, and the stirrer and high-pressure membrane pump were started. After equilibration, infrared spectra of the alkyne/*n*-hexane/CO solution in the high-pressure cell were recorded. A solution of 100 mg of  $\text{Rh}_4(\text{CO})_{12}$  dissolved in 100 mL of *n*-hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO, and then added to the autoclave. Infrared spectra of the alkyne/*n*-hexane/CO/ $\text{Rh}_4(\text{CO})_{12}$  solution in the high-pressure cell were recorded. If this was a CO only experiment, spectra were recorded at 30 min intervals in the range 1600–2200  $\text{cm}^{-1}$ . For CO and  $\text{H}_2$  experiments, 2.0 MPa hydrogen was further added. Spectra were recorded at 30 min intervals in the range 1600–2200  $\text{cm}^{-1}$ .

A considerable number of spectral subtractions were performed on each reaction spectrum in order to subtract the absorbance of the *n*-hexane solvent, dissolved CO,  $\text{Rh}_4(\text{CO})_{12}$ , and the alkynes.

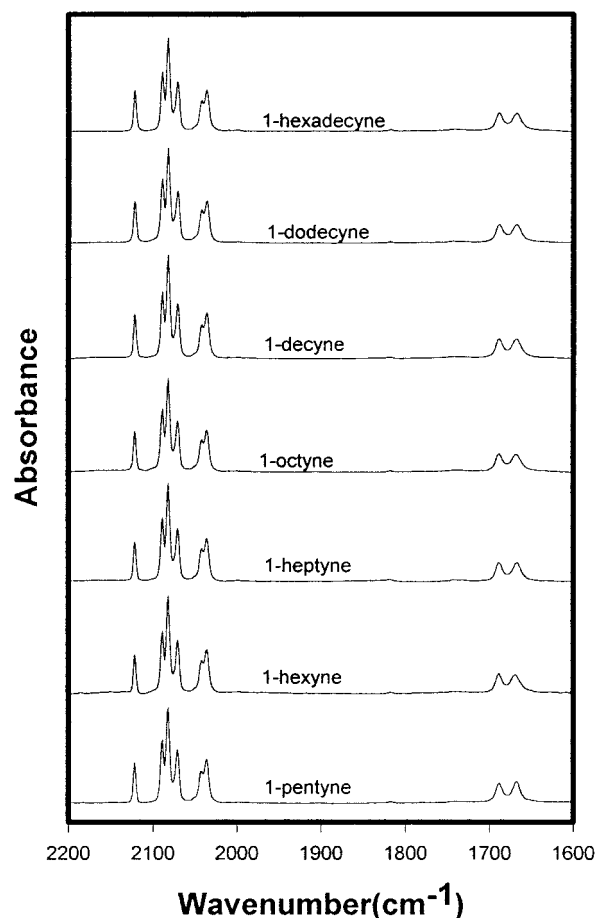
The solubility of CO under these reaction conditions was approximately 0.033 mole fraction, and the solubility of  $\text{H}_2$  was approximately 0.018 mole fraction.<sup>9</sup> Consequently, the moles in each experiment were 1.51 mol of *n*-hexane, 0.05 mol of CO, and 0.03 mol of  $\text{H}_2$ . Since the amount of  $\text{Rh}_4(\text{CO})_{12}$  used in the experiments was ca. 100 mg, and since the concentration of alkynes was low, the corresponding in-situ measured initial concentrations of  $\text{Rh}_4(\text{CO})_{12}$  in the experiments was ca.  $8 \times 10^{-5}$  mole fraction.

## Results

**Terminal Alkynes.** Seven alkynes were used in the series of experiments involving terminal alkynes. These were 1-pentyne, 1-hexyne, 1-heptyne, 1-octyne, 1-decyne, 1-dodecyne, and 1-hexadecyne. The spectra collected under CO reaction conditions and under CO and  $\text{H}_2$  reaction conditions were essentially identical. After a few hours, quantitative conversion of  $\text{Rh}_4(\text{CO})_{12}$  was observed for all reactions. Figure 1 shows the spectra of the seven CO reaction mixtures after subtraction of background, hexane, CO, and alkyne. As shown by Figure 1, the resultant spectra are essentially identical for all alkynes used.

The weak vibration at  $1820\text{ cm}^{-1}$  is due to the bridging carbonyls on  $\text{Rh}_6(\text{CO})_{16}$ . This weak absorbance is seen in this set of experiments as well as experiments with symmetric disubstituted alkynes, asymmetric disubstituted decynes, and other alkynes. In addition, there is a very weak vibration at ca.  $2000\text{ cm}^{-1}$  in these spectra as well as all other spectra. Due to the magnitude of this vibration, as well as its position ca.  $35\text{ cm}^{-1}$  lower than the lowest terminal CO vibration, this band is most likely due to the isotopomers, i.e., the 1.1% natural abundance of  $^{13}\text{C}$ .<sup>20</sup>

The spectra obtained in the present series are similar in both the positions of the absorbance maxima and the relative intensities. Both are tabulated in Table 1. As indicated by Table 1 there appears to be six primary terminal CO vibrations and two clear vibrations at low  $\text{cm}^{-1}$ .



**Figure 1.** Mid-infrared spectra of alkyne–rhodium complexes after subtraction of hexane, CO, and free alkyne. Homologous series of monosubstituted alkynes from 1-pentyne to 1-hexadecyne.

**Symmetric Disubstituted Alkynes.** Five alkynes were used in the series of experiments involving symmetric disubstituted alkynes. These were 2-butyne, 3-hexyne, 4-octyne, 5-decyne, and 6-dodecyne. The spectra collected under CO reaction conditions and under CO and  $\text{H}_2$  reaction conditions were essentially identical. After a few hours, quantitative conversion of  $\text{Rh}_4(\text{CO})_{12}$  was observed for all reactions. Figure 2 shows the spectra of the five CO reaction mixtures after subtraction of background, hexane, CO, and alkyne. As shown by Figure 2, the resultant spectra are not identical. In fact, as the molecular weight of the alkynes increases, more bands become visible.

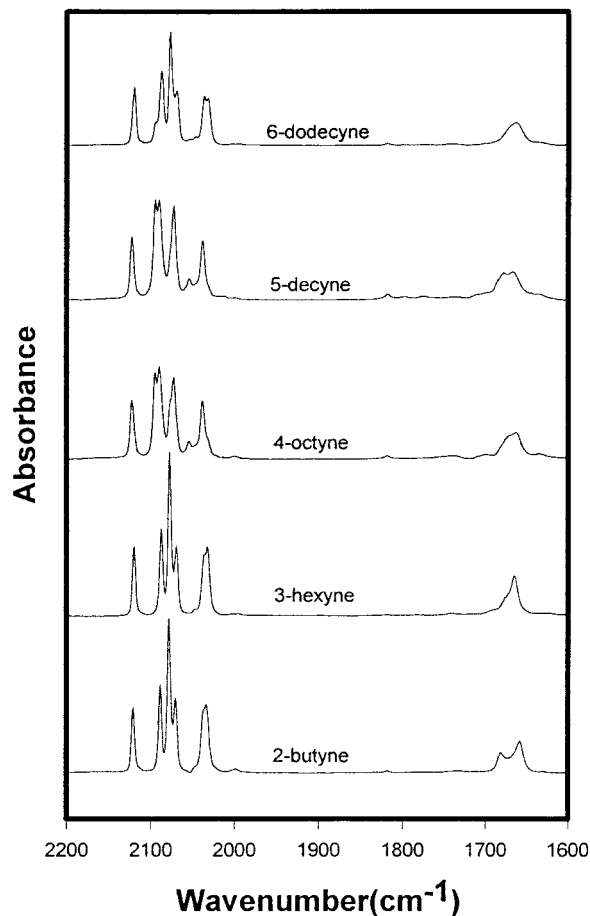
The spectra are only a little similar in the positions of the absorbance maxima as well as the relative intensities of the terminal CO vibrations. However, clear systematic trends are apparent. For example, the result of the 2-butyne experiment is almost identical to the terminal alkyne reactions. However, as the molecular

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**Table 1. Relative Infrared Absorbance of Terminal Alkyne Complexes**

alkyne	$\nu_{\text{CO}}$ (cm <sup>-1</sup> ) above, relative intensity below						$\nu$ (cm <sup>-1</sup> )	
1-pentyne	2122	2089.4	2082.4	2071	2043	2037	1689	1668
	0.41	0.66	1	0.55	0.32	0.45	0.20	0.22
1-hexyne	2122	2089.2	2082.2	2070.6	2042.5	2036.4	1689	1669
	0.40	0.64	1	0.54	0.33	0.45	0.20	0.18
1-heptyne	2121.6	2089	2082	2070.5	2043	2036.3	1689	1667.5
	0.40	0.65	1	0.53	0.32	0.42	0.19	0.18
1-octyne	2120	2089.2	2082	2070.5	2043	2036.3	1689	1667.5
	0.43	0.67	1	0.53	0.34	0.45	0.20	0.19
1-decyne	2122	2089.2	2082	2070.6	2042.5	2036.3	1689	1668
	0.42	0.64	1	0.52	0.31	0.44	0.19	0.19
1-dodecyne	2121.7	2089	2082	2070.6	2042.3	2036.4	1689	1667.6
	0.45	0.68	1	0.56	0.33	0.46	0.19	0.19
1-hexadecyne	2121.7	2089	2082	2070.7	2042.6	2036.2	1689	1668
	0.44	0.64	1	0.52	0.32	0.44	0.19	0.19



**Figure 2.** Mid-infrared spectra of alkyne–rhodium complexes after subtraction of hexane, CO, and free alkyne. Homologous series of symmetric disubstituted alkynes from 2-butyne to 6-dodecyne.

weight increases, more terminal bands become apparent (although they are small) and a new band at 1630 cm<sup>-1</sup> appears. The results are tabulated in Table 2.

**Asymmetric Disubstituted Decynes** Five alkynes were used in the series of experiments involving asymmetric disubstituted alkynes. These were 1-decyne, 2-decyne, 3-decyne, 4-decyne, and 5-decyne. The spectra collected under CO reaction conditions and under CO and H<sub>2</sub> reaction conditions were essentially identical. After a few hours, quantitative conversion of Rh<sub>4</sub>(CO)<sub>12</sub> was observed for all reactions. Figure 3 shows the spectra of the five CO reaction mixtures after subtraction of background, hexane, CO, and alkyne. As shown by Figure 3, the resultant spectra are not identical.

The spectra are only a little similar in the positions of the absorbance maxima as well as the relative intensities of the terminal CO vibrations. However, a clear systematic trend is apparent. For example, the result of the 2-decyne experiment is almost identical to the 1-decyne reaction. However, as the triple bond becomes more internal, more terminal CO bands become apparent (although the intensity of the new bands is low) and the band at 1630 cm<sup>-1</sup> appears. The results are tabulated in Table 3.

**Other Alkynes.** Five other alkynes were used in a comparative series of experiments. These were cyclohexylacetylene, 3,3-dimethylbut-1-yne, 1-phenyl-1-propyne, diphenylacetylene, and phenylacetylene. The spectra collected under CO reaction conditions and under CO and H<sub>2</sub> reaction conditions were essentially identical. After a few hours, quantitative conversion of Rh<sub>4</sub>(CO)<sub>12</sub> was observed for all reactions. Figure 4 shows the spectra of the five CO reaction mixtures after subtraction of background, hexane, CO, and alkyne. As shown by Figure 4, the resultant spectra are not identical.

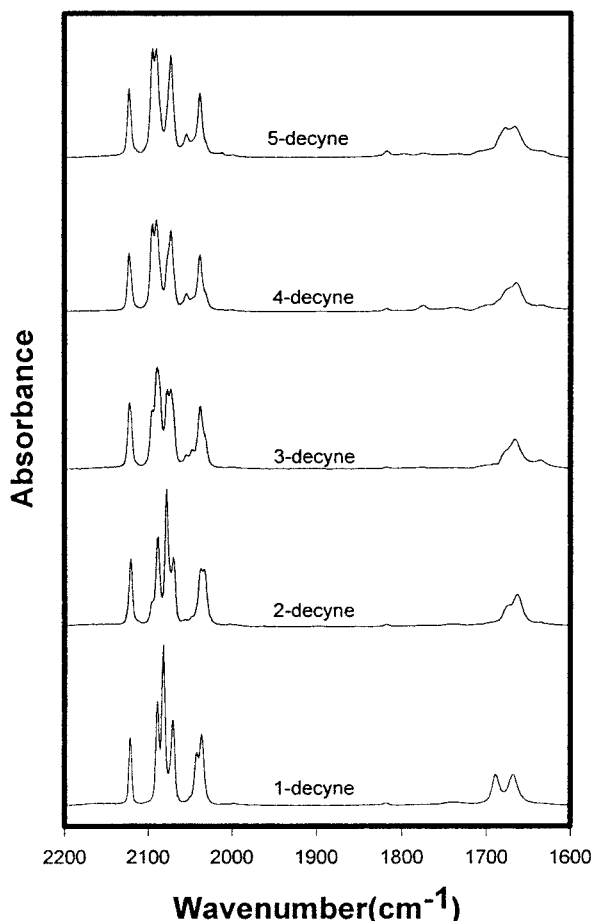
The terminal alkynes, namely cyclohexylacetylene and 3,3-dimethylbut-1-yne, produced spectra typical of terminal alkynes. Phenylacetylene produced a spectrum with only five terminal CO bands, where obvious coalescence of two bands at 2089 cm<sup>-1</sup> occurs. Furthermore, the disubstituted alkynes, namely diphenylacetylene and 1-phenyl-1-propyne, did not produce a spectrum with a visible band at 1630 cm<sup>-1</sup>. The results are tabulated in Table 4.

**Analysis and Deconvolution of Monosubstituted Alkyne Products** As already shown in Figure 1 and Table 1, the terminal alkynes 1-pentyne to 1-hexadecyne (and cyclohexylacetylene and 3,3-dimethylbut-1-yne) lead to almost exactly the same infrared spectrum. The reaction of 1-dodecyne was taken as a characteristic result. A PEAKFIT solution for the terminal CO region is shown in Figure 5. The PEAKFIT basis functions were chosen as Gauss–Lorentz areas. The fit was very good, and Figure 5 clearly shows six strong terminal CO vibrations for a new complex, and one terminal CO vibration at 2074.5 cm<sup>-1</sup> for the ubiquitous Rh<sub>6</sub>(CO)<sub>16</sub>. The characteristic vibrations are 2036.1, 2042.5, 2070.5, 2082, 2089.2, and 2121.7 cm<sup>-1</sup>. Their relative intensities are 0.42, 0.32, 0.51, 1, 0.67, and 0.48. All the bands have widths at half-height of ca. 5 ± 1 cm<sup>-1</sup>, indicative of sharp terminal CO vibrations.

A PEAKFIT solution for the low-cm<sup>-1</sup> region is shown in Figure 6. The PEAKFIT basis functions were chosen

**Table 2. Relative Infrared Absorbance of Symmetric Disubstituted Alkyne Complexes**

alkyne	$\nu_{\text{CO}}$ (cm <sup>-1</sup> ) above, relative intensity below											
	$\nu$ (cm <sup>-1</sup> )											
2-butyne	2121.1		2088.9	2078.4	2070.6		2048.3sh	2037.4	2033	1681	1658.2	1631
	0.41		0.55	1	0.48		0.40	0.40	0.44	0.13	0.20	0.01
3-hexyne	2120		2088	2077.9	2069.6		2047.6	2036.9	2032.7	1676.7	1665	1628
	0.42		0.44	1	0.42		0.04	0.36	0.42	0.13	0.24	0.01
4-octyne	2122.7	2095.4	2090.5	2077.3sh	2073.2	2055.1	2047.5	2038.7	2032.8sh	1687sh	1663	1635
	0.61	0.94	1	0.61	0.86	0.20	0.14	0.64	0.22	0.20	0.28	0.06
5-decyne	2123	2095.1	2091	2076.6sh	2072.9	2054.6	2047.3	2038.5	2034sh	1678.3	1667.2	1633
	0.61	1	0.98	0.51	0.94	0.21	0.15	0.60	0.22	0.27	0.28	0.06
6-dodecyne	2120	2095.1	2087.2	2077	2069.5	2054.4	2047.8	2036.7	2031.9	1674sh	1663.5	1632.8
	0.50	0.18	0.64	1	0.47	0.04	0.06	0.40	0.38	0.14	0.20	0.03

**Figure 3.** Mid-infrared spectra of alkyne–rhodium complexes after subtraction of hexane, CO, and free alkyne. Homologous series of alkynes from 1-decyne to 5-decyne.

as Gauss–Lorentz areas, and again a very good fit was obtained. The characteristic vibrations are 1668.1 and 1688.8 cm<sup>-1</sup>. However, the bands are different, with widths at half-height of ca. 13.6 and 9.9 cm<sup>-1</sup>, respectively. This suggests that two different types of moieties are present.

**Analysis and Deconvolution of Disubstituted Alkyne Products.** As already shown in Figures 2–4 and Tables 2–4, the reactions of the disubstituted alkynes lead to complex infrared spectra. We took the reaction of 6-dodecyne as our characteristic result. A PEAKFIT solution for the terminal CO region is shown in Figure 7. The PEAKFIT basis functions were chosen as Gauss–Lorentz areas. The fit was very good, and Figure 7 clearly shows a strong pattern of six strong terminal CO vibrations at 2031.6, 2037.2, 2069.1, 2077.2, 2087.4, and 2120.5 cm<sup>-1</sup>, with relative intensities of 0.37, 0.38, 0.46, 1, 0.51, and 0.52. Figure 7 also

shows a weaker pattern of five weak terminal CO vibrations at 2046.8, 2055.0, 2084.9, 2090.0, and 2095.0 cm<sup>-1</sup> with relative intensities of 0.20, 0.10, 0.69, 1, and 0.72, and one terminal CO vibration at 2073.4 for the ubiquitous Rh<sub>6</sub>(CO)<sub>16</sub>. All the bands have widths at half-height of ca. 5 ± 1 cm<sup>-1</sup>, indicative of terminal CO vibrations.

A PEAKFIT solution for the low-cm<sup>-1</sup> region is shown in Figure 8. The PEAKFIT basis functions were chosen as Gauss–Lorentz areas, and again a reasonably good fit was obtained. The characteristic vibrations are 1670.2, 1661.4, and 1635.2 cm<sup>-1</sup>. However, the bands are different with widths at half-height of ca. 18.8, 17.3, and 11 cm<sup>-1</sup>, respectively. This suggests two things, namely, broadening of the first two bands when larger substituents are placed on the alkynes and at least two and possibly three different types of moieties present.

**Preliminary Conclusions.** The tables of spectroscopic characteristics as well as the analysis of the deconvoluted infrared spectra suggest that there are only two different types of alkyne–rhodium complexes present in this study.

For one pattern, the infrared spectrum is characterized by six terminal vibrations and two low cm<sup>-1</sup> vibrations. The six terminal vibrations are almost exactly the same, in both position and relative intensity, for both monosubstituted and disubstituted alkyne complexes. The low-cm<sup>-1</sup> vibrations are well separated at 1668 and 1689 cm<sup>-1</sup> in the case of monosubstituted alkyne complexes, but start to coalesce and become broader for disubstituted alkyne complexes. This is the only pattern for monosubstituted alkyne complexes, and it is the predominant pattern (corresponding to the major product) for disubstituted alkyne complexes.

For the second pattern, the infrared spectrum is characterized by five relatively weak terminal vibrations (corresponding to a minor product) and one weak low-cm<sup>-1</sup> vibration. The pattern only appears for disubstituted alkyne complexes. The low-cm<sup>-1</sup> vibration at 1630 cm<sup>-1</sup> is particularly interesting because it is the correct wavenumber for a C=C vibration.

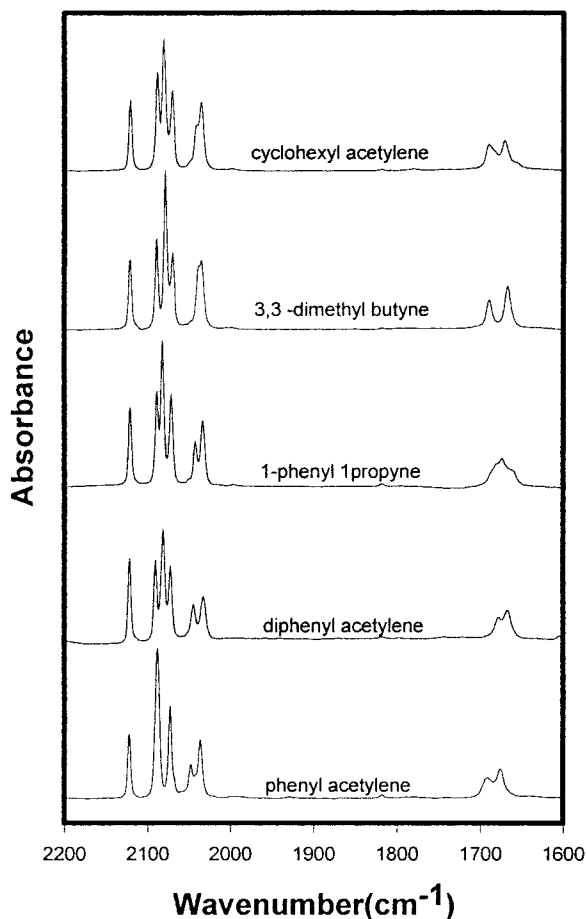
## Discussion

The homogeneous catalytic chemistry of alkynes and the stoichiometric organometallic chemistry of alkyne complexes is quite extensive.<sup>21</sup> Accordingly, the discussion of the results is best approached by first mentioning some of the catalytic aspects, followed by comparisons

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**Table 3. Relative Infrared Absorbance of Decyne Complexes**

alkyne	$\nu_{\text{co}}$ (cm <sup>-1</sup> ) above, relative intensity below								$\nu$ (cm <sup>-1</sup> )			
1-decyne	2122		2089.2	2082	2070.6	2050.6	2042.5	2036.3		1689	1668	
	0.42		0.64	1	0.52	0.04	0.31	0.44		0.19	0.19	
2-decyne	2121.1	2095.7sh	2089	2078.1	2069.9	2056.2	2048.1	2037.6	2033	1674	1663	1635.2
	0.48	0.16	0.65	1	0.50	0.04	0.06	0.40	0.39	0.14	0.22	0.01
3-decyne	2122	2095.3	2089.3	2077.1	2073	2054.9	2047.6	2037.9	2033sh	1678.1sh	1666.4	1636.2
	0.65	0.57	1	0.78	0.79	0.13	0.19	0.57	0.34	0.17	0.29	0.08
4-decyne	2122.8	2095	2090.1	2077.1sh	2073	2054.6		2038.3	2031.7sh	1675.9	1665	1632.3
	0.65	0.96	1	0.60	0.88	0.19		0.63	0.19	0.20	0.28	0.05
5-decyne	2123	2095.1	2091	2072.9	2054.6			2038.5		1678.3	1667.2	1633
	0.61	1	0.98	0.94	0.21			0.60		0.27	0.28	0.06



**Figure 4.** Mid-infrared spectra of alkyne–rhodium complexes after subtraction of hexane, CO, and free alkyne. Assortment of miscellaneous monosubstituted and disubstituted alkynes.

to known alkyne complexes which are inconsistent with our results, and finally by comparisons with known alkyne complexes that appear consistent with the spectroscopic results. Given the very broad area covered by organometallic alkyne complexes, we try to restrict discussion to pertinent cobalt and rhodium complexes as far as possible.

**Relevant Homogeneous Catalytic Aspects of Alkynes.** As already mentioned in the Introduction, alkynes can be hydroformylated by phosphine-modified rhodium complexes. Although no hydroformylation of alkynes by  $\text{Rh}_4(\text{CO})_{12}$  was observed in this study when using a mixture of CO and molecular hydrogen at 293 K and although no other catalytic transformations of alkynes by  $\text{Rh}_4(\text{CO})_{12}$  were observed in the presence of CO alone, the potential for catalytic activity cannot be underestimated.

Various combinations of alkynes and rhodium complexes have been observed to lead to catalytic transformations. Such transformations include (I) the dimerization of alkynes such as 1-octyne to give free 7-methylenepentadec-8-yne in the presence of  $\text{RhCl}(\text{PPh}_3)_3$  at 343 K,<sup>22</sup> (II) the cyclotrimerization of alkynes to give substituted benzenes by rhodium carbonyl complexes again in the absence of CO at 333 K (which is closely related to the well-documented cobalt-catalyzed cyclotrimerization reaction),<sup>23</sup> (III) the synthesis of furan-2(5*H*)-ones by  $\text{Rh}_4(\text{CO})_{12}$  in the presence of alkynes and 100 atm CO at 373 K,<sup>24</sup> (IV) the synthesis of substituted cyclopentanones by  $\text{Rh}_4(\text{CO})_{12}$  in the presence of alkynes, CO, and  $\text{H}_2\text{O}$ ,<sup>25</sup> (V) the cross-hydrocarbonylation of alkynes and ethylene in the presence of  $\text{Rh}_4(\text{CO})_{12}$ , CO, and  $\text{H}_2$  at 423 K to form  $\alpha,\beta$ -unsaturated ethyl ketones,<sup>26</sup> and (VI) the reaction of alkynes and ethylene in the presence of  $\text{Rh}_4(\text{CO})_{12}$  and CO to form 5-ethyl-3,4-disubstituted-2(5*H*)-furanones.<sup>27</sup>

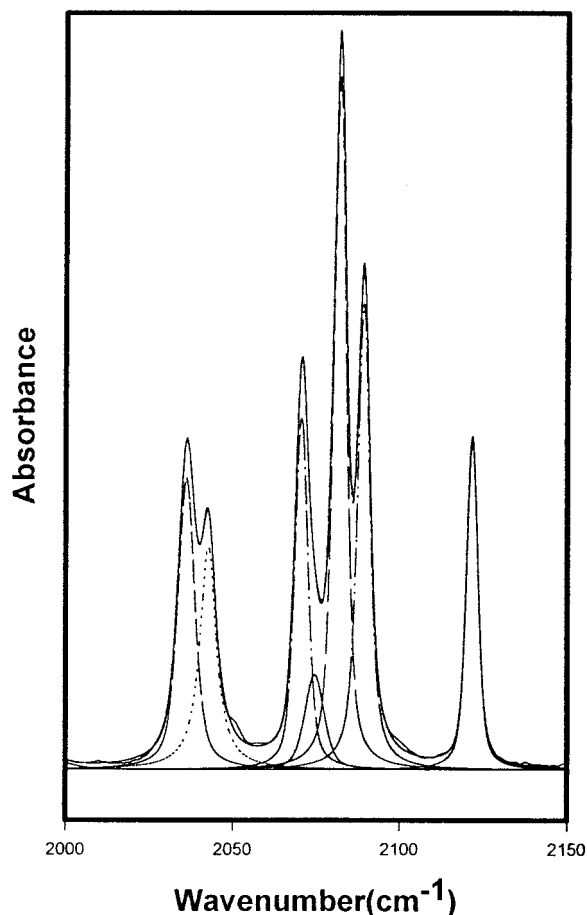
**Inconsistent Alkyne Complexes.  $\text{Rh}_4(\text{CO})_{10}$  ( $\text{R}^1\text{C}_2\text{R}^2$ ).** The reaction of tetranuclear cluster  $\text{Rh}_4(\text{CO})_{12}$  with alkynes in the absence of CO has been reported on at least two occasions.<sup>28</sup> Iwashita and Tamura monitored the reaction of diphenylacetylene with  $\text{Rh}_4(\text{CO})_{12}$  in the infrared in *n*-hexane as solvent. They observed the intermediate formation of a bridged carbonyl species which they tentatively assigned to be  $\text{Rh}_4(\text{CO})_{10}(\text{PhC}_2\text{Ph})$ . Subsequently, Booth et al. performed the same reaction and isolated  $\text{Rh}_4(\text{CO})_{10}$ -( $\text{PhC}_2\text{Ph}$ ) with predominant spectral characteristics of 2087(s), 2068(vs), 2056(vs), 2043(vs), 2016(vs), 1845(s), and 1825(s)  $\text{cm}^{-1}$ , where the last two vibrations are due to bridging carbonyls. A similar complex was also prepared from  $\text{CF}_3\text{C}_2\text{CF}_3$ . Our spectroscopic results indicate that no bridging carbonyls are present in our species.

Importantly, both groups reported that the reaction of other hydrocarbon-substituted alkynes with  $\text{Rh}_4(\text{CO})_{12}$  in the absence of CO leads to a host of very labile and nonisolatable complexes. If benzene is used as solvent, catalytic cyclotrimerization of diphenylacetylene to hexaphenylbenzene occurs.

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 (27) Hong, P.; Mise, T.; Yamazaki, H. *Chem. Lett.* **1981**, 989.  
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**Table 4. Relative Infrared Absorbance of Miscellaneous Alkyne Complexes**

alkyne	$\nu_{\text{co}}$ (cm <sup>-1</sup> ) above, relative intensity below				$\nu$ (cm <sup>-1</sup> )				
phenylacetylene	2122.7	2088.5		2073.6	2048	2036.8	1692	1676.4	
	0.45	1		0.59	0.21	0.41	0.13	0.20	
diphenylacetylene	2122.2	2090.9	2082	2072.9	2045.2	2033.2		1678	1667.3
	0.77	0.74	1	0.66	0.30	0.40		0.20	0.26
1-phenyl-1-propyne	2121.7	2089.4	2082.5	2071.9	2042.6	2033.6	1680.9sh	1674.1	1661.3sh
	0.55	0.65	1	0.63	0.29	0.46	0.17	0.20	0.12
3,3-dimethylbutyne	2121.7	2089.2	2079	2070	2039	2035.2	1690		1668
	0.45	0.58	1	0.46	0.38	0.42	0.18		0.26
cyclohexylacetylene	2121.1	2088.5	2080.7	2070.2	2041.3	2035.1	1690.2	1671	
	0.53	0.76	1	0.59	0.32	0.50	0.18		0.21

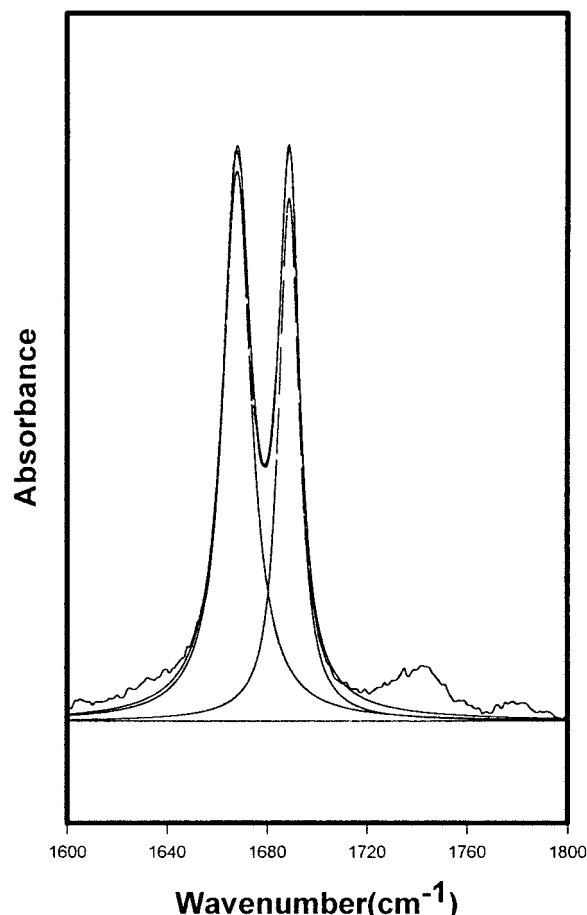
**Figure 5.** Deconvolution of terminal CO region of 1-dodecyl rhodium complex spectrum using Gauss–Lorentz areas.

**Metallocyclopentadiene Complexes.** Both mono-substituted and disubstituted alkynes are known to insert multiple times on a wide variety of coordinatively unsaturated mononuclear complexes, dinuclear complexes, etc., to form metallocyclopentadienes. Thus in the case of rhodium, mononuclear rhodium cyclopentadiene complexes of the form  $\text{RhClL}_2\{\text{C}_4(\text{CF}_3)_4\}$  ( $\text{L} = \text{AsPh}_3, \text{AsMePh}_2, \text{AsMe}_2\text{Ph}$ , etc.) have been synthesized,<sup>29</sup> as well as  $\text{RhClL}_2\{\text{C}_4(\text{CO}_2\text{CH}_3)_4\}$  ( $\text{L} = \text{AsPh}_3$ ),<sup>30</sup> and in the case of dinuclear complexes,  $(\eta\text{-C}_5\text{H}_5)_2\text{Rh}_2\{\mu\text{-}\eta^2, \eta^4\text{-C}_4(\text{CF}_3)_2\text{HR}\}$  has been made.<sup>31</sup> Given the conjugated structure of metallocyclopentadienes, a complex vibration in the range 1500–1400 is to be expected. Such a vibration is not present in our spectra.

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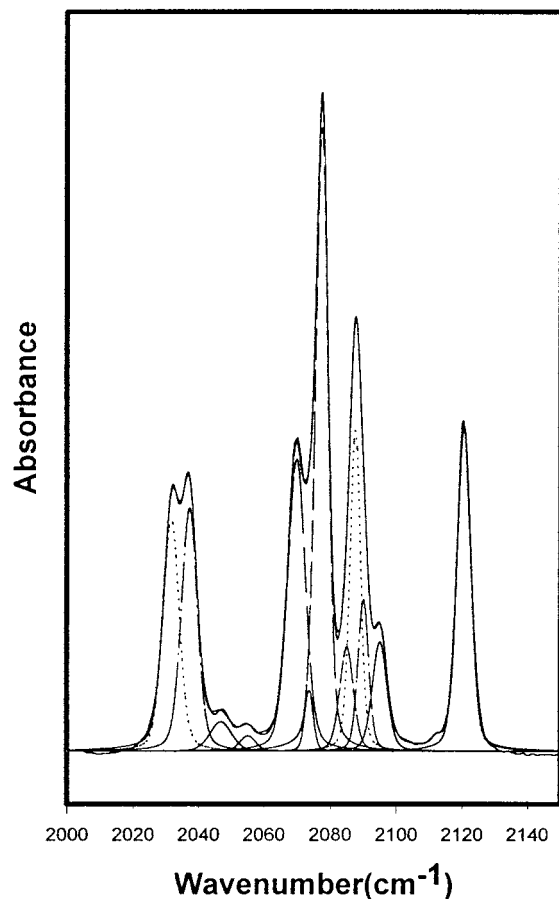
**Figure 6.** Deconvolution of low-cm<sup>-1</sup> region of 1-dodecyl rhodium complex spectrum using Gauss–Lorentz areas.

**$\sigma$ -Alkenyl Complexes.** Both monosubstituted and disubstituted alkynes are known to react with metal hydrides to yield  $\sigma$ -alkenyl complexes. Examples involving rhodium include the reaction of  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  with diphenylacetylene to yield  $(\text{CO})\text{Rh}(\text{PPh}_3)_2(\text{PhC}_2\text{HPh})$ <sup>32</sup> and the reaction of  $\text{RhCl}_2\text{H}(\text{PPh}_3)_2$  with acetylene to yield  $\text{RhCl}_2(\text{PPh}_3)_2(\text{C}_2\text{H}_3)$ .<sup>33</sup> In such cases the C=C vibration appears at ca. 1567 cm<sup>-1</sup>. The existence of  $\sigma$ -alkenyl complexes of arbitrary nuclearity in the present study seems remote since the infrared spectra can be generated in both the absence and presence of molecular hydrogen. Furthermore, no other source for the generation of metal hydrides in the system consisting of rhodium carbonyl/alkyne/CO is readily apparent.

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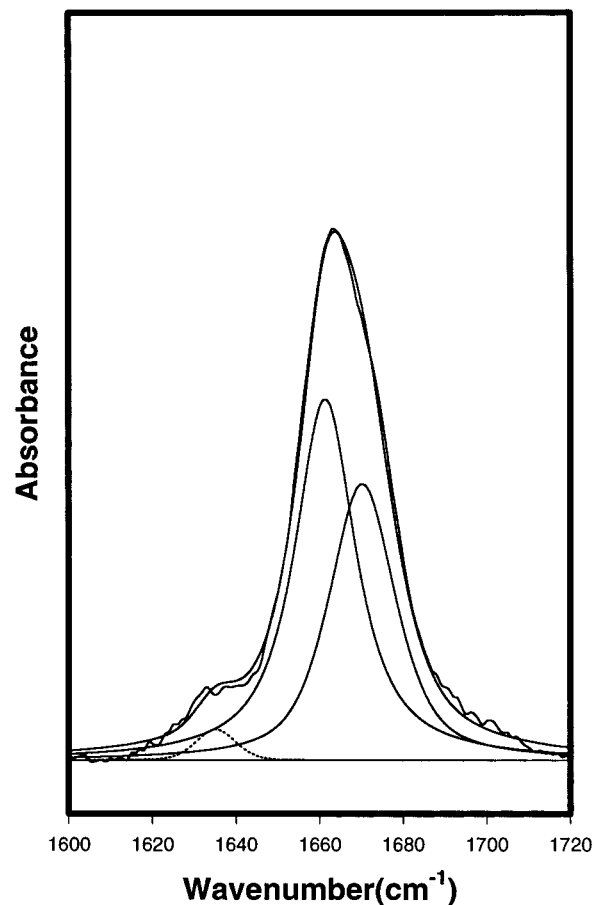


**Figure 7.** Deconvolution of terminal CO region of 6-dodecyl rhodium complex spectrum using Gauss-Lorentz areas.

Multiple alkyne insertions into  $\sigma$ -alkenyl complexes have also been noted. Thus  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  has been shown to react with  $\text{CF}_3\text{C}_2\text{CF}_3$  to yield  $(\text{CO})\text{Rh}(\text{PPh}_3)_2(\text{CF}_3\text{C}_2\text{HCF}_3)$ , which further reacts with  $\text{MeCO}_2\text{C}_2\text{CO}_2\text{Me}$  to yield  $(\text{CO})\text{Rh}(\text{PPh}_3)_2(\text{MeCO}_2\text{C}_2\text{CO}_2\text{MeF}_3\text{C}_2\text{HCF}_3)$ .<sup>34</sup>

**$\sigma$ -Alkynyl Complexes.** Monosubstituted alkynes are known to react with metal hydrides via the elimination of molecular hydrogen to yield  $\sigma$ -alkynyl complexes. Examples involving rhodium include the reaction of  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  with propyne to yield  $(\text{CO})\text{Rh}(\text{PPh}_3)_2(\text{C}\equiv\text{C}-\text{CH}_3)$ <sup>35</sup> and the reaction  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  with 1-hexyne to yield  $(\text{CO})\text{Rh}(\text{PPh}_3)_2(\text{C}\equiv\text{C}-\text{C}_4\text{H}_9)$ . In such cases, a weak  $\text{C}\equiv\text{C}$  vibration appears at ca. 2100–2130  $\text{cm}^{-1}$ . The existence of  $\sigma$ -alkynyl complexes of arbitrary nuclearity in the present study can be ruled out entirely since the 6-terminal-CO pattern in the infrared spectra can be generated for both monosubstituted and disubstituted alkynes.

**$\pi$ -Alkyne Complexes.** Coordinately unsaturated complexes can react with both monosubstituted and disubstituted alkynes to give the corresponding  $\pi$ -bonded alkyne complex, and numerous such complexes involving Pt, Rh, Ir, and Ni are known and have been characterized in detail.<sup>36</sup> All have a  $\text{C}\equiv\text{C}$  vibration



**Figure 8.** Deconvolution of low- $\text{cm}^{-1}$  region of 6-dodecyl rhodium complex spectrum using Gauss-Lorentz areas.

located at ca. 1700–1900  $\text{cm}^{-1}$ . For example, the complex  $\text{ClRh}(\text{PPh}_3)_2(\pi\text{-PhC}_2\text{Ph})$  has a characteristic vibration at 1916  $\text{cm}^{-1}$ .<sup>37</sup> There was no infrared spectroscopic evidence to suggest that  $\pi$ -bonded alkyne complexes exist in the present study.

**“Lactone” Complexes.** Cobalt carbonyls react in the presence of alkynes and CO to form “lactone” complexes of the general form  $\text{Co}_2(\text{CO})_7(\text{R}^1\text{R}^2\text{C}_4\text{O}_2)$ , i.e.,  $\mu_2$ -carbonyl- $\mu_2$ -spiro-[2,3-substituted-2-butenolide-4-ylidene]bis[tricarbonylcobalt][Co-Co] derivatives.<sup>38</sup> The lactone structure has a  $\text{C}=\text{C}$  conjugated to a  $\text{C}=\text{O}$  group. The typical wavenumber for the carbonyl in the lactone group is ca. 1775  $\text{cm}^{-1}$ . Our spectra are inconsistent with a lactone structure.

**Consistent Alkyne Complexes.**  $\text{Co}_2(\text{CO})_6\{\mu\text{-}\eta^2\text{-(R}^1\text{C}_2\text{R}^2)\}$ . Both monosubstituted and disubstituted alkynes react with  $\text{Co}_2(\text{CO})_8$  to give the product  $\text{Co}_2(\text{CO})_6\{\mu\text{-}\eta^2\text{-(R}^1\text{C}_2\text{R}^2)\}$ .<sup>39</sup> This is one of the most extensively documented types of organometallic alkyne complexes.<sup>40</sup> Crystallographic studies firmly establish the geometry as  $\text{Co}_2(\text{CO})_6\{\mu\text{-}\eta^2\text{-(R}^1\text{C}_2\text{R}^2)\}$ , at least in the diphenylacetylene complex.<sup>41</sup> Infrared analyses confirm

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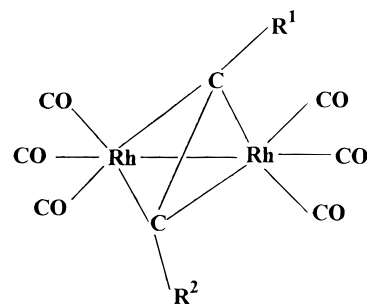
that the alkyne vibration is more like a C=C vibration, i.e., ca. 1630  $\text{cm}^{-1}$ , at least for the disubstituted complexes with aliphatic groups.<sup>42</sup> In addition, there are usually only five terminal CO vibrations instead of six for these complexes, despite their  $C_s$  or  $C_1$  symmetry.<sup>39b,e</sup> For example, the alkyne complex formed from but-2-yne has absorbance maxima at 2086(s), 2045(vs), 2023-(vs), 2011(vs), 2006(sh), and 1978(w)  $\text{cm}^{-1}$ , or approximate relative intensities of 0.75, 1.0, 1.0, 1.0, 0.1, and 0.25.

**$\mu\text{-}\eta^1$  and  $\mu\text{-}\eta^2$  Alkynyl Dirhodium Complexes.** Dickson et al. prepared a number of dirhodium complexes of the general formulas  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})\{\mu\text{-}\eta^1\text{-(RC}_2\text{R)}\}$  and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})\{\mu\text{-}\eta^2\text{-(RC}_2\text{R)}\}$ , where (R = CH<sub>3</sub>, CF<sub>3</sub>, or Ph) in the absence of additional CO.<sup>43</sup> It should be noted that the  $\mu\text{-}\eta^1$  alkynyl complexes assume a terminal arrangement for all the carbonyl ligands, whereas the  $\mu\text{-}\eta^2$  alkynyl complexes prefer a bridged arrangement for at least one carbonyl ligand. In the former case, the vibration for  $\{\mu\text{-}\eta^1\text{-(RC}_2\text{R)}\}$  appears at 1630  $\text{cm}^{-1}$ , and in the latter case the vibration for  $\{\mu\text{-}\eta^2\text{-(RC}_2\text{R)}\}$  appears at a lower wave-number such as 1592  $\text{cm}^{-1}$ . Also, the  $\mu\text{-}\eta^1$  alkynyl complex  $\text{Rh}_2\text{Cl}_2\{\mu\text{-}\eta^1\text{-(CF}_3\text{C}_2\text{CF}_3)\}$  has a prominent vibration at 1638  $\text{cm}^{-1}$ .<sup>44</sup>

**$\text{CoRh}(\text{CO})_6\{\mu\text{-}\eta^2\text{-(PhC}_2\text{Ph)}\}$ .** Diphenylacetylene has been shown to react with  $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$  at 293 K to give  $\text{CoRh}(\text{CO})_6\{\mu\text{-}\eta^2\text{-(PhC}_2\text{Ph)}\}$ .<sup>45</sup> The infrared spectrum showed terminal CO vibrations at 2095(m), 2060(vs), 2044(s), 2034.5(s), 2015(m), and 2009.5(m)  $\text{cm}^{-1}$  in *n*-hexane. Unfortunately, no low  $\text{cm}^{-1}$  were reported, but the NMR is consistent with the structural assignment.

**$(\mu\text{-}\eta^1\text{-CORC}_2\text{R})$  Dinuclear Complexes.** A few examples exist for the insertion of CO into a metal–alkyne bond in dinuclear complexes leading to the formation of  $(\mu\text{-}\eta^1\text{-CORC}_2\text{R})$  dinuclear complexes. These include the complex  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})\{\mu\text{-}\eta^1\text{-(HC}_2\text{TMS)}\}\{\mu\text{-}\eta^1\text{-(COCF}_3\text{C}_2\text{CF}_3)\}$ , for which spectroscopic evidence is available.<sup>46</sup> Furthermore, in the case of cobalt both the complexes  $\text{Co}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{-(COHC}_2\text{H)}\}$  and  $\text{Co}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{-(COHC}_2\text{HCO)}\}$  have been postulated due to the formation of  $\text{CH}_2=\text{CHCOOEt}$  and  $\text{EtOCHCH}=\text{CHCHCOOEt}$  upon treatment with EtOH.<sup>47</sup>

**The Tentative Assignment.** Given the above observations, we propose a tentative assignment for our complexes. The spectral pattern consisting of five terminal CO vibrations and a vibration at ca. 1630  $\text{cm}^{-1}$



**Figure 9.** Structure of the proposed  $\text{Rh}_2(\text{CO})_6\{\mu\text{-}\eta^2\text{-(R}^1\text{C}_2\text{R}^2)\}$  complexes.

and that only arises in the case of disubstituted alkynes is treated first. This pattern strongly suggests a simple alkyne-bridged dirhodium carbonyl complex, probably of the formula  $\text{Rh}_2(\text{CO})_6(\text{R}^1\text{C}_2\text{R}^2)$  and quite possibly of the geometry  $\text{Rh}_2(\text{CO})_6\{\mu\text{-}\eta^2\text{-(R}^1\text{C}_2\text{R}^2)\}$ , where no bridging CO ligands are evident. By analogy with the complexes  $\text{Co}_2(\text{CO})_6\{\mu\text{-}\eta^2\text{-(R}^1\text{C}_2\text{R}^2)\}$ , such complexes have only five of the six bands predicted from the  $C_s$  or  $C_1$  symmetry, even for the symmetric alkyne-substituted complexes.<sup>39b,e</sup> Figure 9 shows the proposed structure for these complexes.

A question naturally arises concerning the reason that this complex exists in the case of the disubstituted alkyne complexes, but not in the case of monosubstituted alkyne complexes. The most straightforward explanation seems to be that CO insertion can take place on the disubstituted alkyne complexes under 2.0 MPa CO; however, conversion is not complete. In other words, CO insertion into the {Rh–CH} bond in the monosubstituted alkyne complexes is much more facile, and the equilibrium is shifted entirely toward the insertion product under 2.0 MPa CO. The presence of long alkyl and aryl substituents on the alkyne moiety appears to considerably hinder CO insertion. Given the above considerations, we tentatively assign the spectral pattern consisting of six terminal CO vibrations and two low  $\text{cm}^{-1}$  to the CO insertion product.

The reaction of the monosubstituted alkynes with rhodium carbonyl gave an infrared spectrum consisting of six terminal CO vibrations and two low- $\text{cm}^{-1}$  vibrations of almost equal absorptivity. This was true for the entire homologous series from 1-pentyne to 1-hexadecyne and for 3,3-dimethylbutyne. Cyclohexylacetylene gave a very similar spectral pattern, and phenylacetylene gave a pattern with only five terminal CO vibrations, where the relative intensities clearly indicate coalescence of two bands. The appearance of six terminal CO vibrations is consistent with the further loss of symmetry elements upon CO insertion into the {Rh–CH} bond and the expected  $C_s$  or  $C_1$  symmetry. This lowering of the symmetry would result in six terminal CO vibrations in a complex with the formula  $\text{Rh}_2(\text{CO})_6\text{-(CO–HC}_2\text{R}^1)$ .

Furthermore, we note again that the two low- $\text{cm}^{-1}$  bands are not identical. The band at 1689  $\text{cm}^{-1}$  has a relatively narrow width at half-height and that band at 1668  $\text{cm}^{-1}$  is somewhat broader. The positions of these bands, their widths at half-height, and their approximately equal integral absorbance suggest that the band at 1689  $\text{cm}^{-1}$  belongs to a C=O moiety, the band at 1668  $\text{cm}^{-1}$  belongs to a C=C moiety, the two

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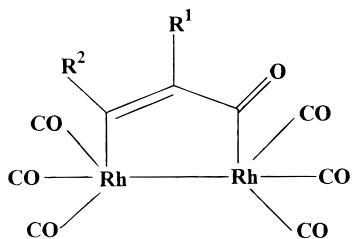
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**Figure 10.** Structure of the proposed  $\text{Rh}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{-(CO-R}^1\text{C}_2\text{R}^2)\}$  complexes.

groups are conjugated, and the stoichiometry is 1:1 for these functional groups. Given the precedence of the complex  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CO})\{\mu\text{-}\eta^1\text{-(HC}_2\text{TMS)}\}\{\mu\text{-}\eta^1\text{-(COCF}_3\text{C}_2\text{CF}_3)\}$ , it would seem that our species is most probably  $\text{Rh}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{-(CO-HC}_2\text{R}^1)\}$ . The conjugation of C=O with C=C would exist in a rather electron-rich environment, assuming the presence of a Rh–Rh bond (which would be predicted by electron-counting rules). Assuming an electron-rich environment, it is instructive to compare the characteristic vibrations of 1689 and 1668  $\text{cm}^{-1}$  seen in these complexes for C=O and C=C, respectively, with the characteristic vibrations of 1679 and 1650  $\text{cm}^{-1}$  seen in the extremely electron-rich compound *p*-benzoquinone for the same groups.<sup>48</sup>

A few outstanding details should be addressed concerning the low- $\text{cm}^{-1}$  bands. First, the C=O vibration occurs at a higher wavenumber in the monosubstituted alkyne complexes than in the disubstituted alkyne complexes. Second, in the case of the disubstituted alkyne complexes, the low- $\text{cm}^{-1}$  vibrations slowly coalesce as the molecular weight of the substituents increases. Third, there is definite signal broadening. These characteristics are most readily seen in the sequence of complexes 1-decyne to 5-decyne (Figure 2). In particular, we note that the C=C vibration is essentially stationary, whereas the C=O vibration only undergoes a shift to lower  $\text{cm}^{-1}$  with increasing substituent length. To explain this result, we look at the series of organic compounds 2-cyclohexen-1-one, 2-methyl-2-cyclohexen-1-one, 3-methyl-2-cyclohexen-1-one, and 2,3-dimethyl-2-cyclohexen-1-one. In this series, the C=O vibrations occur at 1691, 1681, 1681, and 1673  $\text{cm}^{-1}$  and the C=C vibrations occur at 1618, 1641, (unknown), and 1634  $\text{cm}^{-1}$ , respectively.<sup>49</sup> Therefore substitution leads to a systematic shift in the C=O vibration toward lower  $\text{cm}^{-1}$ . In addition, increased alkyl substituent length should further the trend. Increasing alkyl substituent length should also lead to additional steric influences and a broadening of the bands, which is also apparent in these complexes. Therefore, we tentatively assign the probable structure  $\text{Rh}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{-(CO-R}^1\text{C}_2\text{R}^2)\}$  to the disubstituted alkyne complexes. Figure 10 shows the proposed structure for these complexes.

Finally, it would appear that high-pressure NMR would be the most direct means of conclusively determining the structure of these complexes, since they cannot be isolated.

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**Comment on the Mechanism of Formation.** The formation of dirhodium carbonyl alkyne complexes from tetrarhodium dodecacarbonyl and alkynes most likely follows one of the following two mechanisms. **Mechanism 1:** It is well-known that the dinuclear complex  $\text{Rh}_2(\text{CO})_8$  is readily formed from  $\text{Rh}_4(\text{CO})_{12}$  under CO, although its concentration is very low at ambient temperatures.<sup>50</sup> Given the presence of equilibrated  $\text{Rh}_2\text{-(CO)}_8$  in solution and the frequent and facile dissociation of carbonyl ligands, reaction of an alkyne with a coordinatively unsaturated dirhodium carbonyl species could easily explain the mechanism of formation for the species under consideration. **Mechanism 2:** The detailed studies of unmodified rhodium-catalyzed hydroformylations of alkenes starting with  $\text{Rh}_4(\text{CO})_{12}$ , mentioned previously in the Introduction, have shown that CO-assisted polyhedron opening seems to be the common initial step in the induction kinetics. This is then followed by molecular hydrogen attack on the opened cluster. In the present case dealing with the formation of dirhodium alkyne complexes, it may be possible that  $\text{Rh}_4(\text{CO})_{12}$  is opened by CO and then alkynes attack the opened cluster directly, resulting in the dirhodium alkyne complexes without formally going through dirhodium carbonyl intermediates.

## Conclusions

The in-situ infrared spectroscopic results strongly suggest that only two types of alkyne rhodium complexes result from the reaction of alkynes with  $\text{Rh}_4\text{-(CO)}_{12}$  under CO and CO/ $\text{H}_2$  at 293 K in *n*-hexane solvent, i.e., under reaction conditions resembling hydroformylation. Indeed, analysis of the deconvolution results shows that only two repeating absorbance patterns occur throughout the study. A large number of possible species were discounted by simple inspection and comparison of the spectral patterns; these included metallocyclopentadienes, metal  $\sigma$ -alkenyl complexes, metal  $\sigma$ -alkynyl complexes, metal "lactone" complexes, etc.

The reaction of the monosubstituted alkynes consistently gave a final product involving six terminal  $\nu_{\text{CO}}$  vibrations in the region 2030–2121  $\text{cm}^{-1}$  and two strong vibrations at ca. 1668 and 1686  $\text{cm}^{-1}$ , and the disubstituted alkynes consistently gave a final spectrum consistent with the superposition of the aforementioned spectrum, plus a spectrum involving five terminal  $\nu_{\text{CO}}$  vibrations in the region 2046–2095  $\text{cm}^{-1}$  and one strong vibrations at ca. 1630  $\text{cm}^{-1}$ . Due to the band positions and absorptivities, we tentatively propose that these species are substituted dirhodium carbonyl species, specifically  $\text{Rh}_2(\text{CO})_6\{\mu\text{-}\eta^2\text{-(R}^1\text{C}_2\text{R}^2)\}$  for the spectral pattern consisting of five terminal CO vibrations and arising only in the case of disubstituted alkynes. The spectral pattern consisting of six terminal CO vibrations is tentatively assigned to  $\text{Rh}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{-(CO-HC}_2\text{R}^1)\}$  and  $\text{Rh}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{-(CO-R}^1\text{C}_2\text{R}^2)\}$  for the terminal alkynes and disubstituted alkynes, respectively. In other words, the present complexes appear to be the rhodium

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analogues of the well-known dicobalt carbonyl alkyne complexes.

The stability of the present alkyne complexes under CO even in the presence of molecular hydrogen appears to be the primary reason that the presence of trace quantities of alkynes can poison alkene hydroformyla-

tions. The alkynes react with the rhodium in the system and prevent the availability of rhodium for the alkene hydroformylations.

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