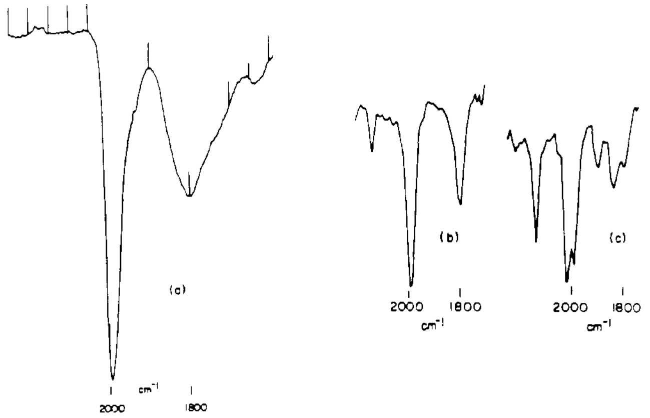

Figure 7. Infrared spectra of $[Rh_{10}As(CO)_{22}]^{3-}$ in solutions of sulfolane (tetrahydrothiophene 1,1-dioxide): (a) at ambient conditions; (b) under 537 atm of CO–H_2 at 150 °C; (c) under 862 atm of CO–H_2 at 150 °C.

oxide–hydrogen mixtures has attracted our attention for some time[28–30] in an attempt to understand their role in the homogeneous catalytic conversion of CO–H_2 into oxygenated organic products.[31–35] These studies have relied mainly on the use of infrared spectroscopy when conducted under high pressure.[4] They show that $[Rh_{10}As(CO)_{22}]^{3-}$ is stable under 537 atm of CO–H_2 (1:1 ratio) up to 150 °C as indicated by comparison of the infrared pattern of the anion under ambient and at the former conditions (Figure 7). An increase in the pressure to 862 atm results in spectral changes (Figure 7) that are indicative of the presence of other carbonyl-containing species together with the initial anion. The absorption at 1895 cm^{-1} (±5 cm^{-1}) probably belongs to $[Rh(CO)_4]^-$,[4] while the remaining new bands at 2010 and 1830 cm^{-1} resemble those previously assigned to $[Rh_9P(CO)_{21}]^{2-}$.[3] The existence of an arsenic-containing analogue of the latter cluster is plausible and the following reaction can be proposed on the basis of a similar reaction for $[Rh_{10}P(CO)_{22}]^{3-}$.[19]

$$\underset{1990,\ 1815\ \text{cm}^{-1}}{[Rh_{10}As(CO)_{22}]^{3-}} + 3CO \rightleftharpoons \underset{2010,\ 1835\ \text{cm}^{-1}}{[Rh_9As(CO)_{21}]^{2-}} + \underset{1895\ \text{cm}^{-1}}{[Rh(CO)_4]^-}$$

We have been able to isolate and characterize $[Rh_9As(CO)_{21}]^{2-}$, confirming the tentative assignment of the infrared pattern above.[36]

Acknowledgment. The publication approval of this work by Union Carbide Corp. is appreciated. The continuous encouragement received from Dr. G. L. O'Connor is also recognized. The NMR spectra were obtained by Dr. R. C. Schoening and the high-pressure infrared spectra by Dr. W. E. Walker, both of Union Carbide Corp. at this location.

Registry No. $[PhCH_2N(C_2H_5)_3]_3[Rh_{10}As(CO)_{22}]\cdot C_4H_8O$, 75802-04-9; $[C_6H_5CH_2N(C_2H_5)_3]_2[Rh_9As(CO)_{21}]$, 75802-02-7; $[Rh(CO)_4]^-$, 44797-04-8; $Rh(CO)_2acac$, 14874-82-9; Ph_3As, 603-32-7.

Supplementary Material Available: Complete listings of structural factors, thermal and positional parameters, and interatomic distances and angles (60 pages). Ordering information is given on any current masthead page.

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Contribution from Union Carbide Corporation,
South Charleston, West Virginia 25303

Rhodium Carbonyl Cluster Chemistry under High Pressure of Carbon Monoxide and Hydrogen. 3. Synthesis, Characterization, and Reactivity of $HRh(CO)_4$

JOSÉ L. VIDAL* and W. E. WALKER†

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The fragmentation of $Rh_4(CO)_{12}$ in dodecane solutions under 1241–1379 atm of carbon monoxide at 5–12 °C has been established by high-pressure infrared spectroscopy to give $Rh_2(CO)_8$. Noticeable spectral changes are caused by the introduction of small amounts of hydrogen (1542 atm, CO:H_2 = 4.5:1). Fourier subtraction of the spectra of these two species left bands at 2070 (m), 2039 (vs), and 2008 (w) cm^{-1}. By analogy to the spectra previously observed for $HIr(CO)_4$ and $HCo(CO)_4$ this pattern is assigned to $HRh(CO)_4$, a species that has eluded previous attempts of detection. The reaction of $[M(CO)_4]^-$ (M = Co, Rh, Ir) with protonic acids in tetraglyme–toluene under high pressure of carbon monoxide resulted in the formation of $HM(CO)_4$ (M = Co, Rh, Ir), with the reaction having been readily detected in the case of iridium with phosphoric acid (Ir:P = 0.38:4.12), while a stronger acid such as sulfuric acid was required for cobalt (Co:S = 0.95:29.9) and rhodium (Rh:S = 0.90:29.4) for the detection of a similar reaction. These results suggest that the proton affinity of these ions varies as $[Ir(CO)_4]^- > [Co(CO)_4]^- > [Rh(CO)_4]^-$. The differences in the acid strength of the corresponding conjugate acids, $HM(CO)_4$ (M = Co, Rh, Ir), was determined under high pressures of CO–H_2 by reaction with amines of different basicities such as *N*-methylmorpholine (p*K*(water, 25 °C) = 7.4) and *N*,*N*-dimethylaniline (p*K*(water, 25 °C) = 4.8) after formation of the tetracarbonylmetal hydrides, "in situ." $HIr(CO)_4$ is not deprotonated in a detectable fashion by *N*-methylmorpholine (Ir:N = 1:10), while $HCo(CO)_4$ is deprotonated by this amine (Co:N = 2.4:1.0) but not by *N*,*N*-dimethylaniline (Co:N = 2.4:3.0). By contrast $HRh(CO)_4$ readily undergoes deprotonation with this amine (Rh:N, = 2.7:1.0). These results correspond to the following trend in Brønsted acidity: $HRh(CO)_4 > HCo(CO)_4 > HIr(CO)_4$.

Introduction

Homogeneous catalysis with transition metals is a rapidly expanding area[1] and several operating industrial processes are now based on these types of catalysts.[2] The elements of the cobalt triad–Co, Rh, and Ir—have probably been the most

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† Deceased.

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studied in this respect, with a broad scope of reactions reported to be catalyzed by complexes of these elements.[1-6] Reactions in which these kind of catalysts have been especially useful are those involving carbon monoxide. For instance, the hydroformylation of olefins with cobalt and rhodium has resulted in an attractive route to aldehydes.[7] Moreover, the formation of ethylene glycol from CO–H_2 occurs in the presence of rhodium carbonyl complex catalysts;[8] $HM(CO)_4$ (M = Co, Rh) has been either mentioned or proposed as the active species in some of these cases.[9-12]

The formation of $HCo(CO)_4$ in the reaction of $Co_2(CO)_8$ with hydrogen occurs under relatively mild conditions,[13] e.g., 100 atm of CO–H_2 at 50 °C,[14] while more drastic conditions were used for the formation of $HIr(CO)_4$ in the reaction of $Ir_4(CO)_{12}$ with CO–H_2, e.g., 315–430 atm of CO–H_2 and 22–200 °C.[14] The intermediacy of $Ir_2(CO)_8$ could not be detected in the latter case, although such species could be expected to be a suitable intermediate (eq 1) as suggested by its formation under more favorable conditions[15] and by analogy with the previous reaction of dicobalt octacarbonyl.

$$M_4(CO)_{12} \overset{CO}{\rightleftarrows} M_2(CO)_8 \overset{H_2}{\rightleftarrows} HM(CO)_4 \qquad (1)$$

Similar behavior was considered to be also possible in the case of rhodium. In fact, $Rh_4(CO)_{12}$ has been previously found to react in solid carbon monoxide matrices, giving $Rh_2(CO)_8$.[15] Moreover, the initial report by Whyman[16] indicates that $Rh_4(CO)_{12}$ shows similar reactivity in hydrocarbon solutions, but it was not possible, then, to get evidence for the formation of $HRh(CO)_4$.

High-pressure infrared spectroscopic studies have been conducted with some of these systems. Spectral evidence for the presence of $HCo(CO)_4$ under high pressure of CO–H_2 has been reported in several instances.[16-19] By contrast, although the existence of $HRh(CO)_4$ was initially proposed in 1943,[20a] others have been unable to confirm it.[20b] The infrared spectral pattern of such species is expected to be similar to those previously reported for the cobalt and iridium analogues. Whyman[14,16] has also tried to obtain spectroscopic evidence for such species under 430 atm of CO–H_2 but the complexity of the infrared pattern precluded in his case the detection of the hydridotetracarbonylrhodium complex, in contrast to his straightforward results for $HCo(CO)_4$ and $HIr(CO)_4$. King et al.[21] have recently suggested that an infrared absorption at 2019 cm^{-1} detected under high pressure during the catalytic carbonylation of ethylene could result from the presence of $HRh(CO)_4$.

Our laboratory has been interested for some time in the homogeneous catalysis of carbon monoxide reactions carried out by rhodium complexes.[7,8,22-25] It was of general interest to establish the infrared spectrum of $HRh(CO)_4$, specifically under high pressures of CO–H_2. An additional incentive was provided by the recently reported ability of $HCo(CO)_4$ to hydrogenate carbon monoxide to methanol[26] and the qualitative parallel between the behavior of cobalt and rhodium homogeneous catalysts in some reactions.[26,27]

We have reexamined the behavior of $Rh_4(CO)_{12}$ in dodecane solution under CO–H_2 using Fourier-transform infrared techniques. Previous results obtained under similar conditions had shown the usefulness of this technique for the spectroscopic study of mixtures and comparison with the spectra of the species more likely present in the specific cases.[28,29] We report for the first time the infrared spectrum of $HRh(CO)_4$ and compare it with those of $HCo(CO)_4$ and $HIr(CO)_4$ reported previously. In addition, we present evidence related to the differences in Brønsted acid–base properties of $[Co(CO)_4]^-$, $[Rh(CO)_4]^-$, and $[Ir(CO)_4]^-$, as well as some observations related to the interconversions of $Rh_4(CO)_{12}$, $Rh_2(CO)_8$, and $HRh(CO)_4$ under CO–H_2. It was of interest to determine the variation of the basicity of the tetracarbonylmetalate monoanions in the cobalt triad because of the potential role that the acidity of their conjugate acids, $HM(CO)_4$, could play in some catalytic reactions in which these species are or could be involved.[3] Although a monotonical increase in basicity is observed for main-group hydrogen compounds upon going down in the periodic system, a different behavior has been reported with some series of complexes for the elements of the iron group.[30,31] Comparative studies of the acidities of metal carbonyl mononuclear and polynuclear hydrido carbonyl complexes for the iron triad (Fe, Ru, Os) have been recently reported.[32]

Experimental Section

The solvents were purified by conventional means and distilled before use; they were stored under argon and transferred via syringe. $Rh(CO)_2acac$ was obtained from Johnson Matthey Ltd., $Ir(CO)_2acac$ and $Co_2(CO)_8$ were from Strem Chemical Co., and potassium hydroxide was from Merck. All were used as available, except for $Co_2(CO)_8$, which was purified by sublimation.

A description of the high-pressure equipment including the high-

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pressure infrared cell and spectrometer, together with the usual operation procedure, has already appeared.[28] Elemental analyses were conducted by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Synthesis of Benzyltriphenylphosphonium Salts of $[Co(CO)_4]^-$, $[Rh(CO)_4]^-$, and $[Ir(CO)_4]^-$.[33] **(a) $[Co(CO)_4]^-$.** Sodium amalgam (50.00 g, 2% sodium) was placed in an argon-purged 300-mL round-bottom flask equipped with a magnetic stirrer. Dry tetrahydrofuran, 100 mL, was then added followed by $Co_2(CO)_8$ (3.42 g), and the system was stirred for 1.5 h. The mixture was filtered through a fritted-disk funnel packed with a high-porosity filtering aid. The filtrate was added to an aqueous solution of benzyltriphenylphosphonium chloride (6.0 g, in 100 mL of water). The precipitate quickly settled to the bottom. The solid was separated by decantation and washed with water until no traces of chloride were detected, followed by several washes (10 × 10 mL) with 2-propanol. The final product was vacuum dried, for a yield of 4.89 g or 31.3%. Anal. Calcd for $C_{29}H_{22}O_4PCo$: C, 66.40; H, 4.24; O, 12.21; P, 5.91; Co, 11.24. Found: C, 65.77, 65.73; H, 4.30, 4.19; P, 5.54, 5.18; Co, 11.80, 11.57.

(b) $[Ir(CO)_4]^-$. Hexamethylphosphoramide, 100 mL, was added to 250-mL Schlenk tube. $Ir(CO)_2(acac)$ (0.8020 g, 2.34 mmol) was added to the degassed solvent, and the mixture was stirred under carbon monoxide until all of the solid had dissolved. Dry and finely ground KOH (8.017 g, 0.143 mol) was then added, and stirring was continued for 10 h. The final mixture was allowed to settle, and the upper liquid was transferred via syringe into an argon-purged 500-mL Schlenk tube, which contained an aqueous solution of benzyltriphenylphosphonium chloride (12.00 g in 180 mL of water) cooled to ~5 °C. The addition resulted in a precipitate from which the supernatant liquid was decanted, and the precipitate was washed several times with water (10 × 10 mL), 2-propanol (10 × 10 mL), and hexane (10 × 10 mL). The product was then dissolved in 50 mL of acetone, precipitated by addition of 100 mL of hexane, and vacuum dried; yield 0.81 g or 52.7%. Anal. Calcd for $C_{29}H_{22}O_4PIr$: C, 52.95; H, 3.38; O, 9.74; P, 4.72; Ir, 29.21. Found: C, 53.12, 53.35; H, 4.39, 4.31; P, 4.30, 4.40; Ir, 29.60.

(c) $[Rh(CO)_4]^-$. The experimental procedure was similar to that described for $[Ir(CO)_4]^-$. The following amounts of reagents have been used: $Rh(CO)_2(acac)$, 3.006 g, 11.8 mmol; KOH, 6.00 g, 0.107 mol; dimethyl sulfoxide as solvent, 90 mL. The final product, 4.00 g, corresponds to a yield of 59.7%. Anal. Calcd: C, 61.26; H, 3.90; P, 5.46; Rh, 18.11. Found: C, 61.46, 61.73; H, 4.09, 4.23; P, 5.40, 5.46; Rh, 18.00, 17.80. The infrared spectra of the three salts in sulfolane or acetonitrile solutions consist of a single strong band centered at 1890 cm^{-1} (±2) cm^{-1}). By contrast, different frequencies are observed for this band in less polar solvents, e.g., tetraglyme or tetraglyme-toluene mixtures: $[Co(CO)_4]$, 1890 cm^{-1}; $[Rh(CO)_4]^-$, 1900 cm^{-1}; and $[Ir(CO)_4]^-$, 1895 cm^{-1}.

High-Pressure Experiments. The procedures followed for handling the solutions and collecting the spectra are those already described.[28,29] A general description including some relevant specific details is given below for the different types of experiments.

The solutions of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ in dodecane or tetraglyme–toluene were charged via syringe under reduced pressure to a reactor previously purged with carbon monoxide, while $Ir_4(CO)_{12}$ was always added as a slurry to an open reactor, which was then closed and purged several times with carbon monoxide. The temperature of the systems was maintained at 25 °C, and the pressure was adjusted to the desired values by compressing CO–H_2 gas from a mixing autoclave. At this point, the temperature was increased to reaction conditions and a variable period was allowed for thermal equilibration. The spectra were recorded as previously described.[28]

Acidifications of solutions of $[PhCH_2PPh_3][M(CO)_4]$ (M = Co, Rh, and Ir) have been carried out by a similar procedure. For these cases, the solutions of the salts in tetraglyme–toluene (80 plus 40 mL) were added to the evacuated reactor. Reaction conditions were approached as above. The solutions of mineral acids in 5 mL of tetraglyme were contained in a 10-mL-capacity high-pressure tube attached to the autoclave, and they were injected into the reaction system by pressurization of this vessel with CO–H_2. The concentration of acid inside the reactor was determined by measurement of the amount of solution left behind in the injection tube. For the reactions of $HM(CO)_4$ with amines a similar experimental procedure was followed.

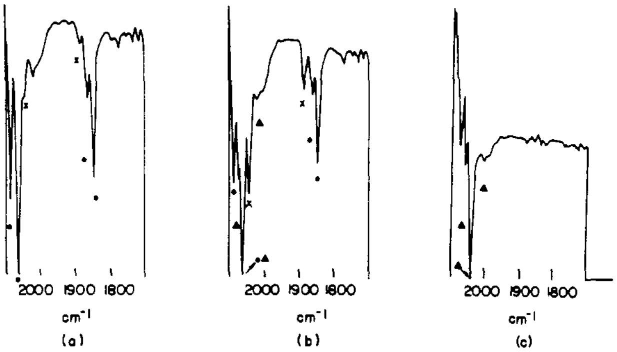

Figure 1. Infrared spectra of a solution of $Rh_4(CO)_{12}$ in dodecane at 5 °C: (a) spectrum under 1379 atm of CO; (b) spectrum under 1542 atm of CO and H_2 with a CO:H_2 ratio of 4.5:1; (c) Fourier subtraction of spectrum a from spectrum b; ×, infrared bands of $Rh_4(CO)_{12}$; ●, infrared bands of $Rh_2(CO)_8$; ▲, infrared bands of $HRh(CO)_4$. The difference in pressure between these two spectra is responsible for the evidently less than perfect subtraction above 2080 cm^{-1}.

(a) Reactions of Neutral Metal Carbonyls. $Co_2(CO)_8$ (1.17 mmol), $Rh_4(CO)_{12}$ (0.94 mmol), and $Ir_4(CO)_{12}$ (0.37 mmol) were dissolved in 125 mL of dodecane during the studies of their reactivities with carbon monoxide or carbon monoxide–hydrogen mixtures.

(b) Generation of $HM(CO)_4$ from $[PhCH_2Ph_3](M(CO)_4]$. For the case of cobalt a solution containing 0.95 mmol in 125 mL of tetraglyme–toluene (6:1, or 107 mL of the former solvent and 18 mL of the latter) was mixed alternatively with 6.44 or 29.9 mmol of anhydrous phosphoric acid at 50 °C and 10 000 psi of carbon monoxide. Another aliquot of the salt solution was treated with sulfuric acid, 29.6 mmol, under the same conditions.

The protonation of $[Rh(CO)_4]^-$ was tested by reacting a solution of the anion, 0.90 mmol, in 125 mL of tetraglyme–toluene (6:1) with 29.4 mmol of concentrated sulfuric acid in 4 mL of the same solvent at 100 °C and 10 000 psi of carbon monoxide. In the case of iridium, similar reactivity was studied by using a solution containing 0.38 mmol of $[Ir(CO)_4]^-$ in 125 mL of tetraglyme–toluene (6:1) and reacting it with 4.12 mmol of anhydrous phosphoric acid dissolved in 3 mL of the same solvent.

(c) Reactions of $HM(CO)_4$ with Amines. The studies were carried out with a solution of 125 mL of tetraglyme–toluene (6:1) containing 1.17 mmol of $Co_2(CO)_8$ to which *N*-methylmorpholine and *N*,*N*-dimethylaniline (1.00 mmol in each case) were added by injection into the reactor in neat form while 0.25 mmol of $Ir_4(CO)_{12}$ was used as a slurry in this solvent and 10.0 mmol of *N*-methylmorpholine was used in this case.

The dodecane studies were carried out by employing standard solutions of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ prepared by dissolving 1.20 and 0.91 mmol, respectively, in 125 mL of the solvent or slurries in the case of $Ir_4(CO)_{12}$. The use of standardized solutions allow for quantitative comparison of the spectra. The amounts of amine used in these cases were injected into the reactor in a neat form. We used *N*-methylmorpholine and *N*,*N*-dimethylaniline (1.00 mmol each) in the case of cobalt, 10.0 mmol of *N*-methylmorpholine in the runs with iridium, and 1.00 mmol of *N*,*N*-dimethylaniline or methylamine for the rhodium studies.

Results and Discussion

The reaction of $Rh_4(CO)_{12}$ with carbon monoxide results in the formation of $Rh_2(CO)_8$, together with small remaining amounts of the starting cluster even under 1379 atm of carbon monoxide at 12 °C (Figure 1). The infrared pattern is consistent with those previously reported for the bridging form of $Rh_2(CO)_8$.[15-19,34] The variation of the relative amounts of $Rh_4(CO)_{12}$ and $Rh_2(CO)_8$ with temperature and pressure of carbon monoxide as observed by us upon gradual variation

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(33) These syntheses are based on initial work by Z. C. Mester. Modifications of the initial procedures involving choice of cation, preciptitating cosolvents, and purification steps were introduced by J. L. Vidal to obtain analytically pure salts as required for this and other applications.

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Table I. Comparison of the Infrared Spectra for $HM(CO)_4$

compd	abs, cm^{-1} ^{a} (intens)			ref
$HCo(CO)_4$	1992 (w)	2030 (s)	2075 (m)	this work^c
	1996 (vw)	2029 (s)	2052 (m)	17^b
$HRh(CO)_4$	2008 (vw)	2039 (s)	2070 (m)	this work^c
$HIr(CO)_4$	1995 (w)	2030 (s)	2070 (m)	this work^c
	1999 (w)	2031 (s)	2054 (m)	17^b

^{a} ±1 cm^{-1}. ^{b} Heptane has been used as a solvent. ^{c} Dodecane is the solvent in this case.

of the pressure of carbon monoxide and temperature (1241 atm, 12 °C; 1379 atm, 12 °C; 1379 atm, 5 °C) is consistent with the presence of the expected equilibrium between the species as defined by eq 1.[35] These and previous observations[15,21] suggest that a nearly complete fragmentation of $Rh_4(CO)_{12}$ should be expected in the range of 0 to −15 °C under our conditions. The persistence of the initial cluster skeleton even under conditions as favorable toward formation of species of lower nuclearity as those employed here is, in part, a probable consequence of the relative energies of the rhodium–rhodium and rhodium–carbon monoxide bonds,[28,29] although the effect of the changes in entropy are also adverse for the fragmentation reaction.

The introduction of hydrogen into these systems was carried out after the initial cluster was converted to $Rh_2(CO)_8$ as above. Addition of small amounts of hydrogen (total pressure 1524 atm, $CO:H_2$ = 4.5:1) resulted in noticeable changes, particularly an increase of the absorptions at 2040 cm^{-1} and the appearance of a weak band at 2010 cm^{-1} (Figure 1b). It is possible to conclude from this spectrum and its comparison with those of $Rh_4(CO)_{12}$ (2076, 2072, 2045, and 1885 cm^{-1}) and $Rh_2(CO)_8$ (2087, 2062, 1852, 1832 cm^{-1}) that there is a decrease in the concentration of the latter species, a parallel increase in the amount of the former cluster, and the generation of a new species. This spectrum did not change in the next 12 h, denoting that chemical equilibria between the species present have been established.[35] Larger amounts of hydrogen (1524 atm, $CO:H_2$ = 2:1) resulted in an increase of the bands assigned to $Rh_4(CO)_{12}$. The dominant tendency is, thus, for $Rh_2(CO)_8$ to recluster back to $Rh_4(CO)_{12}$ in decreasing the carbon monoxide partial pressure. Other species in solution were elucidated by means of Fourier subtraction of the spectral features corresponding to $Rh_4(CO)_{12}$ and $Rh_2(CO)_8$ obtained under pure carbon monoxide from the spectra obtained in the presence of hydrogen (Figure 1c). This left a pattern resembling those previously reported for $HCo(CO)_4$ and $HIr(CO)_4$.[14,16] Similar results have been obtained from $Rh_4(CO)_{12}$ as the predominant species before the addition of hydrogen.

The spectral features left after the Fourier subtractions above (Figure 1c) are assigned to $HRh(CO)_4$ by analogy with the spectra reported for similar complexes of cobalt and iridium.[14,16] This assignment has been checked by direct comparison with the spectra of $HCo(CO)_4$ and $HIr(CO)_4$ obtained by us. It is evident that the spectra are very similar in the three cases; the maxima occur at slightly higher frequencies in the case of rhodium (Table I). A similar trend in the relative frequencies of the carbonyl absorptions with respect to the position of the elements in the periodic system has been noted in group 7B for the $HM(CO)_5$ species (M = Mn, Tc, Re).[36] The overlapping of these bands in the case of $HRh(CO)_4$ with the terminal bands of $Rh_4(CO)_{12}$ could have indeed precluded their detection in previous attempts, as already suggested by Whyman.[16] We have also observed that the conditions required in our case for the generation of $HCo(CO)_4$ (100 °C and 670 atm of 1:1 $CO–H_2$) and of $HIr(CO)_4$ (200 °C and 670 atm of 1:1 $CO–H_2$) from $Co_2(CO)_8$ and $Ir_4(CO)_{12}$, respectively, are relatively more severe than those reported by Whyman.[14,16] This could very well be a consequence of the differences in the solubility of carbon monoxide in the different solvents, e.g., heptane[17] and dodecane as suggested by the weaker intensity of the absorption of free carbon monoxide at 2130 cm^{-1} in the latter solvent under otherwise identical conditions.

These results show the differences in the behavior of $M_4(CO)_{12}$, $M_2(CO)_8$, and $HM(CO)_4$ species for these three elements. A more difficult fragmentation of the tetranuclear species into the binuclear carbonyl complex occurs upon going down the triad (Co ≪ Rh < Ir). As a result of this, the tendency of the binuclear species to reclustering parallels this trend in reverse, with evidence for it lacking under these conditions for cobalt. A different stability order is observed with the hydride complexes, $HCo(CO)_4 \gtrsim HIr_4(CO)_4 > HRh(CO)_4$. For the latter complex we have determined that a relative minor increase in the partial pressure of carbon monoxide (from 1262 to 1320 atm) results in a drastic decrease in the amount of hydride present. We ascribe this effect to the inhibition by carbon monoxide of the reaction between hydrogen and binuclear rhodium species. This is consistent with an increase in the fragmentation of $Rh_4(CO)_{12}$ under higher pressures of carbon monoxide (vide supra) to form $Rh_2(CO)_8$. The equilibria between $HRh(CO)_4$ and $Rh_2(CO)_8$ plus H_2 (eq 1) could account for the interconversion between the hydride and binuclear rhodium species that we have observed as results of changes in temperature and hydrogen partial pressure.[35] Similar proposals have recently been made by King et al.,[37] and analogies for these possibilities are found in the behavior of cobalt.[13]

Protonation of $[M(CO)_4]^-$. Another pathway for the formation of $HM(CO)_4$ is the protonation of the anions with mineral acids, as is well-known with $[Co(CO)_4]^-$ [38] (eq 2). The

$$[M(CO)_4]^- + H^+ \rightarrow HM(CO)_4 \qquad (2)$$

protonation of $[M(CO)_4]^-$ (M = Rh, Ir) was first described by Hieber and Lagally[20,39] as yielding $HM(CO)_4$. Other workers[20] were not able to confirm this earlier report even under the most favorable conditions and concluded that clusters were formed upon acidulation, with this behavior being especially evident in the case of rhodium.

We expected that formation of detectable amounts of hydridotetracarbonylmetal complexes could be feasible, particularly for rhodium, by placing the anion under high pressure of carbon monoxide at relatively low temperatures and then bringing the acid into contact with it. This was based on the thermodynamic preference for a metal–carbon monoxide bond over a metal–metal bond and the fact that $[M(CO)_4]^-$ is the most saturated species with respect to the coordination of carbon monoxide per metal atom (M = Co, Rh, Ir). By operating in this way, we have been able to detect the facile formation of $HIr(CO)_4$ from $[Ir(CO)_4]^-$ by acidification with anhydrous phosphoric acid. Quite unexpectedly, it was found that $[Co(CO)_4]^-$ was not to be protonated under similar

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(35) A report concerning the study of the equilibrium $Rh_4(CO)_{12} + Rh_4(CO)_{12} \rightleftarrows 2Rh_2(CO)_8$ under different conditions of pressure, temperature, and solvents, as well as results concerning the determination of the bond energies of M–H, M–CO, and M–M for M = Rh and Ir, is in progress (J. L. Vidal and W. E. Walker).

(36) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).

(37) R. B. King, C. C. Frazier, R. M. Hanes, and A. D. King, Jr., *J. Am. Chem. Soc.*, **100**, 2925 (1978); R. B. King, *Ann. N.Y. Acad. Sci.*, in press.

(38) H. W. Sternberg, I. Wender, and M. Orchin, *Inorg. Synth.*, **5**, 192 (1957).

(39) W. Hieber and H. Lagally, *Z. Anorg. Chem.*, **245**, 321 (1940).

(40) P. Chini, G. Longoni, and V. Albano, *Adv. Organomet. Chem.*, **14**, 251 (1976); P. Chini and B. Heaton, *Top. Current Chem.*, **71**, 1 (1977).

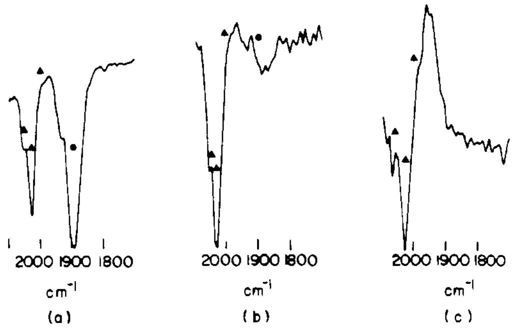

Figure 2. Infrared spectra obtained at 50 °C and 690 atm of carbon monoxide and hydrogen (1:1) for the reaction of (a) 2.34 mmol of $HCo(CO)_4$ with 1.0 mmol of *N*-methylmorpholine, (b) 2.34 mmol of $HCo(CO)_4$ with 1.0 mmol of *N,N*-dimethylaniline, and (c) 1.00 mmol of $HIr(CO)_4$ with 10.0 mmol of *N*-methylmorpholine. These reactions have been conducted in tetraglyme–toluene as solvent: ▲, $HM(CO)_4$; ●, $[M(CO)_4]^-$.

conditions or even in presence of a larger excess of acid. By contrast, formation of $HCo(CO)_4$ was readily achieved upon addition of sulfuric acid under otherwise the same conditions. In agreement with our previous expectations, we found that the protonation of $[Rh(CO)_4]^-$ to $HRh(CO)_4$ proceeds without formation of detectable amounts of clusters upon acidification with sulfuric acid. The infrared spectra of $HM(CO)_4$ species obtained in this way are in good agreement with those observed when these complexes are prepared by reaction of the respective neutral carbonyl complexes with $CO–H_2$.

Reaction of $HM(CO)_4$ with Bases. The results obtained during the protonation studies of $[M(CO)_4]^-$ species indicated a broad difference in the basic characteristic of the anions, as inferred from the ability of $[Ir(CO)_4]^-$ to abstract a proton from phosphoric acid and the seeming inability of $[Co(CO)_4]^-$ to carry out a similar reaction.

We attempted to determined p*K*s for $[M(CO)_4]^-$ (M = Co, Rh, Ir) by reacting their preformed hydride carbonyl complexes (prepared by hydrogenation of the respective neutral carbonyls under $CO–H_2$) with amines at less than equimolar concentrations. The detection of the characteristic infrared absorption for $[M(CO)_4]^-$ anions at 1890 cm^{-1}, generated as described in eq 3, could provide a measure of the equilibrium below. The determination of Beer's law for these systems was carried out as a preliminary step to the studies.

$$HM(CO)_4 + R_3N \rightarrow [M(CO)_4]^- + [R_3NH]^+ \quad (3)$$

The ability of the respective hydrides to protonate amines has been measured by determining the amount of $[M(CO)_4]^-$ generated in each case following the Beer's law results. It has been found that $HCo(CO)_4$ quantitatively transfers the proton to *N*-methylmorpholine (pK_a in water 7.4) as indicated by the formation of 1.0 mmol of $[Co(CO)_4]^-$ upon addition of a similar amount of the amine (Figure 2). The reaction with the same amount of a less basic amine as *N,N*-dimethylaniline (pK_a in water 4.8) results in the generation of only 0.15 mmol of $[Co(CO)_4]^-$. An acid–base equilibrium constant of 1.208×10^{-2} could be then estimated in this case. The larger basicity of $[Ir(CO)_4]^-$ is probably responsible for the inability of its conjugate acid, $HIr(CO)_4$, to protonate *N*-methylmorpholine (Figure 2) even when present in large excess, under otherwise similar conditions as those employed with cobalt. Similar comparative studies with $HRh(CO)_4$ were precluded by the lack of selectivity in the less than quantitative conversion of $Rh_4(CO)_{12}$ into that species (vide supra). No carbonylation of either amine was observed in these reactions. This is consistent with the decrease in the reactivity of $R_{3-x}NH_x$ species toward carbonylation upon increasing the degree of substitution and the fact that most of these reactions occur at 150–270 °C under high pressures of carbon monoxide.[41]

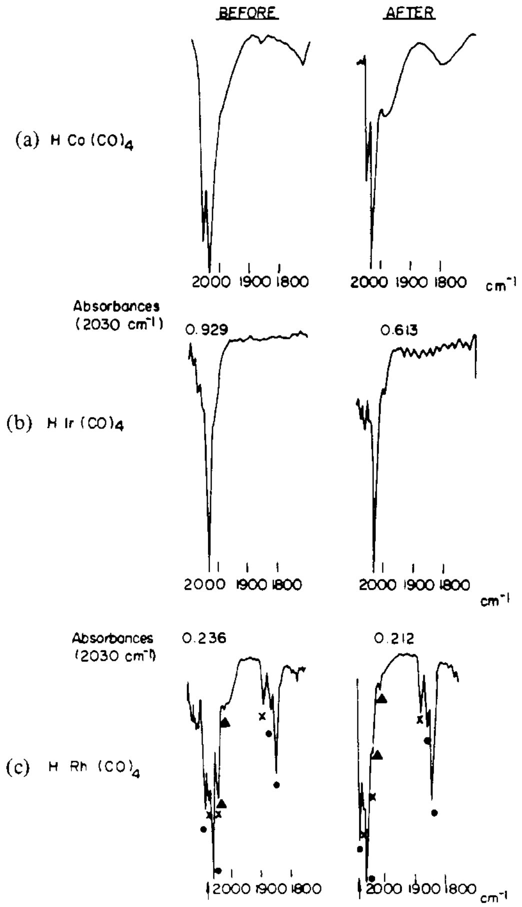

Figure 3. Infrared spectra with the absorbance of the respective bands indicated in dodecane solutions: (a) $HCo(CO)_4$, 2.4 mmol, before and after addition of *N*-methylmorpholine, 1.0 mmol, under 690 atm of 1:1 $CO–H_2$ at 100 °C; (b) $HIr(CO)_4$, 1.5 mmol, before and after addition of *N*-methylmorpholine, 10.0 mmol, under 690 atm of 1:1 $CO–H_2$ at 100 °C; (c) a mixture of $Rh_4(CO)_{12}$, $Rh_2(CO)_8$, and $HRh(CO)_4$ (total rhodium 2.73 mmol) before and after addition of *N,N*-dimethylaniline (1.0 mmol) under 1542 atm of 4.5:1 $CO–H_2$ at 5 °C. In (a) and (b) the absorbances of the "before" spectra are corrected for the amount of solvent injected with the amine. Assignments suggested for the infrared bands: $HRh(CO)_4$, ▲; $Rh_2(CO)_8$, ●; $Rh_4(CO)_{12}$, ×.

The direct comparison of the acid–base chemistry of $HM(CO)_4$ was precluded in the previous attempts of the incomplete fragmentation of $Rh_4(CO)_{12}$. Undersirable side reactions between this cluster and $[Rh(CO)_4]^-$ lead to the formation of small amounts of $[Rh_5(CO)_{15}]^-$ in tetraglyme.[42] We attempted to get a cleaner system by using a solvent in which the ionic species would be less soluble. Initial attempts employing tetraglyme–toluene mixtures were only partially successful, however, as previously discussed. We turned then to dodecane as a more convenient reaction medium. The almost nil solubility of $[Rh(CO)_4]^-$ in this solvent would indeed preclude the occurrence of those side reactions. Moreover, the already alluded lower solubility of carbon monoxide in this solvent was a desirable property to facilitate the Fourier subtractions of the spectra. On the other hand, another convenience in using dodecane was the ready formation of

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(41) I. Wender, and P. Pino, Eds., "Organic Syntheses via Metal Carbonyls", Wiley, New York, 1977: Vol. 1, p 440; Vol. 2, p 565.

(42) We have noticed the formation of small but detectable amounts of $[Rh_5(CO)_{15}]^-$ in these systems. A recent report concerning the formation of this anion in the reaction of $Rh_4(CO)_{12}$ with $[Rh(CO)_4]^-$ offers an explanation to our observation: A. Fumagalli, T. F. Koetzle, F. Takusagawa, P. Chini, S. Martinengo, and B. T. Heaton, *J. Am. Chem. Soc.*, **102**, 1740 (1980).

Chart I

increase in acidity ↓	protonated amine	unreacted amine
$HIr(CO)_4$		$O(CH_2CH_2)_2N(CH_3)$, $PhN(CH_3)_2$
$HCo(CO)_4$	$O(CH_2CH_2)_2N(CH_3)$	$PhN(CH_3)_2$
$HRh(CO)_4$	$O(CH_2CH_2)_2N(CH_3)$, $PhN(CH_3)_2$	

$HM(CO)_4$ (M = Co, Rh, Ir) in this solvent, although in this respect the incomplete conversion of $Rh_4(CO)_{12}$ to $Rh_2(CO)_8$ (vide infra) was of concern and the insolubility of the ionic tetracarbonylmetalate salts was a limitation that only allows for the qualitative comparison of the respective ability of these hydrides to protonate amines.

Fourier subtraction techniques show that $HIr(CO)_4$ (1.5 mmol) does not react with *N*-methylmorpholine (10.0 mmol) while $HCo(CO)_4$ (2.4 mmol) reacts with this amine (1.0 mmol) (Figure 3) but it does not protonate the less basic *N*,*N*-dimethylaniline (1.0 mmol) in a detectable fashion at either 5 or 100 °C. Similar procedures were followed during the study of $HRh(CO)_4$, although the presence of $Rh_4(CO)_{12}$ and $Rh_2(CO)_8$ in this case resulted in a complex pattern already discussed. In any event, the decrease of the bands associated with $HRh(CO)_4$ is observed with *N*,*N*-dimethylaniline (1.0 mmol) (Figure 3). That this decrease does not correspond to a reaction of the hydride with $Rh_4(CO)_{12}$ or any cluster derived from it that could be formed by the presence of the amine is inferred from the constant absorbances for the infrared absorptions of this cluster and $Rh_2(CO)_8$.

With a quantitative evaluation of the relative acidity of $HM(CO)_4$ (M = Co, Rh, Ir) precluded, we turned to qualitative studies for the comparison of the acid–base properties of the $HM(CO)_4$ species. A summary of these observations (Chart I) seems to indicate the larger acidity of $HRh(CO)_4$, although it should be kept in mind that such a conclusion may be affected by our considerations concerning $Rh_4(CO)_{12}$.

The position of $HRh(CO)_4$ is seen to be anomalous, and we do not have a readily available explanation for it. As we already mentioned, a somewhat related behavior has also been reported for the elements in the iron triads. For instance, $[C_5H_5Fe(CO)_2]^-$ is a stronger nucleophile than its ruthenium analogue,[30] and the proton affinity of $[(\eta\text{-}C_5H_5)_2Fe]$ is larger than that of $[(\eta\text{-}C_5H_5)_2Ru]$.[31] It appears, then, that a similar variation in the basicity of the metals, or, more specifically, of their complexes, could be present for both the iron and cobalt triads.

The characterization of $HRh(CO)_4$, a hitherto unobserved species, is also relevant in homogeneous catalysis by rhodium because this species has been proposed to be active in hydroformylation[1–6,13] and in the hydrogenation of carbon monoxide to less oxidized species, e.g., methanol and ethylene glycol.[11]

Acknowledgment. We are indebted to Union Carbide Corp. for permitting the publication of this work, in special to Dr. George L. O'Connor to whom we give recognition for his enthusiastic support in carrying out this investigation.

Registry No. $HCo(CO)_4$, 16842-03-8; $HRh(CO)_4$, 75506-18-2; $HIr(CO)_4$, 25282-12-6; $[PhCH_2PPh_3][Co(CO)_4]$, 42535-64-8; $[PhCH_2PPh_3][Ir(CO)_4]$, 75556-03-5; $[PhCH_2PPh_3][Rh(CO)_4]$, 75556-04-6; $Co_2(CO)_8$, 10210-68-1; $Rh_4(CO)_{12}$, 19584-30-6; $Ir_4(CO)_{12}$, 18827-81-1; $Ir(CO)_2(acac)$, 14023-80-4; $Rh(CO)_2(acac)$, 14874-82-9; $Rh_2(CO)_8$, 29658-60-4.

Supplementary Material Available: High-pressure infrared spectra of the fragmentation of $Rh_4(CO)_{12}$ solutions under CO and CO–H_2, IR spectra of the protonation of $[M(CO)_4]^-$ with protonic acids under CO, and IR spectra of $HM(CO)_4$ (M = Co, Rh, Ir) (3 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

X-ray Structural Characterization and Catalytic Properties of Hydridobis[4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane]rhodium(I)

RICHARD G. BALL, BRIAN R. JAMES,* DEVINDER MAHAJAN, and JAMES TROTTER

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The compound HRh[(+)-diop]$_2$, (+)-diop = (4*S*,5*S*)-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane, crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions a = 17.253 (2) Å, b = 20.976 (2) Å, c = 16.336 (3) Å, and Z = 4. Of the 5726 reflections measured by counter methods (Mo Kα radiation), 3758 $\geq 3\sigma$ were used for the structure determination. Full-matrix least-squares refinement gave a conventional R value of 0.060. The rhodium(I) atom is coordinated to two chelating diop ligands, each with *S*,*S* chirality, and a hydride in a distorted trigonal bipyramid, the hydride (located in a difference Fourier, Rh–H = 1.6 Å) and a phosphorus being at the trans axial sites. The ^{31}P and high-field ^1H NMR data reveal a fluxional structure at room temperature. Kinetic and spectroscopic studies on catalytic hydrogenation of styrene support earlier work on prochiral substrates and are consistent with an "unsaturate" mechanism via a HRh(diop)(diop*) species containing monodentate diop*. Optical induction at the substrate coordination stage is not readily attributed (by studying models) to interaction between the substrate and chiral ligand.

Introduction

Interest remains high in catalytic asymmetric synthesis using transition-metal complexes.[1] Asymmetric hydrogenation has been the most widely studied reaction, using particularly rhodium catalysts containing chiral phosphine ligands, and attempts to explain the mechanism of optical induction have stemmed largely from investigations with these systems.[2–4]

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[1] P. Pino and G. Consiglio in "Fundamental Research in Homogeneous Catalysis", Vol. 3, M. Tsutsui, Ed., Plenum Press, New York, 1979, p 519.

[2] B. R. James, *Adv. Organomet. Chem.*, **17**, 319 (1979).

[3] D. A. Slack, I. Greveling, and M. C. Baird, *Inorg. Chem.*, **18**, 3125 (1979).