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Stepwise Deprotonation of $H_4Ru_4(CO)_{12}$: High-Yield Synthesis and Carbon-13 NMR Spectra of $H_3Ru_4(CO)_{12}^-$ and $H_2Ru_4(CO)_{12}^{2-}$

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A stepwise, systematic procedure is described for the deprotonation of $H_4Ru_4(CO)_{12}$ when it is treated with KH in THF. Reaction with 1 equiv of KH yields the previously reported $H_3Ru_4(CO)_{12}^-$ ion; reaction with 2 equiv of KH yields the new anion $H_2Ru_4(CO)_{12}^{2-}$; and reaction with 3 equiv of KH yields an equimolar mixture of $H_2Ru_4(CO)_{12}^{2-}$ and $Ru_4(CO)_{12}^{4-}$. In this last reaction, the $HRu_4(CO)_{12}^{3-}$ ion is believed to form initially and then decompose to the products which were isolated. Carbon-13 NMR spectra and infrared spectra of the $H_2Ru_4(CO)_{12}^{2-}$ ion indicate the presence of carbonyl bridging. The carbon-13 NMR spectrum under conditions of slow exchange (−80 °C) indicates that this dianion is of C_s point symmetry. From infrared and carbon-13 NMR spectra of the potassium and $(PPh_3)_2N^+$ salts of $H_2Ru_4(CO)_{12}^{2-}$ significant ion pairing is suggested in THF solutions of the potassium salt.

Introduction

One of the principal handicaps to progress in the detailed study and characterization of carbonylate anion clusters has been the lack of specific high-yield syntheses. Preparative procedures which are commonly employed involve reduction of neutral metal carbonyls, with the resulting products usually being mixtures which are difficult to separate. Since carbonylate anions are conjugate bases of transition-metal carbonyl hydrides, a reasonable approach would be to generate these anions through the deprotonation of the neutral parent transition-metal carbonyl hydride cluster since, frequently, the parent hydride is relatively easier to prepare and isolate in pure form than its conjugate base. With but one notable exception,[1] the deprotonation of metal carbonyl hydride clusters has received relatively little attention[2,3] as a synthetic method. Yet, with the proper deprotonating agent such an approach might be the key to the preparation in good yield of new cluster anions and cluster anions prepared previously, but in small yields. In recent years we have successfully used potassium hydride to deprotonate boron hydrides to yield a series of new boron hydride anions.[4] In addition to the purely formal analogies which can be drawn between boron hydrides and metal carbonyl hydride cluster systems,[5] the B–H–B bridge systems in boron hydrides and the M–H–M bridge systems in metal hydrides are chemically similar, in principle. We describe here the adaptation of methods of anion syntheses from boron hydride chemistry[4,6] to metal cluster anion syntheses.

Recent studies[7] of the catalytic activity of $H_4Ru_4(CO)_{12}$ in hydroformylation and the "water gas shift" reaction point to $H_3Ru_4(CO)_{12}^-$ as being an important intermediate in the catalytic cycle. This anion was first prepared by Koepke, Johnson, Knox, and Kaesz[1] by deprotonating $H_4Ru_4(CO)_{12}$ in ethanolic KOH. While this method gives $H_3Ru_4(CO)_{12}^-$ in high yield, a second proton cannot be removed by simply employing a second equivalent of KOH.[26] Using KH as a deprotonating agent we have observed[8] the systematic, stepwise deprotonation of $H_4Ru_4(CO)_{12}$ to give nearly quantitative yields of $H_3Ru_4(CO)_{12}^-$ and the new anion $H_2Ru_4(CO)_{12}^{2-}$. The reactions are apparently clean with respect to cluster degradation, and they are easily monitored by measuring the hydrogen gas evolved.

Results and Discussion

$H_3Ru_4(CO)_{12}^-$. The potassium salt of $H_3Ru_4(CO)_{12}^-$ is prepared quantitatively according to the reaction

$$H_4Ru_4(CO)_{12} + KH \xrightarrow{THF} K[H_3Ru_4(CO)_{12}] + H_2 \quad (1)$$

Deprotonation is complete within 0.5 h at 50–60 °C or 12 h at ambient temperature. Metathesis of $KH_3Ru_4(CO)_{12}$ with $[(Ph_3P)_2N]Cl$ generates $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$, in 70–80% yield.

$$[(Ph_3P)_2N]Cl + K[H_3Ru_4(CO)_{12}] \xrightarrow{CH_2Cl_2} [(Ph_3P)_2N][H_3Ru_4(CO)_{12}] + KCl \quad (2)$$

From a linear least-squares extrapolation to infinite dilution in nitromethane, the equivalent conductance ($\Lambda_0 = 73\ \Omega^{-1}\ cm^2\ mol^{-1}$) of $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$ was shown to be within the range[9] accepted for a 1:1 electrolyte.

The infrared spectrum of $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$ (ν(CO) in THF: 2067 (vw), 2037 (s), 2031 (sh), 2017 (s), 1998 (vs), 1975 (m), 1948 (w), 1930 (w) cm^{-1}) agrees well with that reported for $[Ph_4As][H_3Ru_4(CO)_{12}]$.[1] The infrared spectrum of $K[H_3Ru_4(CO)_{12}]$ (ν(CO) in THF: 2059 (vw), 2037 (s), 2030 (sh), 2009 (vs), 1977 (m), 1948 (m), 1928 (w) cm^{-1}) is similar to that of $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$.

The proton NMR spectrum of $K[H_3Ru_4(CO)_{12}]$ in THF-d_8 at 30 °C consists of a single sharp signal at τ 27.04. This singlet splits into three signals at −93 °C: a doublet at τ 26.04 (J_{H-H} = 2.4 Hz), a singlet at τ 27.54, and a triplet at τ 29.14 (J_{H-H} = 2.4 Hz). These spectra agree well with the spectra of the metal hydride region of $[Ph_4As][H_3Ru(CO)_{12}]$ which have been previously reported and discussed in detail.[1] Two isomers were identified at low temperature: one of C_{3v} symmetry and the other of C_{2v} or C_2 symmetry. At higher temperatures these isomers rapidly interconvert. A recent X-ray study of $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$ has shown that two distinct structural isomers crystallize with μ_2-hydrogen ruthenium arrangements in the $H_3Ru_4(CO)^-_{12}$ ion approximating C_2 and C_{3v} symmetry.[10]

The $^{13}C\{^1H\}$ NMR spectrum of $K[H_3Ru_4(CO)_{12}]$ in THF-d_8 consists of a single sharp signal at 198.2 ppm at 27 °C (Figure 1) which indicates a dynamic process averaging all carbonyl environments. As the temperature is lowered, this signal broadens and is replaced by four new resonances at about −70 °C (δ 201.4, 199.3, 196.5, 193.3). At this point, hydrogen migration is essentially quenched and the carbonyl groups are involved only in localized axial–equatorial exchange (Figure 2), unless extensive, but unlikely, accidental degeneracy exists to account for the deceptively simple spectrum. With only localized axial–equatorial exchange, the C_{3v} and C_2 isomers should each have two sets of symmetry-distinct vertices. The four resonances observed in the $^{13}C\{^1H\}$ NMR spectrum are consistent with the presence of the two isomers. However, we have been unable to assign the signals to isomers of specific symmetry because we could not meaningfully interpret peak area ratios in the temperature range in which these four signals were observed. Presumably different rates of axial–equatorial carbonyl interchange about the symmetry-distinct ruthenium vertices were the source of this problem. In the temperature range −80 to −110 °C, the resonance at 196.5 ppm collapses

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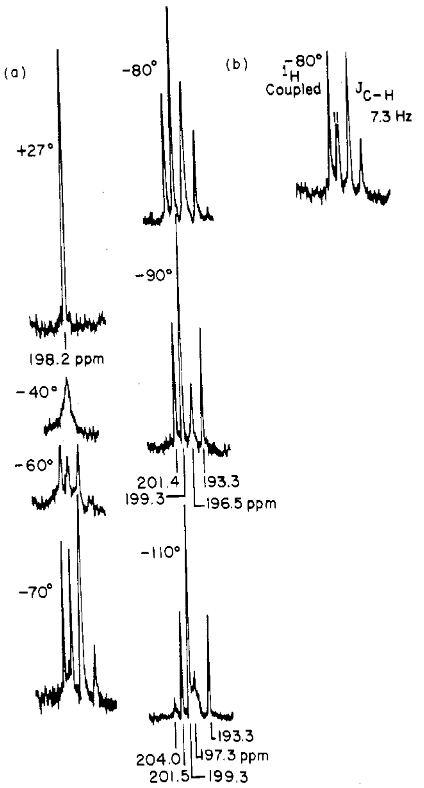

Figure 1. Carbon-13 NMR spectra of $K[H_3Ru_4(CO)_{12}]$ in THF-d_8: (a) proton decoupled; (b) proton coupled.

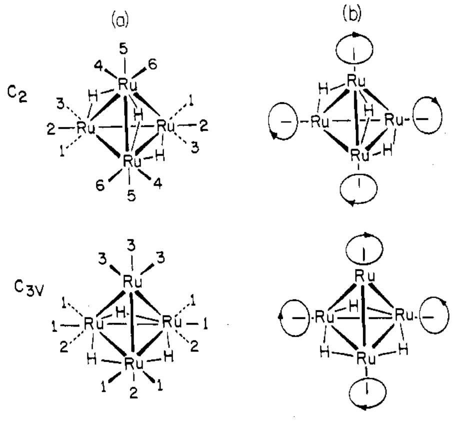

Figure 2. (a) The C_2 and C_{3v} isomers of the $H_3Ru_4(CO)_{12}^-$ ion. (b) Representations of localized axial–equatorial carbonyl exchange.

and is replaced by broad signals at 204.0 and 197.3 ppm, while the remaining three signals sharpen. At the lowest temperature attained, −127 °C in $(CD_3)_2O$, these peaks also begin to collapse. A proton-coupled spectrum at −80 °C reveals that the resonance at 199.3 ppm is clearly coupled to one hydrogen (doublet; J = 7.3 Hz), while the resonance at 193.3 ppm is attenuated but displays no apparent multiplet character.

$H_2Ru_4(CO)_{12}^{2-}$. Reaction of $H_4Ru_4(CO)_{12}$ with 2 equiv of KH gives the new dianion $H_2Ru_4(CO)_{12}^{2-}$ in high yield.

$$H_4Ru_4(CO)_{12} + 2KH \rightarrow K_2[H_2Ru_4(CO)_{12}] + 2H_2 \quad (3)$$

Pure THF solutions of $K_2H_2Ru_4(CO)_{12}$ are orange. When small amounts of $K[H_3Ru_4(CO)_{12}]$ are present, the solutions are tinged red noticeably. From the following metathesis reaction $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$ was prepared in 80% yield.

$$2[(PH_3P)_2N]Cl + K_2[H_2Ru_4(CO)_{12}] \xrightarrow{CH_2Cl_2} [(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}] \quad (4)$$

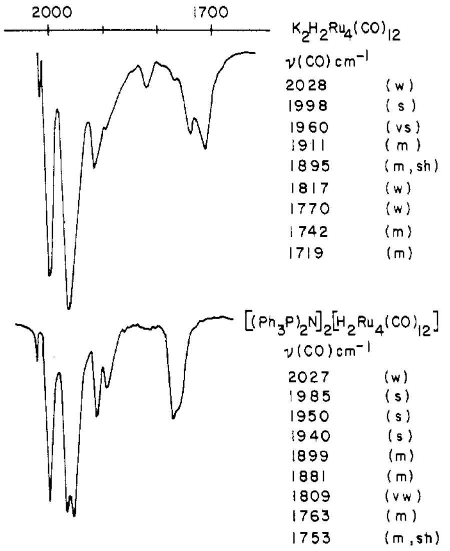

Figure 3. Infrared spectra in THF.

Solutions of $H_2Ru_4(CO)_{12}^{2-}$ salts are stable indefinitely under nitrogen at ambient temperature but, when exposed to air, decompose within 1 h to give an uncharacterized yellow solid. From a linear least-squares extrapolation to infinite dilution in nitromethane, the equivalent conductance (Λ_0 = 167 Ω^{-1} cm^2 mol^{-1}) of $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$ was shown to be within the range[9] accepted for a 2:1 electrolyte.

In contrast to $H_3Ru_4(CO)_{12}^-$ which exhibits only terminal CO infrared absorptions in the range 2100–1900 cm^{-1}, THF solutions of $K_2[H_2Ru_4(CO)_{12}]$ and $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$ also exhibit low-frequency absorptions (1900–1700 cm^{-1}) (Figure 3) which are indicative of bridging carbonyls. Independent evidence for carbonyl bridges is offered by ^{13}C NMR spectra of the $H_2Ru_4(CO)_{12}^{2-}$ ion.

The difference in carbonyl ligation in $H_2Ru_4(CO)_{12}^{2-}$ is presumably due to the larger negative charge on the dianion. This rearrangement might represent a mode of averaging charge distribution throughout the cluster framework.

Chini[11] has found a linear relationship between the fraction of terminal carbonyl groups and the average negative charge per carbonyl group for a series of isoelectronic octahedral carbonyl rhodium clusters. It appears that the ability of a carbonyl ligand to disperse electron density on a metal cluster decreases in the order face bridging > edge bridging > terminal.[11,12] Conversion of terminal into bridging carbonyl groups is consistent with the increase in negative charge in the transformation of $H_3Ru_4(CO)_{12}^-$ into $H_2Ru_4(CO)_{12}^{2-}$. Frequencies of the bridging carbonyl absorptions in $H_2Ru_4(CO)_{12}^{2-}$ probably indicate an edge-bridging mode of attachment, although a face-bridging interaction with the metal tetrahedron cannot be unambiguously excluded by the infrared data alone. A cautious criterion utilized by Chini[11] involves noting the difference between the strongest terminal and bridging carbonyl absorptions. A difference of 150–210 cm^{-1} indicates edge bridges, while one of 210–250 cm^{-1} indicates face bridges. Edge-bridging carbonyls are therefore indicated in $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$ since the difference between the strongest terminal absorptions at 1950 and 1940 cm^{-1} (average 1945 cm^{-1}) and the main bridging absorption at 1763 cm^{-1} is 182 cm^{-1}. Figure 4 depicts the proposed structure of $H_2Ru_4(CO)_{12}^{2-}$ based upon the infrared spectra and the ^{13}C NMR spectra which are discussed below.

A final point of interest in the infrared spectra is that the frequency and intensity differences between the spectra of $K_2[H_2Ru_4(CO)_{12}]$ and $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$ are probably due to significant ion pairing in the potassium salt. Ion pairing has been noted in previous studies[13-16] of alkali

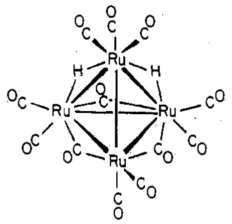

Figure 4. Proposed structure of $H_2Ru_4(CO)_{12}^{2-}$.

Table I. Carbon-13 NMR Data (22.62 MHZ) for $H_2Ru_4(CO)_{12}^{2-}$ Salts

$K_2H_2Ru_4(CO)_{12}$ in THF-d_8			$[(Ph_3P)_2N]_2$-$[H_2Ru_4(CO)_{12}]$ in CD_2Cl_2	
+60 °C	−80 °C	assignt	−80 °C	+30 °C
	281.1	b	280.1	
	280.9	aa′	279.5	
221.5	(222.0)[a]	all CO	(220.4)[a]	220.3
	205.3	cc′; d	204.0	
	205.1	d, cc′	203.8	
	203.3	ee′	201.6	
	200.3	f	198.8	
	200.0	h		
		gg′, h	197.5	
	199.0	gg′		

[a] Weighted average.

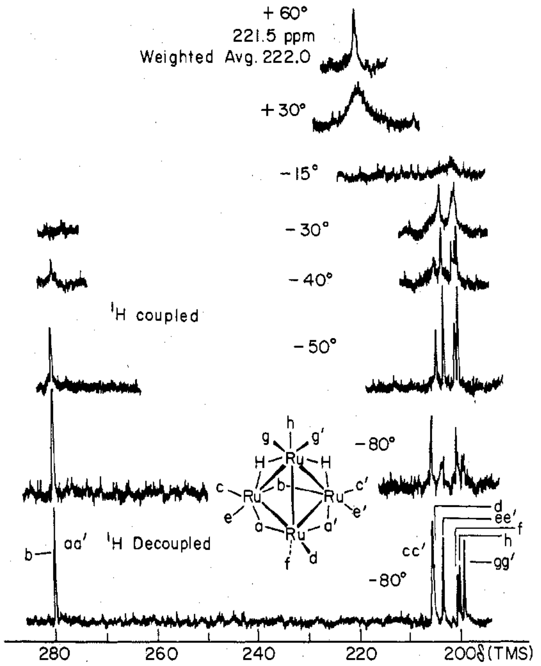

Figure 5. Carbon-13 NMR spectra of $K_2[H_2Ru_4(CO)_{12}]$ in THF-d_8.

metal salts of transition-metal carbonylates. Carbon-13 NMR data (vide infra) of $K_2[H_2Ru_4(CO)_{12}]$ and $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$ are also indicative of ion pairing in the potassium salt.

Proton NMR spectra of $K_2[H_2Ru_4(CO)_{12}]$ in THF-d_8 consist of a single signal. A sharp singlet at τ 29.26 at 30 °C broadens and shifts a little to τ 29.43 as the compound is cooled to −100 °C. The magnitude of the chemical shift of this signal is consistent with the presence of bridging hydrogens as opposed to terminally bonded hydrogens.[2,3]

The ^{13}C NMR spectrum of $K_2[H_2Ru_4(CO)_{12}]$ in THF-d_8 (Figure 5, Table I) at −80 °C is consistent with a structure of C_s symmetry. Nearly 80 ppm chemical shift difference separates the upfield terminal carbonyl resonances from the bridging carbonyls (aa′b) which exhibit the lowest field carbonyl resonance (δ 281.1, 280.9) yet observed for a ruthenium carbonyl species. The resonances at δ 203.3 ($^2J_{^{13}C-Ru-H}$ = 10.3 Hz) and 199.0 ($^2J_{^{13}C-Ru-H}$ = 5.9 Hz) are assigned to carbonyls ee′ and gg′ respectively. trans ^1H–metal–^{13}C coupling is expected to be of greater magnitude than cis coupling.[17] Thus the remaining signal of intensity 2 at δ 205.3 is assigned to the cis carbonyls cc′; proton coupling causes peak attenuation but gives no discernible coupling constant. The upfield resonances at δ 205.1 and 200.3 are relatively unaffected by proton coupling and accordingly are assigned to carbonyls d and f, respectively, since they are farthest removed from the two edge-bridging hydrogens. A selective carbonyl-exchange process which occurs between ca. −80 and −30 °C (Figure 6) allows carbonyls d and f to be differentiated but more importantly establishes that the hydrogens are indeed edge bridging in the static structure.

At about −50 °C the four lowest field signals are broadened and attenuated noticeably with respect to the four highest field resonances. A cyclic exchange mechanism[18] (Figure 6) involving bridging and equatorial carbonyls moving around the Ru_3 basal plane of the metal tetrahedron causes broadening of the signals assigned to a, a′, b, c, c′, and d. This selectivity of signal broadening at intermediate temperatures, −50 to −30 °C, is a consequence of the presence of effectively static edge-bridging hydrogens. So long as these hydrogens are fixed, the breaking and re-forming of carbonyl bridges can occur only about the edges of the unique Ru_3 face, the basal plane of the tetrahedral cluster, since two of the edges of the other faces are occupied by hydrogens. If face-bridging hydrogens were present but fixed, two sets of edges from two Ru_3 faces would be available in the carbonyl-exchange process and in effect would permit the simultaneous participation of all four ruthenium vertices in bridge–terminal interchange once exchange begins. In such a situation a more uniform collapse of ^{13}C resonances would be expected with increasing temperature.

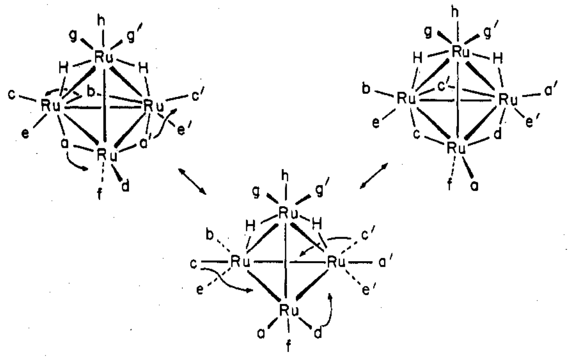

Figure 6. Proposed carbonyl-exchange process in the $H_2Ru_4(CO)_{12}^{2-}$ ion between −80 and −30 °C.

At 60 °C one signal is observed in the $^{13}C\{^1H\}$ NMR spectrum. Its chemical shift is the weighted average of the low-temperature shifts. No unique mechanism for complete exchange averaging is extractable from the data. It is likely that a combination of exchange mechanisms is operative at the higher temperatures. Intranuclear CO and H exchange coupled with localized axial–equatorial carbonyl exchange about each ruthenium vertex is a reasonable route to the averaging of ligand environments.

Comparison of ^{13}C NMR chemical shift data for $K_2[H_2Ru_4(CO)_{12}]$ in THF-d_8 with those of $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$ in CD_2Cl_2 (Table I) indicates that ion-pairing effects are present in the potassium salt. At −80 °C, the $^{13}C\{^1H\}$ NMR spectrum of $K_2[H_2Ru_4(CO)_{12}]$ reveals eight ^{13}C resonances (1:2:2:1:2:1:1:2) compared to seven ^{13}C resonances (1:2:1:2:2:1:3) of $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$ at −80 °C. The highest field signal in the latter spectrum reflects apparent degeneracy of the h, g, g′ resonances either through exchange averaging of these apical carbonyl resonances or through accidental overlap of resonances. When the smaller cation K is present, the environments of h, g, g′ are sufficiently perturbed so that two signals of area ratio 1:2 are produced. Similar effects have been noted previously in the ^{13}C NMR carbonyl chemical shifts of other metal carbonylate systems and have been attributed to the existence of ion pairs.[19,20]

Reaction of 3 Equiv of KH with $H_4Ru_4(CO)_{12}$. Prolonged reaction of $H_4Ru_4(CO)_{12}$ with 3 equiv of KH in THF (4 days at ambient temperature) gives 3-equiv amounts of H_2. Stepwise deprotonation occurs to give $K[H_3Ru_4(CO)_{12}]$ and $K_2[H_2Ru_4(CO)_{12}]$ successively in the first two deprotonation steps. With the removal of the third equivalent of hydrogen we believe that sequence 5 occurs. We were unable to isolate

$$\begin{array}{l} KH + K_2[H_2Ru_4(CO)_{12}] \rightarrow K_3[HRu_4(CO)_{12}] + H_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\downarrow \\ \qquad\qquad {}^{1}/_{2}K_2[H_2Ru_4(CO)_{12}] + {}^{1}/_{2}K_4[Ru_4(CO)_{12}] \end{array} \tag{5}$$

a product of composition $K_3[HRu_4(CO)_{12}]$ but obtained a solution of $K_2[H_2Ru_4(CO)_{12}]$ which contains approximately 50% of the available Ru_4 cluster. A tan-red insoluble solid is also obtained which, from a mass balance, is empirically $K_4[Ru_4(CO)_{12}]$.

Experimental Section

General Data. All manipulations were performed under either vacuum or an atmosphere of prepurified nitrogen.[21] Specific procedures involving the measurement of KH,[22] deprotonation reactions,[6] and vacuum-line filtration[23] apparatus are described in detail elsewhere. Solvents were dried over drying agents before use [CH_2Cl_2 (P_2O_5); CH_3NO_2 ($CaCl_2$); THF and pentane ($LiAlH_4$); $(CD_3)_2O$, THF-d_8, and CD_2Cl_2 (KH)]. These treated solvents were then distilled on a vacuum line into storage vessels which were fitted with Teflon vacuum stopcocks. Hexane which was used for chromatography was stirred over concentrated H_2SO_4 for 2 days. It was then decanted and distilled from CaH_2 under nitrogen.

The solvent $(CD_3)_2O$ (used for low-temperature FT NMR spectroscopy) was prepared from CD_3OD and CD_3I (Stohler Isotope Chemicals) in THF.[24]

Ruthenium carbonyl (Strem Chemicals) was used as received and $H_4Ru_4(CO)_{12}$ was prepared as described previously.[25] Potassium hydride obtained as a mineral oil dispersion (Ventron) was purified, calibrated for activity, and manipulated as described previously.[6,22,23]

Solution infrared spectra were obtained with a Perkin-Elmer 457 spectrometer in matched Perkin-Elmer demountable cells with 0.1-mm Teflon spacers and KBr windows. Spectra were calibrated with polystyrene film.

Mass spectra of gaseous samples were obtained on a modified AEI MS-10 spectrometer. A known mixture of H_2 and CO was used to calibrate a group of instrument settings replicated for all determinations of relative H_2 vs. CO concentrations in unknown samples. Possible carbonyl reduction products such as CH_4 were not observed.

Solutions of the compounds for which conductivity data were desired were air sensitive. Thus, nitromethane solutions of varying concentration (7×10^{-3} to 6×10^{-4} M) were prepared from a stock solution in a drybox equipped with electrical leads connected to an exterior Industrial Instruments Model RC 16B conductivity bridge. Conductivities were measured at 1000 Hz on solutions in a conductivity cell ($K = 0.1$) at 25 °C.

NMR spectra were obtained with a Bruker HX-90 spectrometer operating in the FT mode at 22.6 MHz (^{13}C) or 90 MHz (^1H). Perdeuterated solvents provided both a deuterium lock frequency and internal standard for shift assignments. Carbon-13 and residual proton shifts (relative to Me_4Si) in these solvents were assigned the following values. THF-d_8: ^1H, τ 8.27 and 6.42; ^{13}C, 25.3 and 67.4 ppm. $(CD_3)_2O$: ^1H, τ 6.76; ^{13}C, 57.9 ppm. CD_2Cl_2: ^1H, τ 4.68; ^{13}C, 53.8 ppm. NMR samples were typically 0.2 M concentration. Depending on the temperature, 5000–50 000 transients were sufficient to obtain adequate ^{13}C NMR spectra of the samples which contained ^{13}CO in natural abundance.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

$H_3Ru_4(CO)_{12}^-$ Salts. In a drybox, 0.50 mmol of KH (0.020 g) was added to 0.50 mmol of $H_4Ru_4(CO)_{12}$ (0.372 g) in a 30-mL reaction flask which was fitted with a vacuum stopcock adapter. This apparatus was then connected to a vacuum line and evacuated. Five milliliters of THF was distilled in at −78 °C. Stirring at 60 °C for 1 h afforded a dark opaque red solution of $KH_3Ru_4(CO)_{12}$ and 0.46 mmol of noncondensable gases (98% H_2 and 2% CO by mass spectral analysis). Under a flow of nitrogen gas, 0.48 mmol of $[(Ph_3P)_2N]Cl$ (0.276 g) was added to the reaction flask. The solution was filtered after being stirred for 2 h at ambient temperature to remove precipitated KCl (identified by its X-ray powder pattern). The THF was distilled away under vacuum and replaced with 5 mL of CH_2Cl_2 which was distilled onto the reaction mixture. Ten milliliters of ethanol was slowly distilled into the solution which was maintained at −78 °C. A yellow-orange precipitate of $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$ formed which was filtered and then washed consecutively with ethanol and pentane and then dried overnight under vacuum; yield 0.46 g, 72%. Anal. Calcd for $C_{48}H_{33}NO_{12}P_2Ru_4$: C, 44.97; H, 2.59; Ru, 31.54. Found: C 45.18; H, 2.84; Ru, 31.54. Infrared carbonyl absorptions of the potassium and $(Ph_3P)_2N^+$ salts of $H_3Ru_4(CO)_{12}^-$ in THF agree well with those reported for $[Ph_4As][H_3Ru_4(CO)_{12}]$ except for some broadening in the spectrum of the potassium salt. Samples of $K[H_3Ru_4(CO)_{12}]$ for NMR studies were prepared in THF-d_8 as the reaction solvent. Samples so prepared were filtered under vacuum into 10-mm NMR tubes which were then cooled to liquid nitrogen temperature and sealed off under vacuum.

$H_2Ru_4(CO)_{12}^{2-}$ Salt. The $H_2Ru_4(CO)_{12}^{2-}$ ion was prepared in a manner similar to that described for the preparation of the $H_3Ru_4(CO)_{12}^-$ ion. A 0.48-mmol quantity of $H_4Ru_4(CO)_{12}$ (0.357 g) was reacted with 1.0 mmol of KH (0.040 g) in 5 mL of THF at 50 °C for 0.5 h. During this time the slightly soluble, yellow $H_4Ru_4(CO)_{12}$ was gradually consumed to form an opaque, dark red solution of the more highly soluble $K[H_3Ru_4(CO)_{12}]$. The solution was vigorously stirred for an additional 24 h at room temperature. A total of 1.04 mmol of noncondensable gases (98% H_2 and 2% CO by mass spectral analysis) evolved over the entire reaction period. The solution was filtered and the solvent was pumped away, leaving $K_2[H_2Ru_4(CO)_{12}]$ as a yellow powder. Samples of $K_2[H_2Ru_4(CO)_{12}]$ for NMR studies were prepared by using THF-d_8 as the reaction medium.

In a typical metathesis reaction, 0.40 mmol of $K_2H_2Ru_4(CO)_{12}$ (0.33 g) and 0.80 mmol of $[(Ph_3P)_2N]Cl$ (0.46 g) were stirred in 16 mL of the mixed solvent THF/CH_2Cl_2 (1:1) at room temperature for 1 h. Filtration of the orange-red solution yielded 0.055 g (92%) of KCl which was identified from its X-ray powder diffraction pattern. Solvents were distilled from the filtrate, under vacuum, and then 6 mL of CH_2Cl_2 was added to the crude product. Absolute ethanol, 15 mL, was slowly added to the stirred solution at −78 °C to precipitate yellow $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$ which was filtered, washed consecutively with cold ethanol and pentane, and then dried under vacuum overnight; yield 0.55 g, 76%. Anal. Calcd for $C_{84}H_{62}N_2O_{12}P_4Ru_4$: C, 55.45; H, 3.43; Ru, 22.22. Found: C, 55.35; H, 3.59; Ru, 21.84.

Reaction of 3 Equiv of KH with $H_4Ru_4(CO)_{12}$. A THF-d_8 (3.2 mL) slurry of 0.73 mmol of $H_4Ru_4(CO)_{12}$ (0.542 g) and 2.2 mmol of KH (0.088 g) was stirred under vacuum for 1 h at 45 °C to yield $K[H_3Ru_4(CO)_{12}]$. Stirring was then continued at room temperature for 4 days while gas evolution was monitored. A total of 2.2 mmol of noncondensable gases (98% H_2 and 2% CO by mass spectral analysis) was evolved. Filtration gave a clear, orange filtrate from which solvent removal under vacuum yielded 0.35 g of pure $K_2[H_2Ru_4(CO)_{12}]$ (0.39 mmol) which was identified by its infrared and variable-temperature carbon-13 NMR spectra. The precipitate consisted of 0.28 g of a tannish red solid which on the basis of mass balance is empirically $K_4[Ru_4(CO)_{12}]$ (0.31 mmol). In addition to being insoluble in THF, this solid is insoluble in acetone, CH_3NO_2, HMPA, and THF–18-crown-6.

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Registry No. $H_4Ru_4(CO)_{12}$, 34438-91-0; $K[H_3Ru_4(CO)_{12}]$, 67269-70-9; $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$, 70073-19-7; $K_2[H_2Ru_4(CO)_{12}]$, 67269-69-6; $[(Ph_3P)_2N]_2[H_2Ru_4(CO)_{12}]$, 67430-40-4.

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(26) We have recently discovered that when a large excess of KOH is present in aqueous alcoholic solution, $H_2Ru_4(CO)_{12}^{2-}$ is formed rather than $H_3Ru_4(CO)_{12}^{-}$.

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Intramolecular Hydrogen-Bonding Implications on the Lability of the Molybdenum–Piperidine Bond. Kinetic and Mechanistic Studies of the Reaction of *cis*-$Mo(CO)_4[P(OCH_3)_3]NHC_5H_{10}$ with Carbon Monoxide

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^{13}C NMR and infrared spectral properties in the CO region are provided for the *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ derivative. The effects of intramolecular hydrogen-bonding interactions between the –P–O···H–N– groupings in *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ on the solution dynamics of this species toward amine-displacement reactions are reported. This hydrogen-bonding interaction results in an enhanced stabilization of the piperidine ligand toward dissociative loss as compared with the analogous process in the $Mo(CO)_5NHC_5H_{10}$ derivative, ΔH^* for NHC_5H_{10} dissociation being 3.5 kcal mol^{-1} higher for the former process. The reaction of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ with ^{13}CO was found to afford stereospecifically the equatorially ^{13}CO-substituted derivative $Mo(CO)_4(^{13}CO)P(OMe)_3$. Additionally, *fac*-$Mo(CO)_3(^{13}CO)[P(OMe)_3]NHC_5H_{10}$ was synthesized and observed to react with ^{13}CO to yield exclusively the equatorially ^{13}CO substituted $Mo(CO)_3(^{13}CO)_2P(OMe)_3$ species.

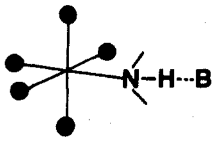
Introduction

Intermolecular hydrogen bonding between a metal-bound amine ligand containing a N–H grouping and added base has been demonstrated to accelerate greatly the rate of amine displacement in substituted metal–carbonyl–amine derivatives.[1] This type of interaction as well explains many of the solvent effects on reaction rates noted in these ligand-substitution processes.[1,2] The reaction can be described in a general manner by eq 1, where B may be either an incoming ligand or the

$$\mathrm{MA + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MA{:}B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MB{:}A \xrightarrow{k_3} MB + A} \quad (1)$$

solvent. Diffusion of MA and B to form the hydrogen-bonding intermediate trapped in a solvent cage has been observed to occur in a fast step with the chemical conversion step being rate determining.

MA:B =



Previously, solid-state structural data have been presented to support the existence of a weak intramolecular N–H···O hydrogen bond in the derivative *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$.[3] In this paper we report kinetic measurements for the dissociative loss of amine (eq 2) in this species in order

$$cis\text{-}Mo(CO)_4[P(OMe)_3]NHC_5H_{10} + CO \rightarrow Mo(CO)_5L + NHC_5H_{10} \quad (2)$$

to assess the role that this interaction plays in the amine-dissociation process. The stereochemical position occupied by the incoming carbon monoxide ligand in eq 2 in addition to scrambling processes in the $[Mo(CO)_4P(OMe)_3]$ intermediate has been investigated with the aid of ^{13}CO.

Experimental Section

Materials. Reagent grade hexane was distilled from $CaSO_4$ under a nitrogen atmosphere. Molybdenum hexacarbonyl was the generous gift of Climax Molybdenum Corp. ^{12}C carbon monoxide was supplied by Matheson, whereas ^{13}CO gas enriched to >90% was obtained from Prochem, B.O.C. Ltd., London. The *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ derivative was prepared from *cis*-$Mo(CO)_4[NHC_5H_{10}]_2$ and $P(OMe)_3$ as previously described.[4]

Kinetic Measurements. Piperidine substitution reactions of *cis*-$Mo(CO)_4[P(OMe)_3]NHC_5H_{10}$ derivatives were carried out in Schlenk storage tubes (25-mL capacity) under a static atmosphere of carbon monoxide in heptane solvent at a variety of temperatures. The tubes were fitted with septum caps secured by copper wire. The reaction

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