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Rhodium Carbonyl Cluster Chemistry under High Pressures of Carbon Monoxide and Hydrogen. 5. Synthesis and Reactivity of $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$

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The mounting interest in transition-metal carbonyl clusters has recently been centered around their behavior as catalysts[1] or as models for surfaces.[2] Consequently, most attention is directed toward clusters usually containing more than four metal atoms.[3,4] A main objective in these studies has been the convenient preparation of large clusters.[5] For instance, the excellent efforts of Chini et al.[6,7] have resulted in the synthesis of species with up to 38 metal atoms, while we have described the single-step high-yield preparation of some of these complexes by high-pressure techniques.[8]

Our interest in the role of rhodium carbonyl clusters in the hydrogenation of carbon monoxide to organic chemicals induced us to study $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$. This study was prompted by the observation of Chini et al. that this cluster releases a mononuclear fragment, upon reaction with halides or nitriles (eq 1), and by the proposed formation of $[\mathrm{Rh_{22}(CO)_{35}H_x}]^{(5-x)-}$ by aggregation with $[\mathrm{Rh_7(CO)_{16}}]^{3-}$.[9,10]

$$[\mathrm{Rh_{15}(CO)_{27}}]^{3-} + 2\mathrm{Br}^- \rightleftharpoons [\mathrm{Rh_{14}(CO)_{25}}]^{4-} + [\mathrm{Rh(CO)_2(Br)_2}]^- \quad (1)$$

Experimental Section

The reagents were obtained from the following commercial sources and used as available: $\mathrm{Rh(CO)_2(acac)}$, Matthey-Bishop; cesium benzoate dihydrate, Strem Chemicals Co; *N*-methylmorpholine, and 1,10-phenanthroline, Aldrich Chemical Co.; tetraglyme, Ansul Chemical Co. Sulfolane was obtained from Phillips Chem. Co., and it was rigorously purified and dried before use. 18-Crown-6 was kindly provided by Dr. Fedor Poppelsdorf of Union Carbide Corp. Carbon monoxide and hydrogen were provided by the Linde Division of Union Carbide Corp.

The high-pressure autoclave used for the synthesis and high-pressure reactions studies has been previously described.[11] The high-pressure autoclave, the high-pressure infrared cell, and the Fourier transform Digilab Nova infrared spectrometer as well as the methods used to collect the spectra have all been described in detail.[12] The infrared studies at atmospheric pressure have been done with a Perkin-Elmer 283 spectrometer while a Varian XL-100 FT NMR spectrometer has been used for the NMR studies. The elemental analysis was conducted at Schwarzkopf Microanalytical Laboratory, Woodside, NY. All of the work has been carried out under argon by the use of Schlenk techniques.

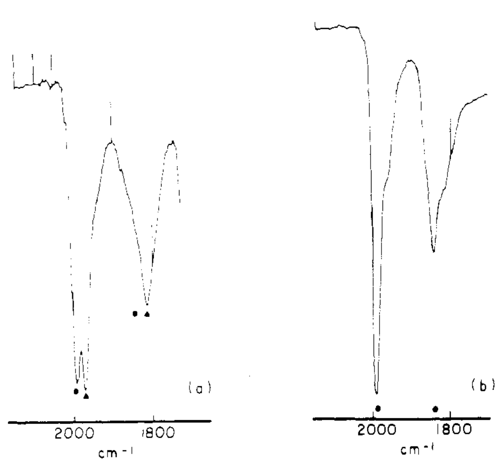

Figure 1. Infrared spectra taken during the high-pressure synthesis of $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$ (a) after 2.0 h reaction time and (b) with $[\mathrm{((C_6H_5)_3P)_2N}]_3[\mathrm{Rh_{15}(CO)_{27}}]$ in acetone solution: ●, $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$ bands; ▲, $[\mathrm{Rh_{14}(CO)_{25}}]^{4-}$ bands.

Synthesis of $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$. This cluster has been prepared by the two procedures described below.

(a) Preparation of the $[\mathrm{Cs}(18\text{-crown-}6)_{\sim 1.6}]^+$ Salt under Atmospheric Pressure. $\mathrm{Rh(CO)_2(acac)}$ (3.132 g, 12.14 mmol) was dissolved together with cesium benzoate dihydrate (0.711 g, 2.45 mmol) in 78 mL of 18-crown-6, which had been previously melted and degassed, in a 250-mL Schlenk tube. This solution was slowly heated to 150 °C while a fast stream of carbon monoxide was bubbled into it. The system was reacted in this way overnight. The resulting mixture was filtered with use of a jacketed frit warmed with steam to remove insoluble material. The residue was thoroughly washed with 2-propanol and then extracted with 280 mL of tetrahydrofuran. The filtrate was concentrated under vacuum to ca. 150 mL and precipitated with 2-propanol. The precipitate was collected by filtration and vacuum-dried. This material (2.247 g) has been characterized as the $[\mathrm{Cs(C_{12}H_{24}O_6)_{1.6}}]^+$ salt of $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$ on the basis of the infrared, $^1\mathrm{H}$, and $^{13}\mathrm{C}$ NMR spectra, and elemental analysis. A yield of 70.0% is calculated for this compound on the basis of rhodium.

(b) Preparation of $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$ under High Pressures of Carbon Monoxide and Hydrogen. A solution of $\mathrm{Rh(CO)_2(acac)}$ (14.0 g, 54.04 mmol) and cesium benzoate dihydrate (3.4 g, 11.7 mmol) was prepared in 840 mL of tetraglyme. Ethylene glycol (40 mL) and *N*-methylmorpholine (10.8 g, 106.9 mmol) were added to the solution, and the mixture was charged into a high-pressure autoclave purged with carbon monoxide and hydrogen. The initial pressure of the reactor was adjusted to ca. 10 atm with a 1:1 mixture of these gases, and the temperature was quickly increased to 150 °C. The stirred mixture was allowed to react under 19 atm and 150 °C for 1 h (Figure 1). The solution was vented, collected into a Schlenk receiver, and filtered. The filtrate was allowed to cool, and it was treated with 4 L of toluene. The solvent mixture was decanted, and the residual oil was washed with 2-propanol, dissolved in 150 mL acetone, and filtered. This filtrate was treated with 150 mL of a solution of $[\mathrm{(Ph_3P)_2N}]\mathrm{Cl}$ in 2-propanol (1 g in 20 mL) and with 600 mL of fresh 2-propanol. The precipitate formed was removed by filtration and washed with 2-propanol (4 × 30 mL) and vacuum-dried. This product (12.3 g) has the infrared spectrum (Figure 1) of $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$, and its elemental analysis is in agreement with that of $[\mathrm{(Ph_3P)_2N}]_3[\mathrm{Rh_{15}(CO)_{27}}]$. Anal. Calcd: C, 41.39; H, 2.32; N, 1.07; P, 4.75; Rh, 39.44, Found: C, 42.01; H, 2.10; N, 1.22; P, 5.02; Rh, 39.85. A yield of 87.0% is calculated for this compound on the basis of rhodium.

Reaction of $[\mathrm{Rh_{15}(CO)_{27}}]^{3-}$ under 10 Atm of Carbon Monoxide and Hydrogen. A solution of $[\mathrm{Cs(C_{12}H_{24}O_6)_{\sim 1.6}}]_3[\mathrm{Rh_{15}(CO)_{27}}]$ (4.0 g,

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(1) K. G. Caulton, M. G. Thomas, B. A. Sosinsky and E. L. Muetterties, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 4274 (1976); C. V. Pittman, Jr., and R. C. Ryan, *CHEMTECH.*, 190 (1978); M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976); G. C. Demitras and E. L. Muetterties, *ibid.*, **99**, 2796 (1977).

(2) E. L. Muetterties, *Science (Washington, DC)*, **196**, 839 (1977); E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79**, 91 (1979); A. K. Smith and J. M. Basset, *J. Mol. Catal.*, **2**, 229 (1977).

(3) J. W. Lauher, *J. Am. Chem. Soc.*, **100**, 5305 (1978); **101**, 2604 (1979).

(4) E. L. Muetterties and E. Band, *Chem. Rev.*, **78**, 639 (1978); E. L. Muetterties, *Angew. Chem., Int. Ed. Engl.*, **17**, 545 (1978).

(5) P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976).

(6) D. M. Washecheck, E. J. Wucherer, L. F. Dahl, A. Ceriotti, G. Longoni, M. Manassero, M. Sansoni, and P. Chini, *J. Am. Chem. Soc.*, **101**, 6111 (1979).

(7) (a) V. G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinengo, and W. M. Anker, *J. Chem. Soc., Chem. Commun.*, 859 (1975); *J. Chem. Soc., Dalton Trans.*, 978 (1979); (b) S. Martinengo, G. Ciani, A. Sironi, and P. Chini, *J. Am. Chem. Soc.*, **100**, 7096 (1978).

(8) J. L. Vidal, R. C. Schoening and J. M. Troup, *Inorg. Chem.*, **20**, 265 (1981).

(9) J. L. Vidal and R. C. Schoening, *Inorg. Chem.*, **20**, 227 (1981).

(10) J. L. Vidal, a report describing the synthesis of the 22 rhodium atom cluster by means of this reaction is in preparation.

(11) J. L. Vidal, R. A. Fiato, L. A. Cosby, and R. L. Pruett, *Inorg. Chem.*, **17**, 2574 (1978).

(12) J. L. Vidal and W. E. Walker, *Inorg. Chem.*, **19**, 896 (1980).

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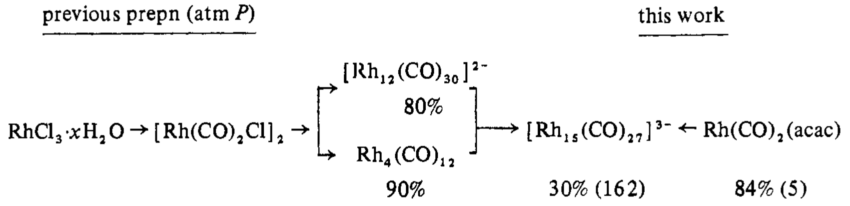
Chart I[a]



[a] % yield (time, h): yields are estimated for each step of procedures in ref 7b and 8. The maximum time requirements have been used for the method in ref 8 [=% (h)] and in this work, while minimum times have been estimated for the procedure in ref 7b [=% (h)].

Table I

reagent	solvent	≃[Rh: reagent atomic ratio]	monitored by
1,10-phenanthroline	acetone	1	IR
N-methylmorpholine	acetone	3	IR
methanol	acetone–sulfolane	4	IR
ethylene glycol	acetone–sulfolane	4	IR
$CsPhCO_2$	acetone–sulfolane	3.7	IR
$CsPhCO_2$	acetone–sulfolane	3.6	IR, ^{13}C NMR

1.01 mmol) in 18-crown-6 was mixed with *N*-methylmorpholine (1.01 g, 10.0 mmol), and the mixture was charged into a high-pressure autoclave purged with argon. The reaction conditions were adjusted to 150 °C and 10 atm of carbon monoxide and hydrogen, and the system was allowed to react for 24 h under these conditions while periodically monitoring the progress of the reaction by high-pressure infrared spectroscopy. The solution was sampled at regular intervals to monitor the changes in rhodium and cesium concentrations from their initial values of 4050 and 1212 ppm, respectively, by means of atomic absorption analyses. The final concentrations of rhodium (2726 ppm) and cesium (205 ppm) correspond to losses of 1324 and 507 ppm, respectively. This indicates an atomic ratio of these two elements of 3.44 in the precipitating solids.

Reactions of $[Rh_{15}(CO)_{27}]^{3-}$ under Ambient Conditions. These reactions were generally studied by preparing a solution of either the cesium or the iminium salt of $[Rh_{15}(CO)_{27}]^{3-}$, ca. 0.3 g, in ca. 4 mL of the solvent of choice to which the reagents were later added. The reactions are shown in Table I and were studied at 25 °C under argon.

The reactions with carbon monoxide or hydrogen were studied with infrared and ^{13}C NMR spectroscopy at 25 °C under atmospheric pressure. They were conducted by dissolving the selected salt of $[Rh_{15}(CO)_{27}]^{3-}$ in the solvent of choice (ca. 0.5–0.7 g in 3 mL) and by bubbling the gas into the solution. A contact time of 65 h was allowed, and the systems were closely monitored. The protonation of $[Rh_{15}(CO)_{27}]^{3-}$ was studied by dissolving 0.5 g of the tetraethylammonium salt (0.13 mmol) in 3 mL of acetone and by treating this solution dropwise with a 0.03 M solution of trifluoromethanesulfonic acid in acetone. The ^{13}C-enriched samples of $[Rh_{15}(CO)_{27}]^{3-}$ salts were prepared by enrichment of the anion at 25 °C under 1 atm of 45% ^{13}C carbon monoxide in acetone solution. The same procedure but with 90% ^{13}C carbon monoxide was followed in the case of the sulfolane solutions.

The single crystals of the tetraethylammonium salt of $[Rh_{15}(CO)_{27}]^{3-}$ used for the determination of the unit cell dimensions were obtained by precipitation of a mixture of the cesium salts of $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{15}(CO)_{27}]^{3-}$ dissolved in acetone with a 2-propanol solution of tetraethylammonium chloride. In this way the tetraethylammonium salts of both clusters are precipitated. Single crystals were grown by slow-vapor diffusion methods using acetone–isopentane. Determination of the unit cell dimensions for the crystals of both clusters and their comparison with the data previously obtained[9] for $[Rh_{14}(CO)_{25}]^{4-}$ conclusively establish the presence of $[Rh_{15}(CO)_{27}]^{3-}$ and the assignment of its infrared pattern. Moreover, the ^{13}C NMR spectrum of the bis(triphenylphosphiniminium) salt of $[Rh_{15}(CO)_{27}]^{3-}$ is in agreement with the one previously assigned by Chini et al.[13] to this cluster.

Table II. Donor Numbers (DN),[a] Dielectric Constants ($\epsilon^{25\,°C}$),[b] and Constants of Formation[c] of the Cesium Complexes of the Solvents Used in Our Study

solvent	DN	ε	log K_f
tetraglyme		~3.5	1.45
18-crown-6		~4.8	4.60
acetone	17.0	20.7	
acetonitrile	14.1	36.2	
sulfolane	14.8	44.0	

[a] Donor numbers are taken from ref 18, p 19. [b] Dielectric constants (given at 25 °C, except for 18-crown-6 and sulfolane, which are both measured at 35 °C) are taken from ref 26, p 101. [c] Constants of formation of the complexes with Cs^+ are taken from ref 19, p 44, and ref 27.

Results and Discussion

The new preparative procedure for $[Rh_{15}(CO)_{27}]^{3-}$ illustrates (Chart I) the advantages of high-pressure techniques in the synthesis of high-nuclearity rhodium carbonyl clusters.[14]

The formal resemblance of an apical rhodium dicarbonyl moiety on the cluster with "$Rh(CO)_2^+$" was initially mentioned and illustrated by Chini et al.[7b,15] in the reaction of $[Rh_{15}(CO)_{27}]^{3-}$ with halides (eq 1). We have found that amines also participate in that reaction to an extent related to the basicity of the amine: *N*-methylmorpholine (pK_a(25 °C) ≃ 7.4); bis(*N*,*N*-dimethylethylenediamine (pK_a(25 °C) ≃ 6.0); 1,10-phenanthroline (pK_a(25 °C) ≃ 4.7). In the case of the two former amines, it has been possible to detect infrared absorptions at 2065 and 2010 cm^{-1} that could be assigned to $[(ligand)_2Rh(CO)_2]^+$ (eq 2) groups by comparison with the

$$[Rh_{15}(CO)_{27}]^{3-} + 2L \rightleftharpoons [Rh_{14}(CO)_{25}]^{4-} + [L_2Rh(CO)_2]^+ \qquad (2)$$

spectra of $Rh(CO)_2(acac)$, $[Rh(CO)_2Cl]_2$, $[Rh(CO)_2X_2]^-$ ($X = Cl^-, Br^-$), and similar species.[16] The same reaction is carried out by cesium hydroxide with the formation of a product characterized as $[Rh_{13}(CO)_{24}H_x]^{(5-x)}$ ($x = 1$)[17] by its infrared spectrum (1960, 1800 cm^{-1}) and solubility properties.

The reactivity of $[Rh_{15}(CO)_{27}]^{3-}$ is affected by the medium. This cluster is stable in low-polarity solvents such as tetraglyme and acetone (Table II), but it forms $[Rh_{14}(CO)_{25}]^{4-}$ in 18-

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(13) P. Chini, personal communication.

(14) Other straightforward syntheses developed by using high-pressure techniques and turning out high yields of clusters have been reported: $[Rh_9P(CO)_{21}]^{2-}$, J. L. Vidal, W. E. Walker, R. C. Schoening, and R. L. Pruett, *Inorg. Chem.*, **18**, 254 (1979); $[Rh_{10}P(CO)_{22}]^{3-}$, J. L. Vidal, W. E. Walker, and R. C. Schoening, *ibid.*, **20**, 238 (1981); $[Rh_{10}As(CO)_{22}]^{3-}$, J. L. Vidal, *ibid.*, **20**, 243 (1981); $[Rh_{12}Sb(CO)_{27}]^{3-}$, J. L. Vidal, L. A. Kapicak, and J. M. Troup, *J. Organomet. Chem.*, in press.

(15) P. Chini, G. Longoni, S. Martinengo, and V. G. Albano, paper presented at the 173rd National Meeting of American Chemical Society, Anaheim, California, 1978.

(16) The following infrared patterns (in cm^{-1}) have been observed for these complexes in solution: $Rh(CO)_2acac$, 2075, 2010; $[Rh(CO)_2Cl]_2$, 2085, 2032; $[Rh(CO)_2X_2]^-$, 2060, 1980. For $[Rh(CO)X_3]^-$ and $[Rh_2(CO)_2X_2]^{2-}$, 2070 and 2080 cm^{-1}, respectively, are reported by L. M. Vallarino, *Inorg. Chem.*, **4**, 161 (1965).

(17) This cluster has been previously characterized by P. Chini et al. in a personal communication.

(18) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions", Springer-Verlag, New York, 1968.

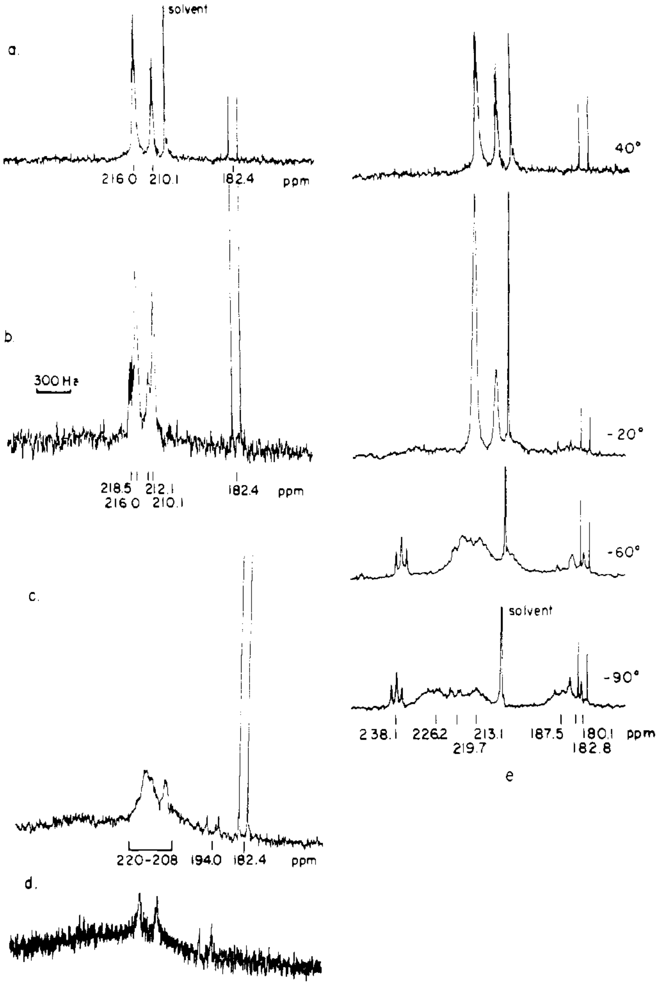

Figure 2. ^{13}C NMR spectra of the $[Cs(18\text{-crown-}6)_{\sim1.6}]^+$ salt of $[Rh_{15}(CO)_{27}]^{3-}$ at 40 °C (a) in perdeuterioacetone, (b) in sulfolane, and (c) after bubbling CO for 3 h into solution b. Spectrum d of $[Rh_{14}(CO)_{25}]^{4-}$ is included for comparison, and part e shows the variable-temperature study of the bis(triphenylphosphiniminium) salt in perdeuterioacetone.

crown-6 and in high-polarity solvents such as sulfolane (eq 2). For instance, the ^{13}C NMR spectrum of $[Rh_{15}(CO)_{27}]^{3-}$ in acetone (216.0, 210.1, and 182.4 ppm) is consistent with that previously observed by Chini et al.,[13] while the release of a "$Rh(CO)_2^+$" fragment in sulfolane is suggested by the relative increase of the resonance at 182.4 ppm (vide infra) and the appearance of additional resonances assignable to $[Rh_{14}(CO)_{25}]^{4-}$ at 218.5 and 212.1 ppm (Figure 2).

These results are explained by a decrease in ion pairing between the cation and $[Rh_{15}(CO)_{27}]^{3-}$ as a consequence of the polarity of the solvent instead of its relative donor ability for the nonchelating solvents (Table II) and the formation by 18-crown-6 of stronger complexes with the cation than those of tetraglyme.[19] In other words, decrease in ion pairing seems to be a sine qua non condition for the release of the coordinatively unsaturated "$Rh(CO)_2^+$" group and its subsequent coordination to the solvent in the absence of other stronger ligands (eq 2). The decrease in ion pairing was detected by the disappearance of the shoulders present in the infrared spectrum in acetone (Figure 1) upon addition of a ligand stronger than 18-crown-6 such as cryptand 322 as previously observed with other transition-metal complexes.[20]

Chart II. Reactions of $[Rh_{15}(CO)_{27}]^{3-}$ with Hydrogen (1 atm, 25 °C)

Acetone

$$[Rh_{15}(CO)_{27}]^{3-} \rightleftharpoons [Rh_{14}(CO)_{25}]^{4-} + \text{“}[Rh(CO)_2]^+\text{”}$$

$$[Rh_{15}(CO)_{27}]^{3-} \xrightleftharpoons[25\ h]{H_2} [Rh_{14}(CO)_{25}]^{4-} + \text{“}[Rh(CO)_2]^+\text{”}$$

$$[Rh_{15}(CO)_{27}]^{3-} \xrightleftharpoons{CsPhCO_2} [Rh_{14}(CO)_{25}]^{4-} + \text{“}Rh(CO)_2]^+\text{”}$$

$$[Rh_{15}(CO)_{27}]^{3-} + PhCO_2^- \xrightarrow[65\ h]{H_2} [Rh_{14}(CO)_{25}]^{4-} + \text{“}[Rh(CO)_2]^+\text{”} + HPhCO_2$$

Sulfolane

$$[Rh_{15}(CO)_{27}]^{3-} \rightarrow \text{no reaction}$$

$$[Rh_{15}(CO)_{27}]^{3-} \xrightarrow[25\ h]{H_2} \text{no reaction}$$

$$[Rh_{15}(CO)_{27}]^{3-} \xrightarrow{PhCO_2^-} \text{no reaction}$$

$$[Rh_{15}(CO)_{27}]^{3-} + PhCO_2^- \xrightarrow[65\ h]{H_2} [Rh_{14}(CO)_{25}]^{4-} + \text{solids} + HPhCO_2$$

quantitative

Chart III

$$[Rh_{15}(CO)_{27}]^{3-} + PhCO_2^- \rightleftharpoons [Rh_{14}(CO)_{25}]^{4-} + [PhCO_2Rh^{I}(CO)_2]$$

$$[PhCO_2Rh^{I}(CO)_2] + D_2 \rightarrow [PhCO_2Rh^{III}(CO)_2(D)_2]$$

$$[Ph(CO)_2Rh^{III}(CO)_2(D)_2 \rightarrow PhCO_2D + [DRh^{I}(CO)_2]$$

$$[DRh^{I}(CO)_2] \rightarrow \text{Rh(precipitates)} + \text{other products}$$

The influence of solvent polarity on the reactivity of $[Rh_{15}(CO)_{27}]^{3-}$ is also manifested in the reactions with carbon monoxide and hydrogen (Chart II). For instance, the thermal fragmentation of this cluster was incomplete even at 140 °C under inert atmosphere while the quantitative formation of $[Rh_{14}(CO)_{25}]^{4-}$ and uncharacterized black solids insoluble in organic solvents occurred when the reaction with hydrogen was conducted in the presence of cesium benzoate. The use of ^{13}C-labeled cesium benzoate and deuterium gas allowed the detection by ^2H and ^{13}C NMR of benzoic acid. The absence of $[Rh_{14}(CO)_{25}H]^{3-}$ from the products of the reaction and the small extent to which cesium benzoate alone is able to transform this cluster or $[Rh_{15}(CO)_{27}]^{3-}$ into $[Rh_{14}(CO)_{25}]^{4-}$ suggest that the interaction between the polynuclear complexes and the benzoate anion[22] may contribute as a minor pathway to the formation of benzoic acid in that reaction. Instead, we suggest that the predominant occurrence of the events below (Chart III) allow one to rationalize our observations. In contrast, the cluster was quantitatively transformed into $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ at 100–200 °C under 200–400 atm of an equimolar mixture of carbon monoxide and hy-

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(19) J. M. Lehn, *Struct. Bonding* (*Berlin*), **16**, 1 (1976).

(20) K. H. Pannell and D. Jackson, *J. Am. Chem. Soc.*, **98**, 4443 (1976); C. D. Pribula and T. L. Brown, *J. Organomet. Chem.*, **71**, 415 (1974); W. F. Edgell, J. Lyford, A. Barbetta, and C. I. Jose, *J. Am. Chem. Soc.*, **93**, 6403 (1971).

(21) B. T. Heaton, C. Brown, L. Longhetti, W. T. Povey, and D. O. Smith, *J. Organomet. Chem.*, **192**, 93 (1980), have reported the following ^{13}C NMR shifts (ppm): $Rh(CO)_2acac$, 183.7; $[Rh(CO)_2Cl]^2$, 180.4; $[Rh(CO)_2Cl_2]^-$, 182.4. Thus, the increase in the intensity of the resonance at 182.4 ppm in the spectra of $[Rh_{15}(CO)_{27}]^{3-}$ in sulfolane relative to acetone is ascribed to the enhanced fragmentation of this cluster (Figure 2, eq 2).

(22) We appreciate the suggestion by Professor G. Longoni, University of Milano, during his review of this manuscript concerning the probable formation of $HPhCO_2$ and $[Rh_{14}(CO)_{25}]^{4-}$ by the reaction of $[Rh_{14}(CO)_{25}H]^{3-}$ with $PhCO_2^-$. We have found that (i) $[Rh_{15}(CO)_{27}]^{3-}$ does not react to an appreciable extent with $CsPhCO_2$, (ii) that $[Rh_{14}(CO)_{25}H]^{3-}$ is only partially converted into $[Rh_{14}(CO)_{25}]^{4-}$ even in the presence of a saturated acetone solution of $CsPhCO_2$, and (iii) that $[Rh_{14}(CO)_{25}H]^{3-}$ was not detected in our NMR studies. These observations provided the basis for our proposal above (Chart III). The occurrence of eq 3 under the more complex conditions used for the high-pressure experiments is ascribed to other reactions possible under these conditions.

drogen. A more gradual fragmentation of $[Rh_{15}(CO)_{27}]^{3-}$ cluster occurred under milder conditions (11 atm of an equimolar mixture of carbon monoxide and hydrogen, 150 °C, *N*-methylmorpholine, Rh:N = ca 5.0, cesium salt, 18-crown-6) as suggested by the sequential changes of the infrared spectra at reaction conditions. The relatively low solubility of $[Rh_{14}(CO)_{25}]^{4-}$ in 18-crown-6, the suggested assignments of the infrared spectra, and the slow precipitation of a material with a Rh:Cs atomic ratio of 3.6 may indicate the formation and precipitation of $[Rh_{14}(CO)_{25}]^{4-}$ (eq 3). These changes

$$\underset{1995,\ 1840\ \mathrm{cm^{-1}}}{[Rh_{15}(CO)_{27}]^{3-}} \xrightarrow[CO]{H_2} \underset{1990,\ 1830\ \mathrm{cm^{-1}}}{[Rh_{14}(CO)_{25}H]^{3-}} \xrightarrow[-H^+]{} \underset{1960,\ 1810\ \mathrm{cm^{-1}}}{[Rh_{14}(CO)_{25}]^{4-}} \quad (3)$$

are attributed to the reaction of $[Rh_{15}(CO)_{27}]^{3-}$ with hydrogen and to the deprotonation by the amine of the resulting species by analogy with the Brønsted acid–base reactions of hydrido carbonyl clusters.[5,7] This proposal is also partially supported by the selective formation of $[Rh_{14}(CO)_{26}]^{2-}$ in the reaction of $[Rh_{15}(CO)_{27}]^{3-}$ with a protonic acid of a weakly electron-donating anion such as trifluoromethanesulfonic acid[23] (eq 4).

$$[Rh_{15}(CO)_{27}]^{3-} + H^+ \xrightarrow[CF_3SO_3H]{PPN^+\ \mathrm{salt}} [Rh_{14}(CO)_{26}]^{2-} \quad (4)$$

Our attempts to study the solution structure of the cluster by ^{13}C and ^{13}C–^{103}Rh NMR[24] were precluded by the complexity of the spectra and the fluxionality of some of these ligands even at −90 °C (Figure 2). The most mobile set of carbonyls (unresolved broad multiplets: 226.2, 213.1, and 187.5 ppm) gives rise to a coalescence band (216.3 ppm) at −20 °C. On the other hand, the rigid set of ligands (edge bridges, symmetric (238.1 ppm, triplet) and asymmetric (219.7, doublet of doublets); terminals (180.1 ppm, doublet and 182.6 ppm, doublet) gives another coalescence band, (210.3 ppm) at a lower temperature of −60 °C. The terminal carbonyls responsible for the doublet at 182.6 ppm do not participate in either scrambling process even at 100 °C. The presence of three independent sets of carbonyls at temperatures higher than −20 °C was confirmed by the observation of characteristic rhodium decoupling frequencies shown in parenthesis for the coalescence bands at 216.3 (3.159 765 and 3.163 425 MHz), 210.3 (3.161 327 and 3.159 470 MHz), and 182.6 ppm (3.162 084 MHz) during ^{13}C–^{103}Rh NMR studies. The detachment of a "$Rh(CO)_2{}^+$" moiety from $[Rh_{15}(CO)_{27}]^{3-}$ may be related to the inability of the terminal carbonyl ligands represented by the resonance at 182.6 ppm to scramble with the other carbonyls.

This work has resulted in the convenient preparation of $[Rh_{15}(CO)_{27}]^{3-}$, and it suggests the importance of ion pairing in determining the reactivity of this cluster. This observation may be technologically relevant because ion pairing has been proposed to affect the behavior of homogeneous catalyst systems based in polynuclear rhodium complexes[25] which convert carbon monoxide and hydrogen into chemicals.[12]

Acknowledgment. The permission for the publication of this work by the management of Union Carbide Corp. is appreciated. The efforts of Mr. R. W. Dykstra in getting the ^{13}C–^{103}Rh NMR spectra are also appreciated.

Registry No. $[Cs(C_{12}H_{24}O_6)_2][Cs_2(C_{12}H_{24}O_6)_3][Rh_{15}(CO)_{27}]$, 79482-76-1; $[(Ph_3P)_2N]_3[Rh_{15}(CO)_{27}]$, 75506-17-1; $Rh(CO)_2(acac)$, 14874-82-9; CO, 630-08-0; H_2, 1333-74-0.

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[23] J. L. Vidal and R. C. Schoening, *J. Organomet. Chem.*, in press.

[24] Professor Brian T. Heaton, University of Kent at Canterbury, England, informed us after this paper was written that he was also studying the solution structure of this cluster using similar techniques.

[25] L. Kaplan, U.S. Patents 3 944 588 (1976), 4 162 261 (1979), 4 224 237 (1980), and 4 197 253 (1980), German Patent 2643971 (1977), and Belgium Patent 867459 (1978).

[26] "The Synthesis and Characterization of Inorganic Compounds", William L. Jolly, Ed., Prentice-Hall, Englewood Cliffs, NJ, 1970, pp 100–102.

[27] G. Chaputt, G. Jeminet, and J. Julliard, *Can. J. Chem.*, **53**, 2240 (1975).

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A Study of the System $[Rh(C_2H_4)_2Cl]_2$–$P[N(CH_3)_2]_3$ and Evidence of *N,N,N',N'*-Tetramethylethylenediamine Formation via Intramolecular $N(CH_3)_2$ Transfer to η^2-C_2H_4. Reaction with CO_2 of the Rhodium Complexes

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Among the trivalent phosphorus derivatives with the phosphorus bonded to nitrogen, the ligand tris(dimethylamino)phosphine has received considerable attention[1–3] owing to some attractive properties, e.g., steric hindrance and peculiar ^1H NMR spectrum. Indeed, the former can influence the geometry of metal complexes, and the latter can result in a useful tool for the identification of different complexes in mixtures.[4]

As an extension of our studies on transition-metal–CO_2 complexes stabilized by phosphorus ligands[5–8] we have prepared complexes of Rh(I) with the ligand $P(NMe_2)_3$ and studied properties and the reaction with CO_2.

Experimental Section

Reactions were carried out in an atmosphere of purified N_2 or CO_2 by vacuum-line techniques. Solvents were dried as reported in the literature and stored under nitrogen. Infrared spectra were run with a Perkin-Elmer 557 spectrophotometer and ^1H NMR spectra with a Varian EM 360 A apparatus. Gas chromatographic analyses were performed with a Hewlett-Packard 5750 instrument, and molecular weights were determined cryoscopically in benzene as previously reported.[9] Reference *N,N,N',N'*-tetramethylhydrazine and *N,N,N',N'*-tetramethylethylenediamine were purchased from Aldrich. CO_2 (99.99% pure) was from Matheson. ^1H NMR resonances are given as δ from internal Me_4Si. Coupling constants are given in hertz.

Preparation of the Complexes. Preparation of $RhCl(C_2H_4)[P(NMe_2)_3]_2$. To a filtered solution of $[RhCl(C_2H_4)_2]_2$ (0.224 g, 0.576 mmol) in toluene (20 mL) was added $P(NMe_2)_3$ (0.364 g, 2.23 mmol) and the solution stirred for 1 h at room temperature under nitrogen and then cooled to 0 °C. Toluene was evaporated in vacuo to half of the original volume and pentane added (10 mL). When the mixture was allowed to stand, at −20 °C, orange crystals deposited, mixed with a finely powdered yellow compound. When the solvent, was

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(1) R. B. King, *Inorg. Chem.*, **2**, 936 (1963); R. B. King, and T. F. Kormowski, *ibid.*, **10**, 1188 (1971).

(2) P. Kalck and R. Poilblanc, *Inorg. Chem.*, **14**, 2779 (1975); J. J. Bonnet, Y. Jeannin, P. Kalck, A. Maisonnat, and R. Poilblanc, *ibid.*, **14**, 743 (1975) and reference therein.

(3) B. Denise and G. Pannetier, *J. Organomet. Chem.*, **161**, 171 (1978).

(4) F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Am. Chem. Soc.*, **92**, 1916 (1970).

(5) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassero, *J. Chem. Soc., Chem. Commun.*, 636 (1975).

(6) M. Aresta and C. F. Nobile, *J. Chem. Soc., Dalton Trans.*, 708 (1977).

(7) M. Aresta and C. F. Nobile, *Inorg. Chim. Acta*, **24**, L49 (1977).

(8) P. Albano, M. Aresta, and M. Manassero, *Inorg. Chem.*, **19**, 1069 (1980).

(9) M. Aresta, C. F. Nobile, and A. Sacco, *Inorg. Chim. Acta*, **12**, 167 (1975).

(10) P. S. Brookes and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1079 (1967).