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Rhodium–Carbonyl Cluster Chemistry under High Pressure of Carbon Monoxide and Hydrogen. 1. Infrared Spectroscopic Study of Homogeneous Systems Active in the Catalytic Synthesis of Polyalcohols from CO and H₂

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The high-pressure infrared study of rhodium catalysts able to carry out in a homogeneous phase the conversion of carbon monoxide and hydrogen to polyols was carried out at 500–1000 atm to determine the nature of the predominant species under conditions milder (50–200 °C) than suitable for optimum catalytic activity (200–290 °C). These studies were conducted by using an infrared cell whose description is attached and a Fourier transform spectrometer to maximize the quality of the spectra and to allow for subtraction of desired features. The catalyst based on $Rh(CO)_2acac$ appears to consist mainly of $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ as the only detectable species under the milder conditions. This is suggested by comparison with the spectra of these two anions under such conditions. Similar results are obtained when solutions of rhodium carbonyl clusters of general formula $[Rh_x(CO)_yH_m]^{n-}$ ($m \geq 0$, $n \geq 0$) such as $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $[Rh_{12}(CO)_{30}]^{2-}$, $[Rh_6(CO)_{15}]^{2-}$, $[Rh_7(CO)_{16}]^{3-}$, and $[Rh_{13}(CO)_{24}H]^{(5-x)-}$ ($x = 2, 3$) are treated in the same way. In contrast, more ambiguous spectral changes are observed upon reaching catalytic conditions, although it was noted that they are reversed, regenerating the pattern assigned to $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ by a decrease in the reaction temperature below 200 °C. The similarity of the high-temperature spectra with those expected for mixtures of high-nuclearity rhodium–carbonyl clusters and the thermodynamic preference for the formation of these species at high temperature, $\bar{D}(Rh–CO)$ and $\bar{D}(Rh–Rh)$ of 39.0 and 26.5 kcal/mol, respectively, suggested that $[Rh_{13}(CO)_{24}H]^{n-}$, $[Rh_{14}(CO)_{25}]^{4-}$, $[Rh_{15}(CO)_{27}]^{3-}$, or related species could be present under those conditions. We have determined whether clusters are the predominant species under catalytic conditions by working with species able to maintain their integrity under these conditions. This has been done spectroscopically, by monitoring the infrared spectra of the systems, and chemically, by determination of the catalyst behavior with temperature and pressure. Species of general formula $[Rh_x(CO)_yE_m]^{n-}$ (E = main-group atom) were tested, and the following resistance to fragmentation was found: $[Rh_6(CO)_{15}C]^{2-} < [Rh_9P(CO)_{21}]^{2-} < [Rh_{17}S_2(CO)_{32}]^{3-}$. It was also established that formation of polyols is occurring at conditions under which the only detectable rhodium–carbonyl complexes are these clusters. It is noted that an infrared absorption at 1890 cm⁻¹ possibly corresponding to $[Rh(CO)]^-$ is not present in these systems while it is detected in those based on $Rh(CO)_2acac$. The catalytic activity (M h⁻¹) of systems based on rhodium–carbonyl clusters with encapsulated heteroatoms is less than that of $Rh(CO)_2acac$ systems: $Rh(CO)_2acac$ (1.9) > $[Rh_6(CO)_{15}]^{2-}$ (1.0) > $[Rh_{17}S_2(CO)_{32}]^{3-}$ (0.53) > $[Rh_9P(CO)_{21}]^{2-}$ (0.1). These results indicate that the latter compounds generate relatively poisoned catalysts. We have also noted the Brønsted acid–base transformation of $[Rh_{13}(CO)_{24}H_3]^{2-}$ into $[Rh_{13}(CO)_{24}H_2]^{3-}$ occurring under high pressure of carbon monoxide upon addition of N-methylmorpholine and the fragmentation of the anions into $[Rh_5(CO)_{15}]^-$ or $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$, respectively, as well as the hydrogenation of the resulting solutions back to the original clusters. The fragmentation of $Rh_6(CO)_{16}$ by carbon monoxide into $Rh_4(CO)_{12}$ and other species probably containing higher carbon monoxide:rhodium ratio was also studied.

The predicted shortage of future oil supplies has brought attention once more to coal as a potential source of energy and as raw material for industry, in the petrochemical industry in particular.[1] Coal was used previously to solve a milder energy crisis occurring during the XVIth Century.[2] Nowadays, the emphasis on the utilization of coal centers on liquefaction and gasification procedures for its utilization by the petrochemical industry. The use of carbon monoxide and hydrogen has offered an attractive pathway for the generation of chemicals from coal since the first reports concerning the synthesis of hydrocarbons and oxygenated products by Sabatier and Senderens[3] and Fischer and Tropsch.[4,5] Research in this field has been restricted mainly to industrial laboratories until recently, and it has been more intense for those concerned with already existing commercial processes such as Sasol.[6]

The attention devoted to synthesis gas chemistry (CO + H₂) by our laboratories has resulted in the synthesis of ethylene glycol and other polyalcohols[7] in presence of homogeneous rhodium catalysts (eq 1). Side products such as methanol,

$$CO + H_2 \rightarrow HOCH_2CH_2OH +$$
$$HOCH_2CH(OH)CH_3, HOCH_2CH(OH)CH_2OH,$$
$$HOCH_2(CHOH)_2CH_2OH \quad (1)$$
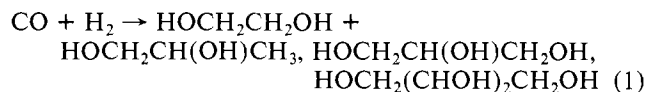
water, and CO₂ are also obtained, among others. Systems based on rhodium–carbonyl clusters[8,9] have been found to be active, and the presence of these species under reaction conditions has been disclosed in some preliminary communications.[10,11] Moreover, rhodium–carbonyl clusters have been also described as present in catalytic systems involved in oxidation of organic substrates,[12] hydroformylation of olefins,[13] and, more importantly yet, in Fischer–Tropsch chemistry.[14–16]

Homogeneous catalysis by transition-metal clusters is attracting increasing attention as shown by reports concerning

(1) N. P. Cochran, *Sci. Am.*, **234**, 24 (1976).
(2) "Coal Technology for Britain's Future", McMillan, London Ltd., London, 1976, p 18.
(3) P. Sabatier and J. B. Senderens, *C. R. Hebd. Seances Acad. Sci.*, **134**, 514 (1902).
(4) F. Fischer and H. Tropsch, *Gesammelte. Abh. Kennt. Kohle*, **10**, 333 (1930); *Brennst.-Chem.*, **4**, 276 (1923).
(5) F. Fischer and H. Tropsch, German Patent 484 337 (1927).
(6) C. D. Frohning and B. Cornils, *Hydrocarbon Process.*, **55**, 105 (1976); J. G. Kronseder, *ibid.*, **55**, 56 (1976).
(7) R. L. Pruett and W. W. Walker, Union Carbide Corp., U.S. Patents 3 833 634 (1974) and 3 957 857 (1976).

(8) J. L. Vidal, Z. C. Mester, and W. E. Walker, Union Carbide Corp., U.S. Patent 4 115 428 (1978).
(9) L. A. Cosby, R. A. Fiato, and J. L. Vidal, Union Carbide Corp., U.S. Patent 4 115 433 (1978).
(10) J. L. Vidal, R. A. Fiato, L. A. Cosby, and R. L. Pruett, paper presented at the Regional Meeting of the American Chemical Society, Charleston, WV, Oct 1977.
(11) J. L. Vidal, D. R. Bryant, L. A. Cosby, W. E. Walker, and R. L. Pruett, paper presented at the 9th Regional Meeting of the American Chemical Society, Charleston, WV, Oct 1977.
(12) G. D. Mercer, J. S. Shu, T. B., Rauchfuss, and D. M. Roundhill, *J. Am. Chem. Soc.*, **97**, 1967 (1975).
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(14) G. C. Demitras and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 2796 (1977).
(15) C. Masters and J. A. v. Doorn, Shell Research Co., U.K. Patent A (1976).
(16) M. G. Thomas, B. F. Veier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976).

the application of clusters of metals other than rhodium to water-shift[17] and Fischer–Tropsch[14] reactions, among others. Simultaneously, studies concerning the catalytic activity of supported cluster catalysts in carbon monoxide systems are also appearing.[18-20] An understanding of the behavior of these complexes, in particular, rhodium–carbonyl clusters, under catalytic conditions such as those reported for the synthesis of ethylene glycol has, therefore, broad implications in catalysis.

This paper describes a systematic study of the behavior of this type of complex with CO, CO/H_2, or H_2, at elevated temperatures and pressures, using infrared techniques to follow these reactions by observing the carbonyl stretching area of the spectra. Similar studies with rhodium carbonyls and analogous transition-metal complexes were first reported by Whyman et al.[21-23] More recently, King et al.[24] described the application of this technique to transition-metal complexes closely related to intermediates proposed for the hydroformylation of olefins. They also mentioned that advances in the implementation of infrared spectroscopy have resulted in the routine experimental application of this technique under high pressure. The presentation of our results obtained routinely under maximum pressures of 500–1000 atm, at temperatures of 100–260 °C, illustrates the previous aspect. In addition, further advantages resulting from using an infrared spectrometer with Fourier-transform capabilities are also implicitly presented.

Experimental Section

The spectra taken at ambient conditions were recorded with a Perkin-Elmer 283 spectrometer using matched liquid cells equipped with calcium fluoride windows.

High-Pressure Infrared and Reactor Equipment. The high-pressure infrared spectra reported in this paper were taken with a Digilab FTS-10 spectrometer. This instrument has a modular design with separate units for the optical system and for the recorder and computer sections. The optical unit and the high-pressure infrared cell are enclosed in a nitrogen-purged Plexiglas box equipped with an air-conditioning unit to keep the instrument temperature below 40 °C when the cell is operated at high temperatures for extended periods. Adjacent to this unit is a 150-mL Magnedrive autoclave reactor supplied by Autoclave Engineering Co. This is connected to the high-pressure infrared cell with $^1/_4$-in. high-pressure tubing wrapped with heating tape and insulation. The temperatures of the line and the reactor are monitored with J-type thermocouples. The entire assembled system is mounted behind $^1/_4$-in. steel-plated walls with a multiplate glass window for the sample area. The controls for liquid flow, gas addition, and temperature are outside this shield for safety reasons.

The high-pressure infrared cell used in this study has been previously described,[25] and a sketch is attached (Figure 1). The cell block (1) is built of stainless steel, and it has four holes (18) for introduction of tubular heaters and one hole (19) for the introduction of a thermistor for the purpose of controlling the temperature of the block. At each end of the block there are plugs (3) with threaded portions (4) to hold them to the block. The opening defined by the plugs (17) has an axis common to the beam of radiation. The solutions to be studied are
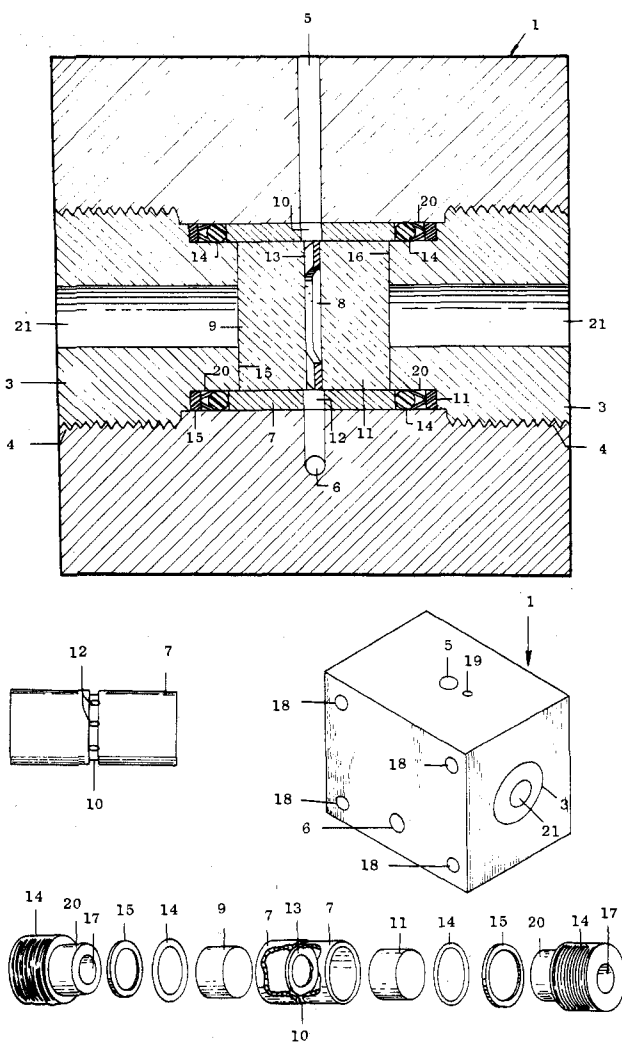

Figure 1. Scheme of the infrared cell used in the high-pressure studies.

introduced through inlet part 5, into the sample area (8), and the gas is removed from the cell via 6. A metal sleeve (7) is located around the sample area. Several holes present in this sleeve (10 and 12) are required to provide ready access of the solutions to the sample area. To ensure a leak-free seal between the threaded portion of the plugs and the metal sleeve there are two O-rings made of Viton (14). Although the primary seal for the cell is provided by the O-rings, a secondary means of sealing (15) is provided to prevent gas leakage via the threaded portion of the plugs. It consists of a K-ring built from a soft material such as copper, capable of being deformed by applied pressure. The metal sleeve circumscribes optically ground infrared-light-transmitting windows 9 and 11. Each window is in contact with the optically flat inner surface (16) of the plugs. The windows are separated before pressurization of the cell by means of a wave ring (13) which is an irregular shaped washer with a springlike quality.

It should be pointed out that the wave ring is simply a device to provide expansive forces necessary to mate the window surfaces with the optically flat surfaces of the plugs. It must be thinner than the available sample thickness as defined by the area within the opening. The ring can be made by cutting washer-shaped pieces from a stainless-steel sheet of appropriate thickness and crimping the washer to provide a spring action when flattened. The K-rings (15) are self-energizing devices under the pressures imposed. They are built of soft material to allow the O-ring to ride in the "V" structure of the K-ring. Any pressure exerted on the O-rings is transmitted to the K-rings, forcing the sides of the "V" structure to seal against the plugs and the cell body. These rings are desirably machined to exact tolerances within 0.001 in. These tolerances can be critical for obtaining a maximum efficiency seal. The combination of the dimensions of the sleeve, rings, secondary sealing means, and plugs is significant also in the same respect. It is desirable that the sealing means be

(17) R. M. Laine, R. G. Rinker, and R. C. Ford, *J. Am. Chem. Soc.*, **99**, 252 (1977).
(18) J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquard, *J. Am. Chem. Soc.*, **94**, 1789 (1972).
(19) H. Knozinger and E. Rumpf, *Inorg. Chim. Acta*, **30**, 51 (1978); J. L. Bilhou, V. Bilhou-Bougnol, W. F. Graydon, J. M. Basset, A. K. Smith, G. M. Zanderighi, and R. Ugo, *J. Organomet. Chem.*, **153**, 73 (1978).
(20) M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 11 (1976).
(21) R. Whyman, *Chem. Commun.* 1194, 1381 (1970).
(22) R. Whyman, *J. Chem. Soc., Dalton Trans.*, 1375, 2294 (1972).
(23) R. Whyman, *J. Organomet. Chem.*, **24**, C35 (1970); **29**, C36 (1971).
(24) R. B. King, A. D. King, Jr., M. Z. Ifbal, and C. C. Frazier, *J. Am. Chem. Soc.*, **100**, 1687 (1978).
(25) W. E. Walker, L. A. Cosby, and S. T. Martin, Union Carbide Corp., U.S. Patent 3 886 364 (1975). Another design of an infrared cell suitable for studies under high pressure has been reported by D. E. Morris and H. B. Tinker, *Rev. Sci. Instrum.*, **43**, 1024 (1977).

Table I. Catalytic Activity of Solutions of Rhodium-Carbonyl Complexes under 1000 atm of CO/H_2, 1:1, at 260 °C[a]

	rate, M h^{-1}	
complex	CH_3OH	$HOCH_2CH_2OH$
$Rh(CO)_2acac$[b]	1.00	1.90
$Cs_2[Rh_6(CO)_{15}C]$	0.60	1.00
$Cs_3[Rh_{17}(S)_2(CO)_{32}]$[c]	0.10	0.53
$Cs_2[Rh_9P(CO)_{21}]$	0.05	0.10

[a] Catalyst system: [Rh] $\simeq 0.019$ M; the solvent used was sulfolane, 75 mL; the only extra additive present was N-methylmorpholine, 5.0 mmol. [b] Work by L. Kaplan. In cesium benzoate, 0.375 mmol. [c] Work by J. L. Vidal and R. A. Fiato.

sized so as to generate approximately 0.01-in. compression; that is, the dimensions of these components must be 10/1000 larger than the available space for them, so as to ensure a maximum seal. This sealing combination has been established to be capable of withstanding pressures of 30 000 psi and should withstand pressures up to 50 000 psi.

The windows for the cell are made of Irtran-2 (Eastman Kodak Co.), and further information about this material and its properties is available in the literature.[24] The thickness of the sample for the spectra reported in this work is about 0.15 mm, but it can be varied by appropriate choice of metal sleeves (7).

General Procedure for High-Pressure Infrared Runs. The same procedure has been followed for all the high-pressure infrared spectra reported in this paper. A first step consists in assembling the cell in the optical system and purging the surrounding box with nitrogen. The desired solution is then charged to the previously evacuated autoclave, which is brought to normal pressure with CO/H_2 and is reevacuated. This cycle is usually repeated three times. Compressed gas from the reservoirs (CO, CO/H_2, or H_2) is now pumped over the stirred solution, and the pressure is adjusted to a previously determined value. The temperature of the cell interior was monitored throughout each experiment and specifically measured before and after recording any spectrum, by using a J-type thermocouple inserted into the thermowell in the cell body. The solution inside the high-pressure autoclave is heated by electrical means, and the temperature is determined by a thermocouple inserted into the bottom of the autoclave. Final pressure adjustments are required once thermal equilibrium has been reached. A purge of several milliliters of solution is passed through the cell before any spectrum is recorded.

Reagents and Solvents. Sulfolane and tetraglyme,[26] $CH_3(CH_2C-H_2O)_4CH_3$, were obtained from Shell Chemical Co. and Ansul Chemical Co., respectively. They were dried by conventional methods, distilled, and stored under argon before use. Other chemicals such as N-methylmorpholine and other amines (Aldrich Chemical Co.) and alkali carboxylates (Strem Chemical Co. and Alfa) were used as obtained. Rhodium-carbonyl complexes were obtained from commercial sources, e.g., $Rh(CO)_2acac$ (Johnson, Mathey, Ltd.), or they were prepared either by modification of known literature procedures, e.g., $Cs_2[Rh_6(CO)_{15}C]$,[8,27] or by known methods as for $[Rh_{13}(CO)_{24}H_x]^{n-}$ (n = 2,3),[28] $[Rh_{12}(CO)_{30}]^{2-}$,[29] and $[Rh(CO)_4]^{-}$.[30] The syntheses of the cesium salts of $[Rh_9P(CO)2]^{2-}$ and $[Rh_{17}(CO)_{32}(S)_2]^{3-}$ have been described elsewhere.[31,32] These compounds were characterized by comparison of their infrared spectra with those in the literature and by elemental analysis and nuclear magnetic resonance studies when required.

(26) Some solvents have been previously reported as suitable media for reaction 1: sulfolane (L. Kaplan, Union Carbide Corp., German Patent 2 559 057 (1976), and references therein), tetraglyme (R. L. Pruett and W. E. Walker, Union Carbide Corp., U.S. Patent 3 957 857 (1976), and sulfolane-tetraglyme (L. Kaplan and W. E. Walker, Union Carbide Corp., German Patent 2 643 971 (1977)).
(27) V. G. Albano, M. Sansoni, P. Chini, and S. Martinengo, *J. Chem. Soc., Dalton Trans.*, 651 (1973); S. Martinengo, G. Ciani, A. Sironi, and P. Chini, *J. Am. Chem. Soc.*, **100**, 7096 (1978); J. L. Vidal, unpublished results (paper in preparation).
(28) P. Chini and S. Martinengo, *Gazz. Chim. Ital.*, **102**, 344 (1972).
(29) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 21 (1969).
(30) V. G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinengo, and M. Auker, *J. Chem. Soc., Dalton Trans.*, 859 (1975).
(31) J. L. Vidal, R. A. Flato, L. A. Cosby, and R. L. Pruett, *Inorg. Chem.*, **17**, 2574 (1978).
(32) J. L. Vidal, W. E. Walker, R. L. Pruett, and R. C. Schoening, *Inorg. Chem.*, **18**, 129 (1979).

Table II. Infrared Spectra of Some High-Nuclearity Rhodium-Carbonyl Clusters[27]

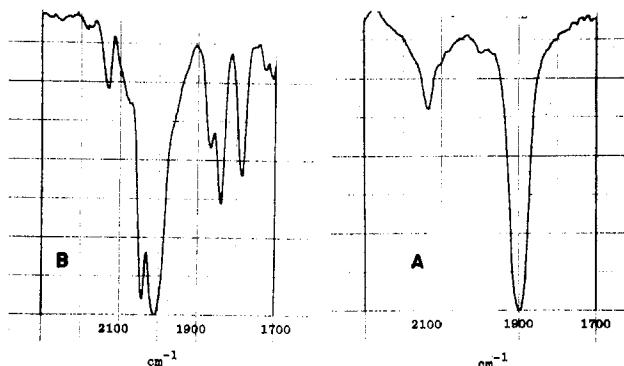| cluster	ν, cm^{-1}	cluster	ν, cm^{-1}
$[Rh_{13}(CO)_{24}H_3]^{2-}$	2020, 1845	$[Rh_{15}(CO)_{28}H]^{3-}$	1990, 1820
$[Rh_{13}(CO)_{24}H_2]^{3-}$	1990, 1825	$[Rh_{14}(CO)_{25}]^{4-}$	1960, 1810

Figure 2. Infrared spectra of (A) $[Rh_{12}(CO)_{30}]^{2-}$ salts in solutions of either sulfolane or tetraglyme under 500–800 atm of CO/H_2, 1:1, at 50–220 °C and (B) $[Rh(CO)_4]^{-}$ salts under similar conditions. These spectra remain constant over the full thermal range for any pressure in the previous interval.

Results and Discussions

This study was prompted by analogies between clusters and heterogeneous catalysts, the potential fragmentation of clusters under the conditions employed in the synthesis of ethylene glycol (Table I), and the need for comparison between the chemistry of rhodium-carbonyl clusters under ambient and high-pressure conditions.

Infrared spectroscopy was the technique of choice because of the relatively simple requirements of equipment, the previous knowledge of the infrared spectra of some rhodium-carbonyl species under ambient conditions, and the sensitivity of the technique. A matter of concern in this respect was the relative reduced fingerprint ability of this technique in the case of rhodium-carbonyl clusters as indicated by the similarities observed for the infrared spectra of some of these species (Table II). Another additional source of concern was the increase in the breadth of the bands noted in some initial tests at temperatures above 220 °C. Both of these limitations will be obvious during the discussion.

The behavior of rhodium-carbonyl complexes with a characteristic infrared pattern in the carbonyl-stretching region at ambient conditions was initially tested. The characteristic pattern of $[Rh_5(CO)_{15}]^{-}$ previously reported by Chini et al.[29] in the reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with carbon monoxide (eq 2) has been generated upon charging solutions of this anion

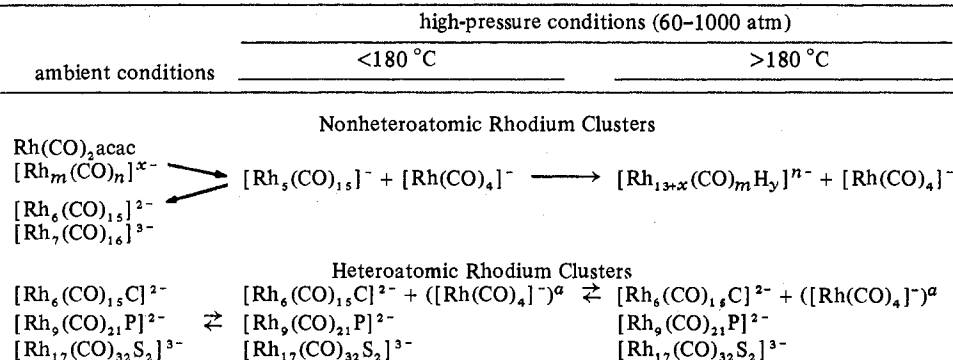$$[Rh_{12}(CO)_{30}]^{2-} + 4CO \rightarrow [Rh_5(CO)_{15}]^{-} \qquad (2)$$
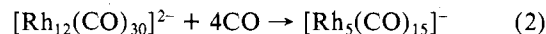
under high pressures of carbon monoxide and hydrogen (Figure 2A). A simpler pattern consisting of a single terminal carbonyl band located at 1895 cm^{-1} (± 3 cm^{-1}) has been observed for solutions of several salts of $[Rh(CO)_4]^{-}$ under the previous experimental conditions (Figure 2B). The same spectrum has been reported for the anion under ambient conditions.[30] Both of these patterns remain unchanged up to 220 °C under 1000 atm of carbon monoxide and hydrogen (1:1).

Solutions of $Rh(CO)_2acac$ containing amines and/or alkali carboxylate salts (Table I) give under maximum pressures of 1000 atm of CO/H_2, 1:1, at temperatures below 180 °C spectra (Figure 3A) that could be assigned to $[Rh_5(CO)_{15}]^{-}$ and $[Rh(CO)_4]^{-}$, by comparison with the spectra of these two complexes under similar conditions (Figure 2A,B). The presence of the latter anion in these systems may result from

Scheme I. Overall Representation of the Behavior of Rhodium–Carbonyl Clusters under Carbon Monoxide and Hydrogen, 1:1

	high-pressure conditions (60–1000 atm)	
ambient conditions	<180 °C	>180 °C

Nonheteroatomic Rhodium Clusters

$Rh(CO)_2acac$
$[Rh_m(CO)_n]^{x-}$ ⟶ $[Rh_5(CO)_{15}]^- + [Rh(CO)_4]^-$ ⟶ $[Rh_{13+x}(CO)_mH_y]^{n-} + [Rh(CO)_4]^-$
$[Rh_6(CO)_{15}]^{2-}$
$[Rh_7(CO)_{16}]^{3-}$

Heteroatomic Rhodium Clusters

$[Rh_6(CO)_{15}Cl]^{2-}$		$[Rh_6(CO)_{15}Cl]^{2-} + ([Rh(CO)_4]^-)^a$	$\rightleftarrows$	$[Rh_6(CO)_{15}Cl]^{2-} + ([Rh(CO)_4]^-)^a$
$[Rh_9(CO)_{21}P]^{2-}$	$\rightleftarrows$	$[Rh_9(CO)_{21}P]^{2-}$		$[Rh_9(CO)_{21}P]^{2-}$
$[Rh_{17}(CO)_{32}S_2]^{3-}$		$[Rh_{17}(CO)_{32}S_2]^{3-}$		$[Rh_{17}(CO)_{32}S_2]^{3-}$

^{a} Observed only after relatively long times.

Figure 3. Infrared spectra of $Rh(CO)_2acac$, $CsPhCO_2$, and N-methylmorpholine solutions in sulfolane: (A) spectrum taken at 500–1000 atm of CO/H_2, 1:1, and 100–180 °C; (B) spectrum taken at 250–270 °C under the same pressure.

the fragmentation reaction of clusters by carbon monoxide known to be facilitated by a basic medium.[33]

The features of the above spectra (Figure 3A) remained unaltered up to 180 or 210 °C under 500 and 840–1000 atm of CO/H_2, 1:1, respectively. An increase in the temperature above these values causes a broadening of the bands, a dramatic reduction in the intensity of the absorption for [Rh(CO)_4]^-, and a negative frequency shift for the terminal carbonyl absorption which now shows a broad maximum at 1995–2000 cm^{-1} (Figure 3B). The broadness of this band and the presence of shoulders at both sides of the maximum indicate that this band could correspond to an envelope. In any case, these changes are reversible and the spectral pattern assigned to [Rh_5(CO)_{15}]^- and [Rh(CO)_4]^- could be regenerated by cooling the systems below 180–220 °C under high pressure. This behavior is general for the systems initially containing Rh-(CO)_2acac, $[Rh_m(CO)_n]^{x-}$, $[Rh_m(CO)_nH_y]^{x-}$, or $[Rh_m(CO)_n]$. The absence of this property could serve as a tool for the diagnosis of changes or perturbations in the nature of the species present at the higher temperatures (vide infra). Obviously, it is not possible to make an unequivocal assignment of the high-temperature pattern or even to suggest with a comfortable degree of confidence the species present, on the basis of only spectroscopic evidence. Nevertheless, additional chemical analogies and evidence are helpful in this respect.

The formation of high-nuclearity rhodium–carbonyl clusters such as $[Rh_{13}(CO)_{24}H_n]^{(5-n)-}$ [28] and side products such as $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{15}(CO)_{28}]^{3-}$, in the reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with hydrogen at high-temperature and normal pressures, could serve as an analogy for the formation of
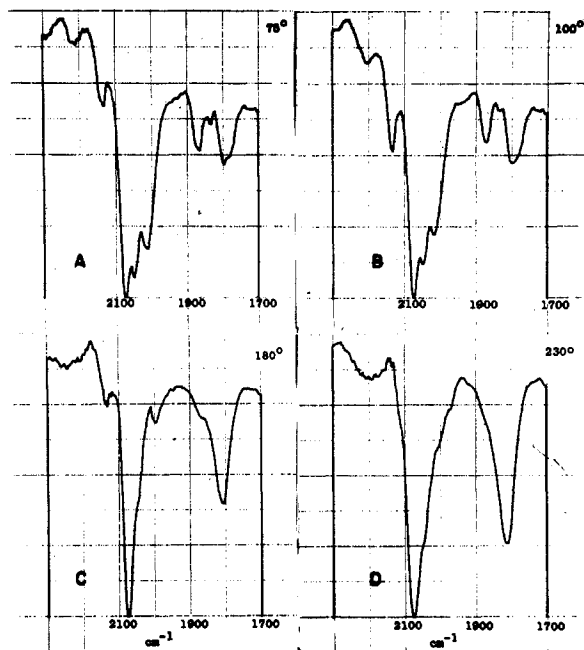

Figure 4. Infrared spectra of $Rh_6(CO)_{16}$–sulfolane solutions under 670 atm of carbon monoxide at (A) 75 °C, (B) 100 °C, (C) 180 °C, and (D) 230 °C.

similar clusters in our systems (vide infra). Likewise, the reaction of $[Rh_{12}(CO)_{30}]^{2-}$ with $[Rh(CO)_4]^-$ could offer an alternative pathway for the formation of the higher nuclearity clusters under suitable conditions. In any case, the infrared spectra of characterized high-nuclearity rhodium clusters (Table II) indicate the potential presence of some of these clusters in our systems.

We have found that other rhodium–carbonyl clusters such as $[Rh_6(CO)_{15}]^{2-}$, $[Rh_7(CO)_{16}]^{3-}$, and $Rh_4(CO)_{12}$ react with high pressure of CO/H_2 mixtures, in the presence of either amine and/or alkali carboxylates, in a similar way to that described above for $Rh(CO)_2acac$. In fact, any rhodium–carbonyl cluster of general formula $[Rh_m(CO)_n]^{x-}$ has been found to behave in an analogous way (Scheme I).

$Rh_6(CO)_{16}$ was also studied because of the high stability of this cluster and the apparent ability of the rhodium skeleton to survive drastic thermal conditions.[34] It has been observed that $Rh_6(CO)_{16}$ also undergoes the previously described transformation into $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ in the presence of amines and/or alkali carboxylates. The reactivity of $Rh_6(CO)_{16}$ with CO has been also tested in absence of these

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(34) G. C. Smith, T. P. Chojnacki, S. R. Dasgupta, K. Iwatate, and K. L. Watters, *Inorg. Chem.*, **14**, 1419 (1975).
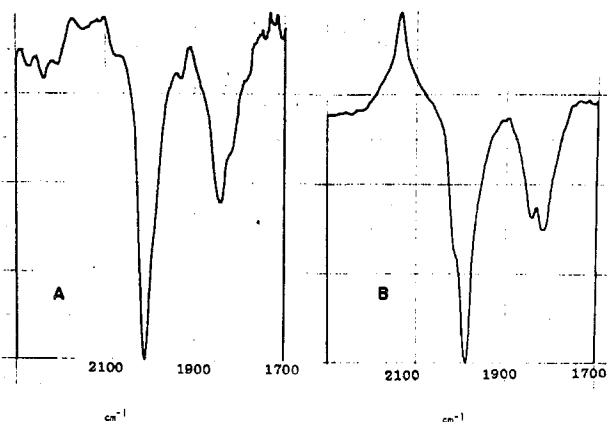
Figure 5. Infrared spectra of sulfolane solutions under 6 atm of CO/H_2, 1:1, at 50 °C for (A) $[Rh_{13}(CO)_{24}H_3]^{2-}$ and (B) $[Rh_{13}(CO)_{24}H_2]^{3-}$ in mixtures with $[Rh_{13}(CO)_{24}H_2]^{2-}$, prepared by addition of N-methylmorpholine to the solution in part A.
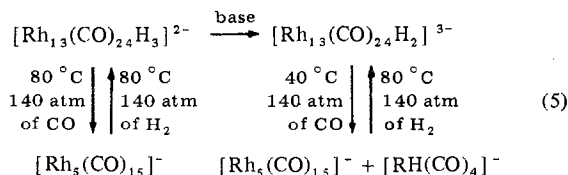
two bases. The probable presence of $Rh_6(CO)_{16}$ in the latter systems (Figure 4) even under 670 atm of carbon monoxide at 180–230 °C may be indicated by the similarity between the infrared spectra of the system with that reported for $Rh_6(CO)_{16}$.[33] The presence of several other bands at lower temperatures is a probable result of the fragmentation of $Rh_6(CO)_{16}$ into species richer in carbon monoxide, consistent with thermodynamic arguments involved in cluster fragmentation by CO (vide infra). In any case, the presence of additional infrared bands under these conditions, e.g., 100 °C, at 2045 and 1785 cm^{-1} is consistent with the formation of $Rh_4(CO)_{12}$[33] caused by reaction with CO (eq 3). The presence of this equilibrium is also suggested by the reversibility of the spectra upon changes in temperature.

$$2Rh_6(CO)_{16} + 4CO \rightleftarrows 3Rh_4(CO)_{12} \quad (3)$$
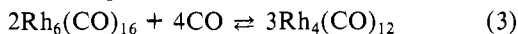
The transformation of rhodium–carbonyl clusters into $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ occurring with either $Rh(CO)_2$acac or $[Rh_m(CO)_n]^{x-}$ (Scheme I) under high pressure of CO/H_2 in the presence of bases (Figures 2 and 3) has been also detected for $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ ($x = 2, 3$). Both of these anions have been found to be stable at room temperature under a low pressure of carbon monoxide (Figure 5). In addition, it has been observed that addition of bases, e.g., N-methylmorpholine, results in the deprotonation of the dianion in a way similar to that previously reported at ambient conditions by Chini et al.[30]

$$[Rh_{13}(CO)_{24}H_3]^{2-} \xrightarrow{\text{base}} [Rh_{13}(CO)_{24}H_2]^{3-} \quad (4)$$
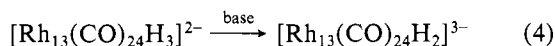
The reaction of these clusters with carbon monoxide has been studied by stepwise increase of temperature and pressure from 25 °C and 6 atm, with the spectra taken after equilibria have been reached. Change of the dianion to $[Rh_5(CO)_{15}]^-$ occurs upon reaching 80 °C and 140 atm (eq 5), but the

$$[Rh_{13}(CO)_{24}H_3]^{2-} \xrightarrow{\text{base}} [Rh_{13}(CO)_{24}H_2]^{3-}$$

$$\begin{array}{cc}
80\ °C & \uparrow 80\ °C \\
140\ atm & 140\ atm \\
of\ CO \downarrow & of\ H_2
\end{array}
\qquad
\begin{array}{cc}
40\ °C & \uparrow 80\ °C \\
140\ atm & 140\ atm \\
of\ CO \downarrow & of\ H_2
\end{array} \quad (5)$$

$$[Rh_5(CO)_{15}]^- \qquad [Rh_5(CO)_{15}]^- + [RH(CO)_4]^-$$

reaction is reversed by replacing CO by hydrogen. Addition of N-methylmorpholine results in the appearance of the bands probably corresponding to $[Rh_{13}(CO)_{24}H_2]^{3-}$. The formation of $[Rh_5(CO)_{15}]^-$ takes place now at 40 °C and 140 atm of carbon monoxide, but it is found that hydrogen is able to reverse this reaction only after 140 atm of H_2 and 80 °C have been reached. The respective cycles have been repeated for a 24-h period.
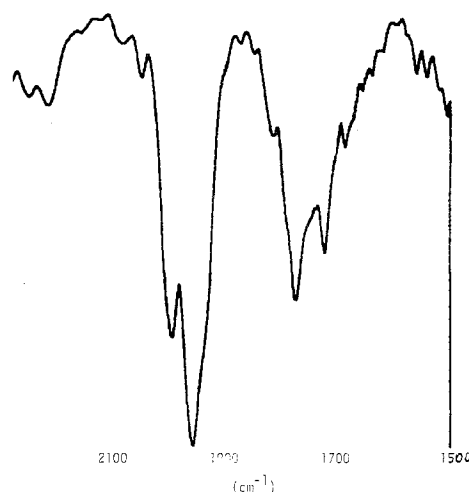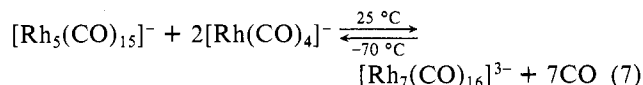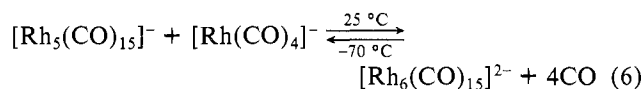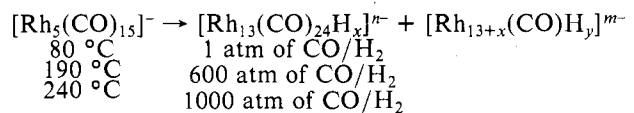

Figure 6. Infrared spectrum of a solution of $Rh(CO)_2$acac, $CsPhCO_2$, and N-methylmorpholine in sulfolane taken at ambient conditions after 1–3 h under 500–1000 atm of CO/H_2, 1:1, at 250–260 °C. This solution has a dark green color.

The trend in the reaction of $[Rh_{13}(CO)_{24}H_x]^{n-}$ clusters with carbon monoxide indicates that the more reduced anion ($n = 3$) undergoes a fragmentation reaction easier. Similar behavior has been noted by Chini et al.[33] for $[Rh_6(CO)_{14}]^{4-}$ and $[Rh_6(CO)_{15}]^{2-}$, and they suggest that this may represent general behavior for rhodium–carbonyl clusters.

The infrared spectra of the solutions suggested here to contain $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ under high pressure of CO/H_2, vide supra (Figure 3), change upon venting the solutions to ambient conditions (Figure 6). The presence of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$ in these solutions is suggested by the similarities between the infrared spectra reported for these anions[33] and those of the vented solutions and by the green color of the solutions. The presence of these two anions in our system is consistent with the report by Chini et al.[33] describing their formation from $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ under 1 atm of carbon monoxide (eq 6 and 7).

$$[Rh_5(CO)_{15}]^- + [Rh(CO)_4]^- \underset{-70\ °C}{\overset{25\ °C}{\rightleftarrows}}$$
$$[Rh_6(CO)_{15}]^{2-} + 4CO \quad (6)$$

$$[Rh_5(CO)_{15}]^- + 2[Rh(CO)_4]^- \underset{-70\ °C}{\overset{25\ °C}{\rightleftarrows}}$$
$$[Rh_7(CO)_{16}]^{3-} + 7CO \quad (7)$$

The inverse effect of temperature and pressure of carbon monoxide on the reactions of rhodium–carbonyl clusters is apparent from these equations. This observation may be useful in the comparison of the chemistry of these complexes under ambient and high pressure. Thus, reactions of rhodium–carbonyl clusters occurring at relatively high temperature under normal pressure could be expected to occur at even high temperatures with increasing CO or CO/H_2 pressures. The reaction of $[Rh_5(CO)_{15}]^-$ with hydrogen is an adequate example suitable for the illustration of these arguments. It has already been mentioned that such a reaction occurs readily at 80 °C under 1 atm of hydrogen.[30] By contrast, the reaction happens at 180–190 °C upon increasing the pressure to 500 atm, and, finally, it requires a temperature of 240 °C under a pressure of $\sim$1000 atm of carbon monoxide and hydrogen (eq 8).
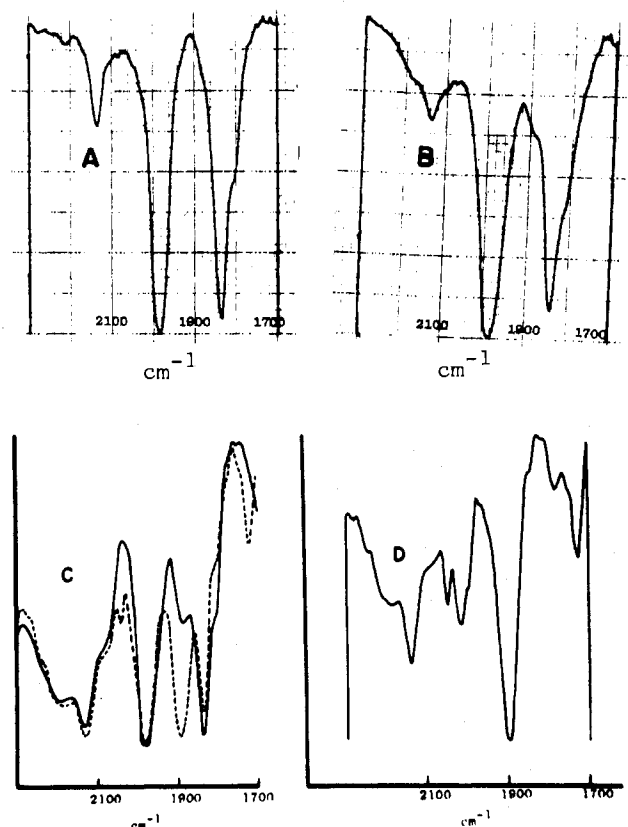
$$[Rh_5(CO)_{15}]^- \rightarrow [Rh_{13}(CO)_{24}H_x]^{n-} + [Rh_{13+x}(CO)H_y]^{m-}$$
$$\begin{array}{ll}
80\ °C & 1\ atm\ of\ CO/H_2 \\
190\ °C & 600\ atm\ of\ CO/H_2 \\
240\ °C & 1000\ atm\ of\ CO/H_2
\end{array} \quad (8)$$

Figure 7. Infrared spectra of sulfolane solutions of $[Rh_6(CO)_{15}C]^{2-}$ salts under 1000 atm of CO/H_2, 1:1, (A) at 100 °C for 4 h, (B) at 260 °C for 0.5 h, and (C) upon cooling to 100 °C after (- - -) 3 h and (—) 0.5 h at 260 °C. Part D is a computer subtraction of the spectra in part C.
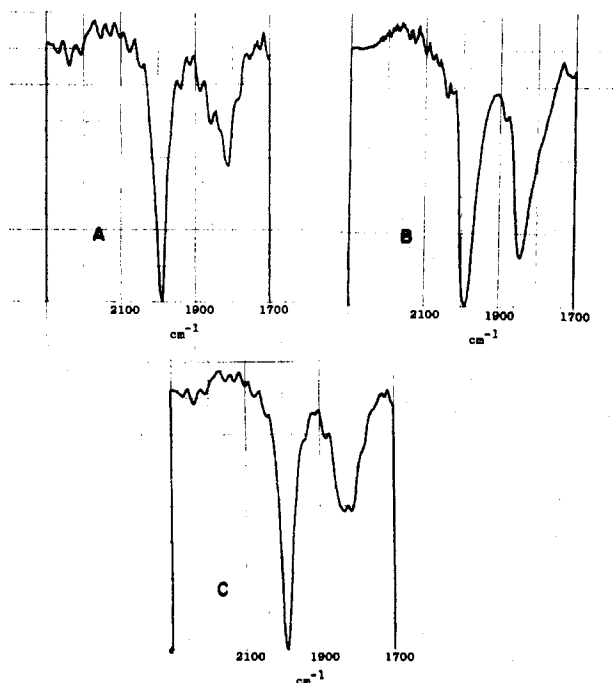

Figure 8. Infrared spectra of sulfolane solutions of (A) $[Rh_{13}(CO)_{24}H_2]^{3-}$ at 25 °C and 50 psi of CO/H_2, (B) $[Rh_6(CO)_{15}C]^{2-}$ under the same conditions, and (C) a solution containing both anions.

The proposal for the formation in these systems of high-nuclearity rhodium–carbonyl clusters, e.g., $[Rh_{13+x}(CO)_3H_y]^{n-}$, as occurring above 180 °C is rudimentarily supported by simple thermodynamic considerations. The tendency to form
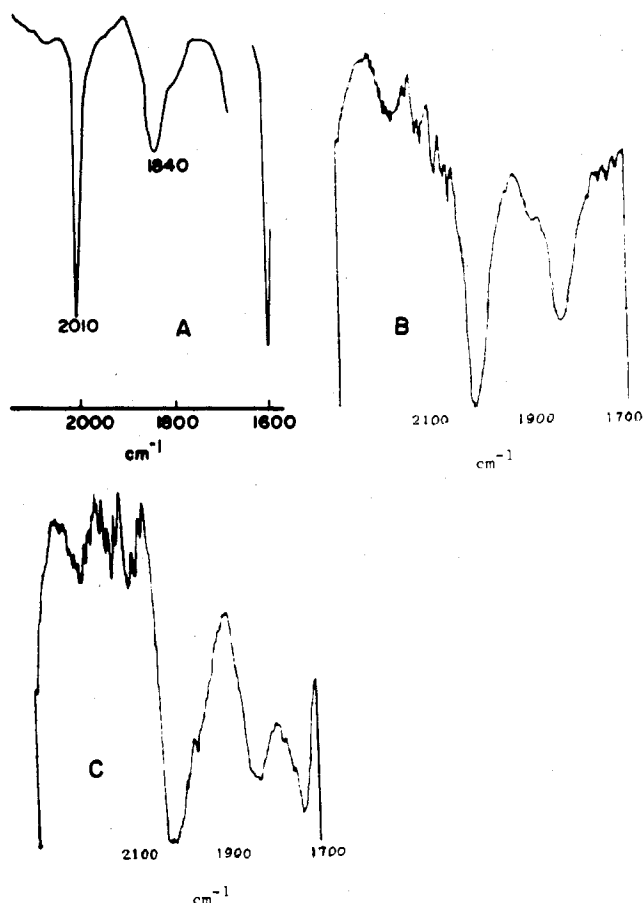

Figure 9. Infrared spectra of $[Rh_9P(CO)_{21}]^{2-}$ salts and *N*-methylmorpholine solutions in sulfolane: (A) spectrum taken at ambient conditions; (B) spectrum of the same solution taken at 160 °C under 1000 atm of CO/H_2, 1:1, with a contact time of 2.0 h; (C) spectrum of the same solution taken at 250 °C after 2.0 h at conditions under the same pressure used in B.

an increasing number of rhodium–rhodium bonds upon increasing temperature could result, at least in part, from the differences in the bond energies for $\bar{D}(Rh-Rh)$ = 26.5 kcal/mol and $\bar{D}(Rh-CO)$ = 39.0 kcal/mol.[35] Moreover, the overall free energy for the hypothetical reaction (eq 9) that could represent schematically the thermally induced condensation of rhodium–carbonyl clusters appears as more favorable with increasing high temperature.

$$Rh-CO + Rh-CO \rightarrow Rh-Rh + 2CO \qquad (9)$$

Rhodium–Carbonyl Clusters with Encapsulated Heteroatoms. An alternative to the complexity in the infrared patterns detected for the catalytic systems above was offered by systems consisting of rhodium–carbonyl clusters with encapsulated heteroatoms such as $[Rh_6(CO)_{15}C]^{2-}$ and $[Rh_{15}(CO)_{28}(C)_2]^{-}$. The presence of the central main-group atom(s) was previously suggested to enhance the stability of these species.[36] These arguments, together with the ability expected for some rhodium polyhedra to encapsulate atoms of covalent radii in the range of 0.7–1.1 Å,[33] plus the known affinity of low oxidation state rhodium for sulfur and phosphorus ligands were the main reasons behind the syntheses of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ [31] and $[Rh_9P(CO)_{21}]^{2-}$.[32]

It was expected that systems based on the heteroatomic clusters above would provide more favorable cases for scru-

(35) P. Chini and B. T. Heaton, *Top. Curr. Res.*, **4**, 3 (1978).
(36) V. G. Albano, M. Sansoni, P. Chini, S. Martinengo, and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 970 (1976).
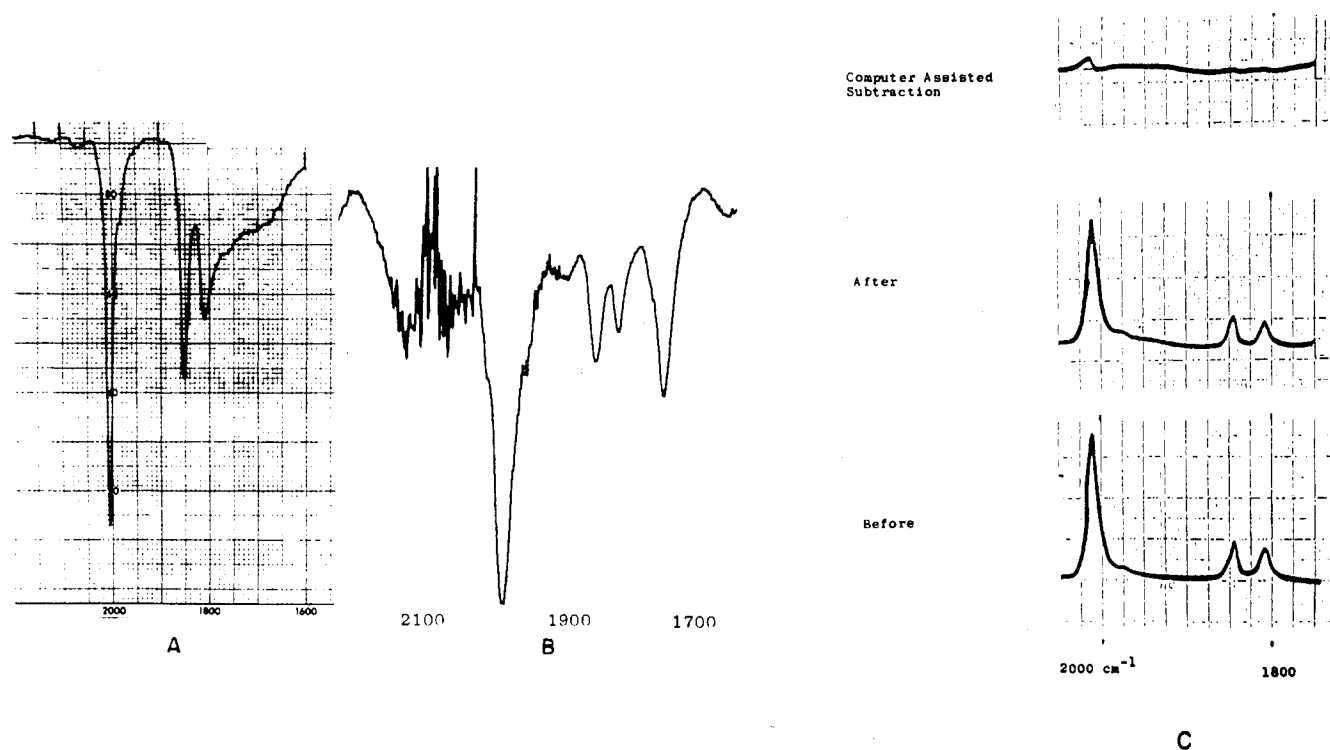
C

Figure 10. Infrared spectra of sulfolane solutions of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ salts and N-methylmorpholine: (A) spectrum at ambient conditions; (B) spectrum of the same solution taken at 250 °C under 1000 atm of CO/H$_2$, 1:1, with a contact time of 3.0 h; (C) absorbance plots for these solutions before and after a catalytic run taken at ambient conditions and the computer-assisted subtraction of these spectra.

tinizing our systems under conditions required for catalytic activity.

High-Pressure Infrared Results Concerning Rhodium–Carbonyl Anionic Clusters with Encapsulated Group 4, 5, and 6 Atoms. The ability of $[Rh_6(CO)_{15}C]^{2-}$ to maintain its chemical integrity after 4 h at 100 °C and 1000 atm of Co/H$_2$, 1:1, is strongly suggested by the similarity between the spectra collected under these conditions and those under ambient conditions[27] (Figure 7). The presence of bases such as N-methylmorpholine does not change these results. Moreover, changes of these spectra are not detectable upon warming these systems to 260 °C for ca. 0.3 h (Figure 6).

In contrast, the appearance of a weak absorption band at 1895 cm^{-1} (Figure 7), possibly belonging to $[Rh(CO)_4]^-$ (Figure 2), is detected after 0.5 h at 260 °C under 1000 atm of CO/H$_2$, only in systems containing bases. The concentration of the monoanion in these systems has been estimated by Beer's law as corresponding to less than 5% of the initially charged metal. These results indicate that fragmentation of $[Rh_6(CO)_{15}C]^{2-}$ is occurring very slowly under these conditions. These results do not allow us either to detect or to speculate about the identity, or even the presence, in this system of any other rhodium–carbonyl complex that could have been generated in this process in addition to $[Rh(CO)_4]^-$.

The thermal reversibility of the spectral changes previously described for the systems containing Rh(CO)$_2$acac, $[Rh_m(CO)_n]^{x-}$, or Rh$_m$(CO)$_n$ (Figures 3 and 6 and Scheme I) supplied us with a test for the fragmentation of these heteroatomic clusters into rhodium–carbonyl species usually present in systems containing nonheteroatomic rhodium–carbonyl clusters.

No changes were detected upon cooling to 100 °C a system containing $[Rh_6(CO)_{15}C]^{2-}$ and N-methylmorpholine after staying 0.5 h at 260 °C under 1000 atm of CO and H$_2$ (Figure 7). In contrast, the same procedure results in the appearance of some additional bands after 3.0 h under the latter conditions (Figure 7). Fourier subtraction of these spectra shows a re-

sulting spectrum (Figure 7) that could correspond to that expected from mixtures of $[Rh_5(CO)_{15}]^-$ (2040, 2015, 1855, and 1785 cm^{-1}) and $[Rh(CO)_{14}]^-$ (1895 cm^{-1}) (Figure 2). Comparison between this spectrum and the ones obtained for the nonheteroatomic species (Figure 3) shows that although these two anions are present in both instances, the intensity ratios of the absorption bands for these two species vary with those of $[Rh_5(CO)_{15}]^-$ being weaker in the $[Rh_6(CO)_{15}C]^{2-}$ system. This indicates that the presence of a heteroatomic rhodium–carbonyl cluster has resulted in different chemistry.

The infrared spectrum of $[Rh_6(CO)_{15}C]^{2-}$ and $[Rh_{13}(CO)_{24}H_x]^{n-}$ ($x = 2, 3$) at ambient conditions indicated that mixtures of these species could be expected to give a spectrum similar to the one obtained from the $[Rh_6(CO)_{15}C]^{2-}$ systems under conditions in which these systems are catalytically active in the synthesis of ethylene glycol (Figure 8B; Table I).[8] This possibility has been discounted on the basis of Fourier overlapping and subtraction of these spectra (Figure 8). This has been additionally supported by the actual recording of the one for a mixture of $[Rh_{13}(CO)_{24}H_2]^{3-}$ and $[Rh_6(CO)_{15}C]^{2-}$ (Figure 8).

$[Rh_9P(CO)_{21}]^{2-}$ is another rhodium–carbonyl cluster with an encapsulated heteroatom found to be stable under high pressures of CO and H$_2$. The spectral pattern detected for this anion at ambient conditions (Figure 9) remains unaltered after 3 h under 1000 atm of carbon monoxide and hydrogen at 160 °C and even after 0.5 h at 250 °C.[32] As in the previous case, Fourier subtraction of these spectra shows no additional carbonyl absorption, as does the study of the systems cooled to 100 °C. These results lead us to conclude the only detectable rhodium–carbonyl complex present in these solutions even under catalytic conditions (Table I).

$[Rh_{17}(S)_2(CO)_{32}]^{3-}$ has been also reported to be stable under 300 atm of CO and H$_2$.[31] A comparison of the infrared spectra of solutions of this anion in the presence of N-methylmorpholine under 1 atm of CO and H$_2$ at 25 °C and under 1000 atm of CO and H$_2$ at 250 °C after 3 h (Figure 10)

Table III. Relative Catalytic Activity of Rhodium Catalysts Based on Clusters

initially added Rh complex	species probably present at conditions[a]		rel catalytic activity
	Rh clusters	$[Rh(CO)_4]^-$	
$Rh(CO)_2acac$	X	X	1.0
$[Rh_6(CO)_{15}C]^{2-}$	X		0.5
$[Rh_{17}S_2(CO)_{32}]^{3-}$	X		0.3
$[Rh_9P(CO)_{21}]^{2-}$	X		0.1

[a] Detected by IR spectroscopy after 0.5–1.0 h under 800–1000 atm of CO and H_2 at 240–260 °C in presence of the promoters, e.g., R_3N and/or alkali carboxylates.

indicates the constancy of the patterns and the absence of any extra absorption corresponding to the stretching vibration of coordinated carbon monoxide. Cooling the latter system to 100 °C does not change the spectrum observed at high temperature. The inability of this system to generate $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ after cooling is in sharp contrast to the previously suggested presence of these two anions in the cases for which nonheteroatomic rhodium–carbonyl complexes are used as precursors of the catalyst. These results could be a consequence of the different nature of the species present under catalytic conditions (Table III) in both types of systems, and this may indicate that $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ is not getting transformed into another detectable species at these conditions. Alternatively, the same species could be present in both cases if the products that could result from the potential fragmentation of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ are transformed further. This possibility could escape undetected by our experimental procedure only if the reversible aggregation of these fragments would be fast and selective enough to preclude any detection of rhodium–carbonyl complexes other than the disulfide anion upon cooling under high pressure of CO/H_2 or under ambient conditions (Figure 10). Fourier subtraction of the spectra taken at ambient conditions for solutions of $[Rh_{17}(S)_2(CO)_{32}]^{3-}$ and *N*-methylmorpholine (Table I) before and after carrying out a catalytic run for 0.3 h under 1000 atm of CO/H_2, 1:1, at 260 °C resulted in very weak residual infrared absorption at 2020, 1870, and 1830 cm^{-1}. The similarity of this pattern to that previously reported for $[Rh_{17}(S)_2(CO)_{32}H_m]^{(3-m)-}$ [31] suggests this material could be responsible for these bands.

An additional effect resulting from the stability of $[Rh_6(CO)_{15}C]^{2-}$, $[Rh_9P(CO)_{21}]^{2-}$, and $[Rh_{17}(CO)_{32}(S)_2]^{3-}$ is evident when these solutions are decompressed to normal pressure. In those cases, the absence of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{15}]^{3-}$ is in sharp contrast to the presence of these species in similarly treated solutions (Table I) initially containing other rhodium–carbonyl complexes, e.g., $Rh(CO)_2acac$, $[Rh_x(CO)_y]^n$, $Rh_4(CO)_{12}$, or $Rh_6(CO)_{16}$. An apparent explanation for this difference in behavior is that while $[Rh_5(CO)_{15}]^-$ and

$[Rh(CO)_4]^-$ are not present at low temperature and high pressure in the case of the former systems, their proposed presence in the latter solutions under similar conditions is consistent with the formation of $[Rh_6(CO)_{15}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$ by reaction of the two anions (eq 5 and 6) upon decreasing the pressure to normal values. These results provide additional circumstantial evidence that could make it possible to rule out the presence of rhodium species usually present in the conventional $Rh(CO)_2acac$ or $[Rh_x(CO)_yH_m]^{n-}$ solutions, when compared with catalytic solutions based on the three heteroatomic rhodium clusters under study.

Additional Remarks

The relative catalytic activity of systems based on $Rh(CO)_2acac$ and on the three heteroatomic rhodium–carbonyl clusters under study (Table III) shows the decreased activity of the latter systems. Thus, it is possible to look upon $[Rh_6(CO)_{15}C]^{2-}$, $[Rh_9P(CO)_{21}]^{2-}$, and $[Rh_{17}(CO)_{32}(S)_2]^{3-}$ as relatively poisoned clusters, with the carbon, phosphorus, and sulfur atoms acting in a certain way similar to their behavior with some poisoned heterogeneous catalysts. The lack of detectable fragmentation products of these clusters under conditions employed for the synthesis of alcohols from CO/H_2 by either chemical or spectroscopic methods may be indicative of the ability of the initial cluster moieties to stand these conditions. The increase in the stability of the complexes $[Rh_6(CO)_{15}C]^{2-}$ < $[Rh_9P(CO)_{21}]^{2-}$ < $[Rh_{17}(CO)_{32}(S)_2]^{3-}$ corresponds to that expected from hard–soft interactions between low-oxidation-state rhodium and the respective atomic ligands. Thus, the enhancement in cluster stability for these species follows, at least partially, the ability of the encapsulated atom(s) to reinforce the linkage between different sections of the clusters, acting in effect as a "glueing agent". Other factors under study at present may also be relevant.[37]

The conditions for the easy formation of $[Rh_9P(CO)_{21}]^{2-}$ and $[Rh_{17}(CO)_{32}(S)_2]^{3-}$ [31,32] suggest that this basic type of species could be more prevalent than considered initially.[38]

(37) J. L. Vidal et al., papers in preparation.
(38) After this paper was submitted, it was reported to us by Professor Paolo Chini that the species previously suggested by his group to be $[Rh_{12}(CO)_{34}]^{2-}$ [29,30,33] is the fact $[Rh_5(CO)_{15}]^-$. Their results are described in a forthcoming publication. Consequently, we have replaced in every instance the former formula by the latter.