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Brønsted Acidities of Carbonyl Hydride Complexes of Iron, Ruthenium, and Osmium: pK_a Values and Deprotonation Rates in Methanol Solution[1]

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Abstract: Reported are kinetics studies of the reaction of methoxide ion with several mononuclear and polynuclear carbonyl hydride complexes $H_xM_y(CO)_z$ of the iron triad. Deprotonation of the hydrides to give the conjugate base anions occurs with moderate second-order rate constants ($\sim 10^1$–10^4 M^{-1} s^{-1}), considerably smaller than those of oxygen or nitrogen acids of comparable thermodynamic strength under similar conditions. The relative slowness of these reactions is interpreted in terms of possible electronic and structural rearrangements of substrate and solvent occurring as the result of the deprotonation. In addition the kinetics technique allows the measurement of the reverse reaction (protonation of the conjugate base by methanol) rate constants which are also comparatively small ($\sim$0.05–25 s^{-1}). The ratio of the forward and reverse rates gives the equilibrium constants from which the pK_a's in methanol can be calculated. In several cases pK_a's were confirmed by buffer/indicator techniques. From these and other published data are drawn the conclusions that bridging hydrides are more acidic than terminal hydrides and that hydrides of the lighter metals are more acidic than those of homologous heavier metals. Furthermore, it is shown that the substituent effect of replacing CO of a cluster by a trimethyl phosphite is to decrease significantly the acidity of that cluster's hydrides.

The metal carbonyls and metal carbonyl hydrides have been the subjects of much recent attention as possible homogeneous catalysts. Of special interest are the roles played by such species in the catalysis of CO, H_2, or H_2/CO mixtures in reactions such as the hydrogenation or hydroformylation of organic substrates,[2] the water gas shift,[3,4] and the hydrogenation of carbon monoxide.[5] In such systems, the metal hydrides may act variously as a hydrogen (H_2), hydride (H^-), or proton (H^+) source, and these properties have been demonstrated qualitatively for a number of metal hydrides.

The Brønsted acidity of metal carbonyl hydrides (e.g., eq 1)

$$H_xM_y(CO)_z + B \rightleftarrows BH^+ + H_{x-1}M_y(CO)_z^- \qquad (1)$$

is well-known. A wide span of acidities is observed ranging from the strong acids such as $HCo(CO)_4$, which is reported to be stronger than nitric acid but weaker than hydrochloric acid in methanol,[6b] to exceedingly weak acids. In some cases the anions of di- and higher-order hydrides can be deprotonated further by very strong bases. For examples, $H_4Ru_4(CO)_{12}$ is deprotonated to $H_3Ru_4(CO)_{12}^-$ with 1 equiv of KOH in ethanol[7] and a second proton is removed to form $H_2Ru_4(CO)_{12}^{2-}$ in more concentrated KOH solutions.[8] With the stronger base KH in tetrahydrofuran, all four protons can be removed to give $K_4Ru_4(CO)_{12}$.[8]

Since hydrogen coordinated to a metal is normally viewed as a hydride (i.e., H^-), protonation and deprotonation reactions can also be considered the simplest oxidative addition/reductive elimination reactions, at least formally. That such redox features are not always mere formalities is indicated by structural changes sometimes accompanying proton transfer. For example, the $Fe(CO)_4^{2-}$ ion has a tetrahedral arrangement of the carbonyls[9] as seen for the isoelectronic d^{10} nickel carbonyl. Upon protonation the resulting $HFe(CO)_4^-$ ion has the trigonal-bipyramidal configuration[10] expected for a d^8 pentacoordinated complex.

Quantitative measurements of equilibrium constants have been made in a few cases. For example, the first and second pK_a's of $H_2Fe(CO)_4$ (eq 2 and 3) have been determined in H_2O by a

$$H_2Fe(CO)_4 \rightleftarrows H^+ + HFe(CO)_4^- \qquad (2)$$

$$pK_a(1) = 4.0\ (20\ °C)$$

$$HFe(CO)_4^- \rightleftarrows H^+ + Fe(CO)_4^{2-} \qquad (3)$$

$$pK_a(2) = 12.7\ (20\ °C)$$

titrimetric technique.[11] However, the number of such measurements are sparse, and even these few measurements have been carried out under widely varying conditions (different solvents, etc.). Furthermore, rates measurements of the protonation/deprotonation steps are even rarer.

In this context, we began a systematic study of thermodynamics and kinetics parameters of transition-metal carbonyl hydrides acting as Brønsted acids. Reported here are studies carried out with various mono- and polynuclear complexes of the iron triad which were chosen for study in part because several of these species have appeared as components of catalysts for the water gas shift reaction.[3] The medium is anhydrous methanol, chosen because the acid/base properties of this solvent are well characterized, because the pK_a's rates of numerous other Brønsted acids have been measured in methanol, and because the hydrides are generally sufficiently soluble in this medium. Notably, in the period since the original communication of our studies[1] in this regard, there has been a recent report of the Brønsted acid/base equilibrium and kinetics of several group 6 plus several osmium carbonyl hydrides in anhydrous acetonitrile.[12]

Experimental Section

Syntheses. $H_4Ru_4(CO)_{12}$,[13] $[Ph_4As][H_3Ru_4(CO)_{12}]$,[7] $H_2FeRu_3(CO)_{13}$,[14] $H_4FeRu_3(CO)_{12}$,[13] $H_2Ru_4(CO)_{13}$,[14] $H_2Os_3(CO)_{10}$,[13] $H_2Os_3(CO)_{11}$,[15] $H_4Os_4(CO)_{12}$,[13] $H_2Os_3(CO)_{12}$,[16] $[Et_4N][HRu_3(CO)_{11}]$,[17] Na_2-

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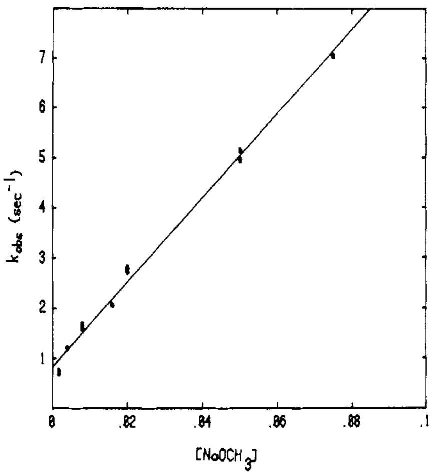

Figure 1. Kinetics plot of observed rate constants for the deprotonation of $H_4Ru_4(CO)_{11}(P(OCH_3)_3)$ in methanol as a function of methoxide concentration.

$[Os(CO)_4]$,[18] $H_2Os(CO)_4$,[19] $[PPN][HOs(CO)_4]$[20] (PPN^+ = bis(triphenylphosphine)nitrogen(1+), $[PPN][HRu(CO)_4]$,[20] $[PPN][DOs(CO)_4]$,[21] $[PPN][DRu(CO)_4]$,[21] $[PPN][HFe(CO)_4]$,[22] $H_2Fe(CO)_4$, and $H_4Ru_4(CO)_{12-x}(P(OCH_3)_3)_x$ (x = 1, 2, 3)[23] were all prepared by published procedures. The deuterated complexes $D_4Ru_4(CO)_{12}$, $[Ph_4As][D_3Ru_4(CO)_{12}]$, and $D_2Os(CO)_4$ were prepared in the manners analogous to those used for the respective perprotio analogues with the following exceptions. For $D_4Ru_4(CO)_{12}$,D_2 gas was used as a reductant in place of H_2 and the complex was recrystallized from CH_2Cl_2/CH_3OD rather than purified by column chromatography. $[Ph_4As][D_3Ru_4(CO)_{12}]$ was prepared by the reaction of $NaOCH_3$ (10 mg) in CH_3OD with $D_4Ru_4(CO)_{12}$ (50 mg) followed by addition of D_2O to effect precipitation. $D_2Os(CO)_4$ was prepared by using D_3PO_4 to protonate $Na_2Os(CO)_4$ followed by repeated trap to trap distillation for purification. In all these cases, the glassware utilized had been pretreated by exposure to D_2O vapor to minimize isotopic exchange with trace H_2O. Analyses were performed at Schwarzkopf Microanalytical Laboratories.

Instrumentation. Infrared spectra were obtained on a Perkin-Elmer Model 683 infrared spectrophotometer calibrated against polystyrene. UV-visible spectra were taken on a CARY 14 recording spectrophotometer in a 1-cm path length quartz cell. The cell had a 10-cm extension which could be fitted with a rubber septum cap to allow samples to be under CO, H_2, or N_2 atmosphere. Methoxide or buffer solutions would be added by syringe through the septum. A Durrum-Gibson D110 stopped-flow spectrophotometer was used for kinetics studies. The drive syringes and observation block were thermostated at 25 ± 1 °C. Optical density changes were monitored at wavelengths ranging from 280 to 450 nm. Solutions were transfered to the drive syringes via disposable polyethylene syringes.

^1H NMR spectra were obtained on Varian Associates CFT-20 and XL-100 NMR spectrometers operating in the pulsed Fourier transform mode with deuterium lock. Deuterated solvent was the lock substance and samples were referenced to residual protons in the solvent.

Calculations were performed on a Digital Equipment Corp. PDP-11/34 computer operating on a time-sharing UNIX system.

The mass spectrum of $D_4Ru_4(CO)_{12}$ was obtained on the departmental AEI MS 902 with a probe temperature of 100 °C and a 70-V ionizing voltage.

Kinetic Studies. Rates of deprotonation were determined with a stopped-flow spectrophotometer. A solution of the metal hydride in methanol was mixed with methanol solutions of sodium or potassium methoxide of various concentrations and the reaction followed by the changes in the optical density (OD) of the resulting solution. All rate determinations were made at 25 ± 1 °C with N_2-saturated solutions except where noted. Alkali metal methoxide solutions were prepared by dissolving freshly cut metal in degassed methanol. Stock solutions (0.1 N) were prepared new for each set of experiments, and concentrations were determined by titrating stock solution aliquots, diluted into degassed water, with standard HCl solutions, using phenopthalein as the indicator. Buffer solutions for equilibrium experiments were prepared from veronal (5,5′-diethylbarbituric acid, pK_a = 12.7 in CH_3OH)[24] or benzoic acid (p_A = 9.4 in CH_3OH)[24] by mixing the acid (0.05 M) with various amounts of standardized methoxide solutions. The pH values of these buffer solutions were determined with indicators of known pK_a in CH_3OH (bromthymol blue, 12.4; phenol red, 12.8).[24] Solutions for deuterium isotope effect kinetics studies were prepared from CH_3OD (99% D) purchased from Stabler Isotope Chemicals.

Table I. Rate Constants for the Reaction

$$H_xM_y(CO)_z + CH_3O^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_{x-1}M_y(CO)_z^- + CH_3OH$$

and pK_a Values Obtained for the Hydrides $H_xM_y(CO)_z$ in Methanol (25 °C)

complex	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}	pK_a[a]
$H_4Ru_4(CO)_{12}$	8.7×10^3	0.08	11.7
$H_4Ru_4(CO)_{11}(P(OCH_3)_3)$	8.4×10^1	0.84	14.7
$H_4Ru_4(CO)_{10}(P(OCH_3)_3)_2$			>15
$H_4Os_4(CO)_{12}$	2.2×10^3	0.05	12.0 (12.3)
$H_4FeRu_3(CO)_{12}$	8.2×10^3	0.1	(11.8)
$H_2Ru_4(CO)_{13}$	8.0×10^3	0.02	(11.1)
$H_2FeRu_3(CO)_{13}$	1.6×10^4	0.05	(11.2)
$H_2Os_3(CO)_{12}$	2.2×10^3	25.	14.7
$H_2Os(CO)_4$	2.3×10^1 [b]	0.76[b]	15.2[b]

[a] pK_a calculated from eq 6; values in parentheses from buffer experiments. [b] Values obtained from linear fit of k_{obsd} vs. $[NaOCH_3]$ linear fit for $[NaOCH_3] < 0.1$ M.

The data from a stopped-flow kinetics run were in the form of absorbance vs. time traces on the storage oscilloscope and were recorded with the oscilloscope camera. These traces were digitized and a computer program was used to obtain a linear least-squares fit to ln $(A - A_\infty)$ vs. time. Plots of the fitted line and of the data were produced to indicate any systematic deviations from linearity. Correlation coefficients were generally better than 0.998. The slope of the line is the negative of the observed rate constant.

For the reaction shown in eq 4, the observed rate constant is given by

$$HA + CH_3O^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + CH_3OH \qquad (4)$$

eq 5. A linear fit of k_{obsd} vs. $[CH_3O^-]$ was calculated, and a plot was

$$k_{obsd} = k_1[CH_3O^-] + k_{-1} \qquad (5)$$

produced to indicate systematic deviations from linearity. An example is shown in Figure 1. The slope of this line is k_1 and the intercept is k_{-1}. The uncertainty in the rate constants is <±10% unless otherwise noted. The pK_a was calculated from these values according to the relationship in eq 6, where pK_s is the negative log of the ion product of methanol (16.7 at 25 °C).[25]

$$pK_a = pK_s - \log (k_1/k_1) \qquad (6)$$

In some cases solutions of both HA and A^- were sufficiently stable to allow equilibrium concentrations determinations by static spectral measurements on the Cary 14 spectrophotometer thermostated at 25 °C. For those cases, the spectrum of the complex was measured in a buffer solution and the pK_a calculated from

$$pK_a = pH - \log ([A^-]/[HA]) \qquad (7)$$

For cases where sufficiently concentrated methoxide solutions (>10^{-4} M) produced nonzero equilibrium concentrations of the acid form of the complex, the A_∞ values of the stopped-flow traces were also used to calculate the pK_a in the same manner. However, in several experiments, buffer solutions were used in the stopped flow to produce solutions of measurable $[A^-]/[HA]$ ratios. In such experiments k_{-1} could be determined by combining eq 6 and 7. In several cases k_{-1} could also be measured directly from the deprotonation rates in the buffer solution and eq 5. For example, with $H_2Ru_4(CO)_{13}$ the value of k_{-1} calculated from

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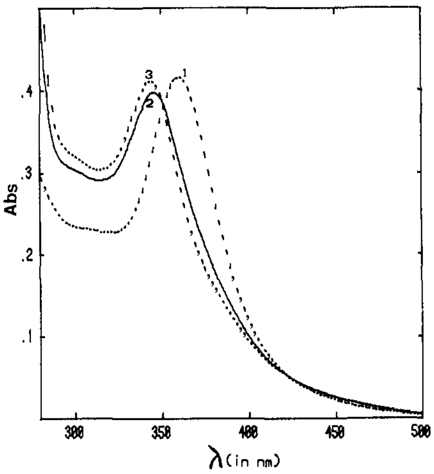

Figure 2. Electronic spectrum of $H_4Ru_4(CO)_{12}$ (2.5×10^{-5} M) (1) in neutral methanol, (2) in pH 12.7 veronal/veronalate buffered methanol, (3) in 2.5×10^{-3} M $NaOCH_3$ in methanol.

the equilibrium data was 1.6×10^{-2} s^{-1} while that measured directly in buffer solution was 2.0×10^{-2} s^{-1}.

Results

Table I summarizes the rate constants and equilibrium data obtained for the various carbonyl hydride complexes studied here. It will be noted that several of these values differ from those published in the original communication,[1,26] although the qualitative conclusions drawn in that earlier work remain valid (see Discussion). A case by case summary of the results follows.

$H_4Ru_4(CO)_{12}$. A solution of $H_4Ru_4(CO)_{12}$ in methanol shows a peak at 362 nm (ϵ 17 500) as seen in Figure 2. Upon addition of $NaOCH_3$ solution the peak shifts to 344 nm (ϵ 17 900) with isosbestic points at 352 and 418 nm. These spectral changes are reversible upon the addition of acetic or triflic acid. The spectrum resulting from the addition of sodium methoxide is identical with that of independently synthesized $[AsPh_4][H_3Ru_4(CO)_{12}]$ in methanol. The pK_a for $H_4Ru_4(CO)_{12}$ was determined to be 11.9 by equilibration in a veronal/veronalate buffer by using the methods described in the Experimental Section. The spectrum of the equilibrium mixture in a buffer solution of pH 12.7 is also shown in Figure 2. In the stopped-flow spectrometer, the expected decrease in absorbance at 380 nm is observed upon mixing the hydride and methoxide solutions. Plots of ln $(A - A_\infty)$ vs. time are linear and the k_{obsd} values determined from these experiments follow the linear relationship described by eq 5, giving a slope (k_1) of 8.7×10^3 M^{-1}/s^{-1} and an intercept (k_{-1}) of 8×10^{-2} s^{-1}. These data yield a pK_a of 11.7 for the compound, in good agreement with the equilibrium results.

It is assumed that the spectral changes observed are indeed due to deprotonation according to eq 8. However, the kinetics and

$$H_4Ru_4(CO)_{12} + CH_3O^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_3Ru_4(CO)_{12}^- + CH_3OH \quad (8)$$

the UV-visible spectral changes presented thus far do not preclude the possibility of formation of a methoxycarbonyl species as in eq 9. Such a reaction would obey the same rate law, and

$$H_4Ru_4(CO)_{12} + CH_3O^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_4Ru_4(CO)_{11}(C(O)OCH_3)^- \quad (9)$$

methoxycarbonyl adduct formation of similar rates has been noted

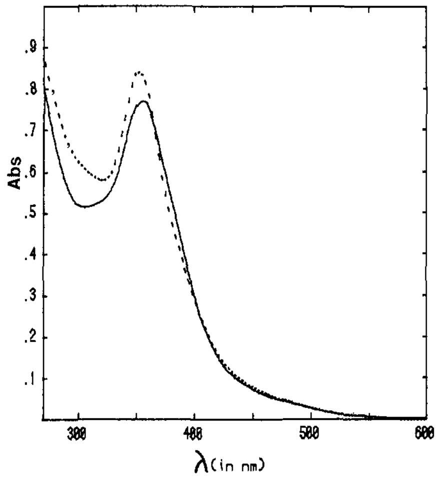

Figure 3. UV-visible spectrum of $H_4Ru_4(CO)_{11}(P(OCH_3)_3)$ (6×10^{-5} M). Dashed curve results upon addition of sodium methoxide (5×10^{-2} M).

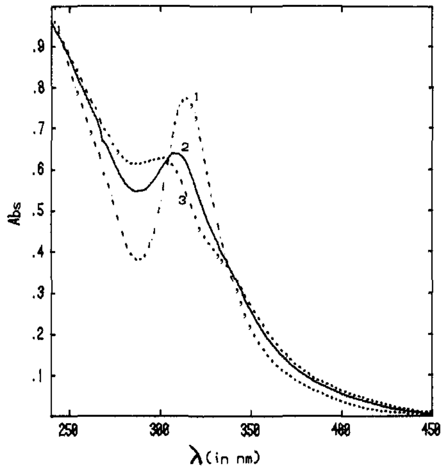

Figure 4. Electronic spectrum of $H_4Os_4(CO)_{12}$ (1) in neutral methanol, (2) in pH 12.7 veronal/veronate buffered methanol, (3) in 5×10^{-2} M $[NaOCH_3]$ in methanol.

with the triangular clusters $M_3(CO)_{12}$ (M = Fe, Ru, or Os).[27] However, this proposal can be discounted for $H_4Ru_4(CO)_{12}$ given that the proton NMR spectrum of the reaction products with sodium methoxide in methanol (singlet at δ −16.9 relative to Me_4Si) is qualitatively identical with that found[7] for the $H_3Ru_4(CO)_{12}^-$ ion in a variety of other solvents at room temperature. When this solution is cooled to −95 °C, the original hydride resonance at δ −16.9 splits into a doublet centered at δ −15.95, a singlet at δ −17.44, and a triplet at δ −19.05 with intensities in the ratio 2/3.9/1. Similar behavior was seen previously in the other solvents[7] and attributed to the presence of two isomers, one of C_{3v} symmetry (δ −17.50) and one of C_2 symmetry (δ −15.95 and −19.05) which interconvert rapidly on the NMR time scale at room temperature but slowly at low temperature.

$H_4Ru_4(CO)_{12-k}[P(OCH_3)_3]_k$ (k = 1, 2, 3). The UV-visible spectrum of $H_4Ru_4(CO)_{11}[P(OCH_3)_3]$ is shown in Figure 3. There is a peak at 356 nm (ϵ 1.24×10^4 M^{-1} cm^{-1}), which shifts to 353 nm (ϵ 1.35×10^4 M^{-1} cm^{-1}) upon addition of sodium methoxide to 2×10^{-2} M. Intermediate $[NaOCH_3]$ gave isosbestic points at 367 and 402 nm. An increase in absorbance is seen at 350 nm which can be followed on the stopped-flow spectrometer. The plot of k_{obsd} vs. $[CH_3O^-]$ gives $k_1 = 8.43 \times 10^1$ M^{-1} s^{-1} and $k_{-1} = 0.84$ s^{-1}. The pK_a is calculated to be 14.7 with these values.

The spectra of the bis- and trisphosphite-substituted clusters displayed maxima at 370 (ϵ 1.6×10^4 M^{-1} cm^{-1}) and 377 nm (ϵ

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(26) After careful reexamination of the original kinetics data (Kresge, C. Ph.D. Thesis, University of California, Santa Barbara, 1979), we conclude that the differences between the results reported in the preliminary communication and in the present article resulted from a failure to appreciate the fragility of certain complexes. It is apparent that in these cases the rate studies were carried out on impure compounds owing to partial decomposition prior to the kinetics measurements. In such cases both metal carbonyls and metal carbonyl hydrides of unknown composition, all of which can react with methoxide ion (ref 27), may have been present in the reaction solution.

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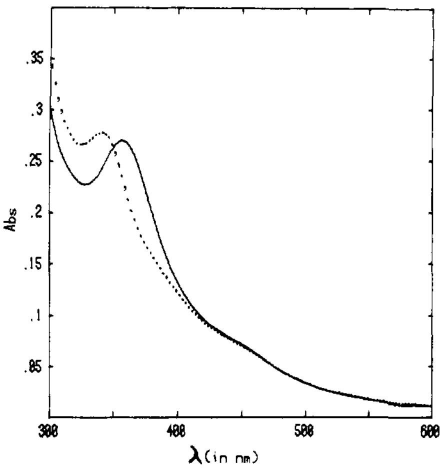

Figure 5. UV-vis spectrum of $H_4FeRu_3(CO)_{12}$ (7.7×10^{-5} M) in methanol. Dashed curve results on addition of $NaOCH_3$ (5×10^{-2} M).

1.9×10^4 M^{-1} cm^{-1}), respectively. The spectral changes seen upon addition of $NaOCH_3$ (to 0.01 M) were insufficient to allow kinetics studies. Since all the other clusters studied showed marked changes in the UV-visible spectrum upon deprotonation, one is left to conclude that the pK_a's of these complexes are greater than 15.

$H_4Os_4(CO)_{12}$. The UV-visible spectrum of $H_4Os_4(CO)_{12}$ in methanol is shown in Figure 4. The neutral hydride has a peak at 313 nm, and addition of $NaOCH_3$ shifts this peak to 340 nm with a shoulder at about 300 nm. Neutralization with acetic acid reverses the spectral changes with isosbestic points maintained at 246, 304, and 337 nm. The same absorbance changes are seen with the stopped-flow spectrometer. Equilibrium studies using veronal buffer solutions indicate a pK_a of 12.3. A kinetics plot of k_{obsd} measured at 320 nm on the stopped-flow spectrometer vs. [CH_3ONa] gives the values $k_1 = 2.22 \times 10^3$ M^{-1} s^{-1} and $k_{-1} = 0.05$ s^{-1}. From these can be calculated a pK_a of 12.0, in fair agreement with the equilibrium result.

$H_4FeRu_3(CO)_{12}$. The spectrum of $H_4FeRu_3(CO)_{12}$ in methanol is shown in Figure 5. The neutral complex displays a peak at 356 nm (ϵ 1.0×10^4). Upon addition of $NaOCH_3$, the peak shifts to 340 nm (9.2×10^3) with an isosbestic point maintained at 350 nm. Plots of k_{obsd}, determined at 370 nm, vs. [$NaOCH_3$] are linear and give $k_1 = 8.2 \times 10^3$ M^{-1} s^{-1}. However k_{-1} is small compared to $k_1[CH_3O^-]$ for all concentrations of sodium methoxide greater than 10^{-4} M, so k_{-1} was determined from the kinetic buffer experiment to be 0.1 ± 0.02 s^{-1}, giving a pK_a value of 11.8.

$H_2Ru_4(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$. The UV-visible spectrum of $H_2Ru_4(CO)_{13}$ in methanol is shown in Figure 6. The kinetics were studied under a carbon monoxide atmosphere since the substrate proved more stable under these conditions. Upon addition of $NaOCH_3$ to a solution of $H_2Ru_4(CO)_{13}$ in methanol, there is an abrupt spectral change followed by a slower change having isobestic points at 398 and 420 nm. The final spectrum is identical with that of the $[HRu_3(CO)_{11}]^-$ ion.[27]

The second reaction is slow on the stopped-flow time scale, so the initial step can be studied in isolation. The plot of k_{obsd} vs. [$NaOCH_3$] for a monitoring wavelength of 400 nm gives a k_1 for the initial step at 8.03×10^3 M^{-1} s^{-1}.

The intercept of this plot (k_{-1}) is not discernible. Furthermore, the oscilloscope traces from which the kinetics data were obtained showed no evidence of an incomplete conversion of $H_2Ru_4(CO)_{13}$, indicating that k_{-1} is much smaller than $k_1[CH_3O^-]$ at all the methoxide concentrations used. Therefore, the k_{-1} and pK_a for $H_2Ru_4(CO)_{13}$ were obtained from equilibrium measurements in buffer solutions. The secondary conversion of $HRu_4(CO)_{13}^-$ to $HRu_3(CO)_{11}^-$ required that these measurements be performed on the stopped-flow spectrometer. When a solution of $H_2Ru_4(CO)_{13}$ is deprotonated with a veronal buffer solution having a pH of 11.9, the absorbance does not go completely to that of $HRu_4(CO)_{13}^-$ determined by deprotonation of the same solution by 10^{-2} M NaOCH$_3$. This indicates that an equilibrium mixture of $H_2Ru_4(CO)_{13}$ and $HRu_4(CO)_{13}^-$ is formed in the buffer solution. The pK_a can be calculated as 11.0 from the known pH of the buffer solution and the observed ratio of the final $H_2Ru_4(CO)_{13}$ and $HRu_4(CO)_{13}^-$ concentrations. From this and k_1, a k_{-1} value of 1.6×10^{-2} s^{-1} is determined.

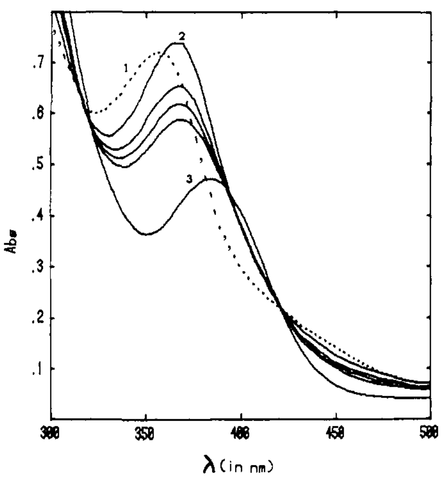

Figure 6. Spectral changes observed on addition of $NaOCH_3$ to a methanol solution of $H_2Ru_4(CO)_{13}$ under 1 atm of CO: (1) spectrum of $H_2Ru_4(CO)_{13}$ (3.4×10^{-2} M) in neutral CH_3OH, (2) spectrum immediately after adding $NaOCH_3$ (5×10^{-2} M), (3) final spectrum after several hours.

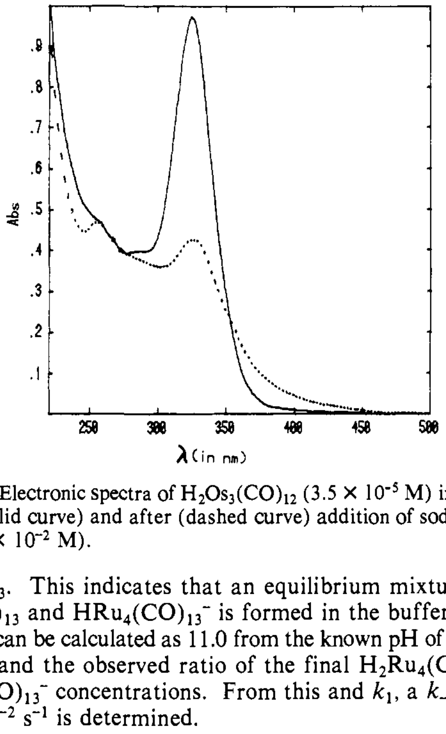

Figure 7. Electronic spectra of $H_2Os_3(CO)_{12}$ (3.5×10^{-5} M) in methanol before (solid curve) and after (dashed curve) addition of sodium methoxide (5×10^{-2} M).

$H_2FeRu_3(CO)_{13}$ exhibits behavior similar to that observed for $H_2Ru_4(CO)_{13}$. Addition of $NaOCH_3$ to $H_2FeRu_3(CO)_{13}$ in CH_3OH under 1 atm of CO causes an abrupt change in the spectrum followed by a slower one, finally giving the spectrum of $HRu_3(CO)_{11}^-$. A plot of k_{obsd} determined at 400 nm vs. [$NaOCH_3$] gives k_1 as 14.7×10^3 M^{-1} s^{-1}, but k_{-1} is not measurable. The latter value was obtained from stopped-flow experiments with buffer solutions which gave $k_{-1} = 0.05$ s^{-1} and a pK_a of 11.2.

$H_2Os_3(CO)_{12}$. The electronic spectrum of $H_2Os_3(CO)_{12}$ in methanol displays a λ_{max} at 324 nm (ϵ 2.8×10^4 M^{-1} cm^{-1}) (Figure 7). Addition of $NaOCH_3$ leads to a large decrease in absorbance at 320 nm which can be followed in the stopped-flow spectrometer. A kinetics plot of k_{obsd} vs. [$NaOCH_3$] gives $k_1 = 2.22 \times 10^3$ M^{-1} s^{-1} and $k_{-1} = 25$ s^{-1}. From these values are calculated a pK_a of 14.7. Using the A_∞ values to estimate equilibrium concentrations gives a pK_a value of 14.8.

$H_2Os(CO)_4$. Addition of $NaOCH_3$ to a methanol solution of $H_2Os(CO)_4$ leads to an absorbance increase at 350 nm which can be followed in the stopped-flow spectrophotometer. Plots of ln ($A_\infty - A$) are linear to four half-lives with initial ($t = 0$) absor-

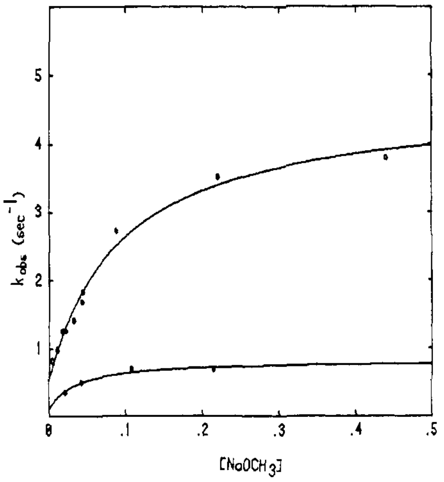

Figure 8. Plots of k_{obsd} vs. [$NaOCH_3$] for $H_2Os(CO)_4$ (upper) and $D_2Os(CO)_4$ in CH_3OH and CH_3O^2H solutions, respectively. Curves drawn for illustrative purposes.

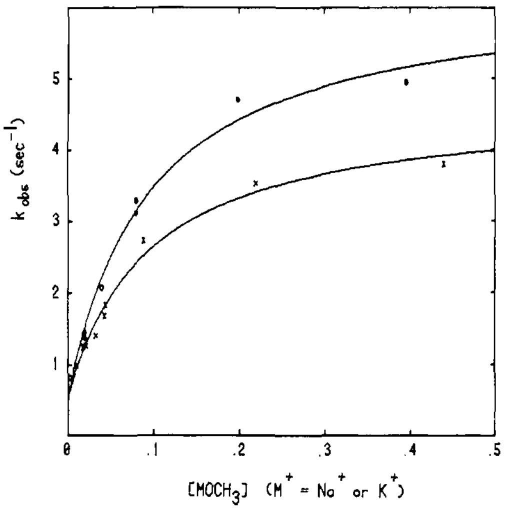

Figure 9. Comparisons of rate constants observed at various methoxide concentrations for the deprotonation of $H_2Os(CO)_4$ in methanol by $KOCH_3$ (upper curve) and by $NaOCH_3$.

bances essentially zero for all [$NaOCH_3$] concentrations. The A_∞ values vary with the methoxide concentration in a manner indicating the presence of both $H_2Os(CO)_4$ and its conjugate base under conditions of lower [$NaOCH_3$]. The plot of k_{obsd} vs. [$NaOCH_3$] (Figure 8) deviates substantially from linearity at higher [$NaOCH_3$]; however, a least-squares linear fit of the data for [$NaOCH_3$] < 0.1 M gives the rate constants $k_1 = 22.5$ M^{-1} s^{-1} and $k_{-1} = 0.76$ s^{-1}. From these data the pK_a of $H_2Os(CO)_4$ in methanol is calculated to be 15.2. Calculations of the equilibrium concentrations of the hydride and its conjugate base drawn from the A_∞ values of the stopped-flow experiments at low [$NaOCH_3$] give a pK_a value of 14.8.

There are several possible interpretations of the nonlinearity of the plot shown in Figure 8. An obvious consideration is the possibility of kinetics effects from ion pairing of Na^+ with either the OCH_3^- reactant or the anionic osmium product at the higher methoxide concentrations. Ion pairing of alkali metal cations with metal carbonyl anions in organic solvents is well established.[28] Furthermore, ion pair association constants K_a of 50–100 M^{-1} have been estimated for $K^+OCH_3^-$ in methanol, a K_a value of 30 M^{-1} determined for $K^+BPh_4^-$ in methanol, and K_a values of 36 and 49 M^{-1}, respectively, have been determined for potassium and sodium ethoxide in ethanol.[29] Given these values, pairing of the alkali methoxides and between metal carbonylates and alkali cations would be extensive for the higher methoxide concentrations used to deprotonate $H_2Os(CO)_4$. That this may be a significant contributor was shown by examining the kinetics of the reaction between $H_2Os(CO)_4$ and $KOCH_3$ in methanol (Figure 9). From plots of k_{obsd} values for [$KOCH_3$] < 0.1 M, values for k_1, k_{-1}, and pK_a were determined as 29 M^{-1} s^{-1}, 0.8 s^{-1}, and 15.1, respectively. Attempts to model these rate/concentration patterns by assuming simple equilibria between the separated ions M^+ and OCH_3^- and one-to-one ion paris proved only marginally successful, suggesting the possibility of higher order ionic aggregates.

An alternative mechanism would be a unimolecular rearrangement of the substrate followed by a second-order reaction with CH_3O^- ($H_2Os(CO)_4 \rightleftarrows$ I, I + $OCH_3^- \rightarrow$ P). The rate behavior with respect to methoxide concentration could be simulated with this model.[1a] However, such a model alone provides no reasonable explanation for the differences between the potassium and sodium methoxide rate studies.

$H_2Ru(CO)_4$. Kinetic studies of the acidity of $H_2Ru(CO)_4$ were not successful due to the thermal instability of the complex. Neat $H_2Ru(CO)_4$ decomposes to an uncharacterized red solid[30] at temperatures above −30 °C, and when [PPN][$HRu(CO)_4$] is dissolved in neutral room-temperature methanol, the electronic spectrum observed appears to be that of the $HRu_3(CO)_{11}^-$ ion. When [PPN][$HRu(CO)_4$] is dissolved in 0.1 M sodium methoxide/methanol, the cluster formation is slowed but proceeds within minutes to completion. A dry THF solution of [PPN][$HRu(CO)_4$] is thermally stable at room temperature. When a small amount of water is added to the latter solution (0.1 mL in 3.5 mL), formation of $HRu_3(CO)_{11}^-$ occurs within minutes. This cluster formation apparently is occurring through solvolysis of the anion, perhaps as in eq 10–12.

$$HRu(CO)_4^- + ROH \rightleftarrows H_2Ru(CO)_4 + RO^- \quad (10)$$

$$HRu(CO)_4^- + H_2Ru(CO)_4 \rightarrow [HRu_2(CO)_8^-] + H_2 \quad (11)$$

$$[HRu_2(CO)_8^-] + H_2Ru(CO)_4 \rightarrow HRu_3(CO)_{11}^- + CO + H_2 \quad (12)$$

The thermal stabilities of $H_2Ru(CO)_4$ and $H_2Fe(CO)_4$ are similar, yet solutions of [PPN][$HFe(CO)_4$] in neutral methanol do not undergo comparably rapid decomposition. Acidification of such a solution causes formation[31] of the $HFe_3(CO)_{11}^-$ ion. Substitution for CO on $H_2Ru(CO)_4$ is slower than on $H_2Fe(CO)_4$.[32] Thus, the instability of [PPN][$HRu(CO)_4$] in neutral methanol implies either that $HRu(CO)_4^-$ is a stronger nucelophile than $HFe(CO)_4^-$ or that $HRu(CO)_4^-$ is a stronger base than is $HFe(CO)_4^-$. It has been shown that the nucleophilicity of organometallic anions parallels their basicity.[33] Therefore, if the cluster formation indeed occurs via eq 10, the thermal instability of $HRu(CO)_4^-$ in methanol suggests that $H_2Ru(CO)_4$ is a considerably weaker acid than $H_2Fe(CO)_4$. The pK_a of the latter complex in methanol has been estimated[1b] as 6.9 from the potentiometric titration data reported by Hieber and Hübel.[6b] Thus we conclude that for $H_2Ru(CO)_4$ the pK_a is significantly greater than 7.

$D_4Ru_4(CO)_{12}$. The reaction of $D_4Ru_4(CO)_{12}$ with $NaOCH_3$ was studied on the stopped-flow spectrometer in CH_3OD solution.[34] The plot of k_{obsd} vs. [$NaOCH_3$] was linear but the intercept (hence k_{-1}) was indeterminate. The slope k_1 equaled 1.0×10^4 M^{-1} s^{-1}.

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(34) The isotopic purity of the deuterated substrate in these studies will be largely determined by that of the CH_3OD solvent (99% D) given the facile exchange between the solvent and substrate.

According to this, the calculated kinetic isotope effect $k_1(H)/k_1(D)$ is 0.8 ± 0.2; however, it should be noted that the solvent was different in the two experiments (CH_3OH and CH_3OD, respectively).

The ^1H NMR behavior of $[AsPh_4][H_3Ru_4(CO)_{12}]$ in CD_3OD was discussed previously with regard to the solution structure of the hydride anion. This same solution was allowed to warm in an attempt to obtain a value of $k_{-1}(D)$ through the exchange rate as monitored by the disappearance of the hydride signal. However, widely varying results were obtained, and the procedure failed to give a reliable value for $k_{-1}(D)$.

$D_2Os(CO)_4$. Stopped-flow experiments were performed sodium methoxide to dedeuterate $D_2Os(CO)_4$ in CH_3OD solution.[34] A plot of k_{obsd} vs. $[NaOCH_3]$ is shown in Figure 8. The curves are analogous to these for the perprotic system but rates for the deuterated complex are substantially lower at each concentration of methoxide including the intercept. A plot of $k_{obsd}(H)/k_{obsd}(D)$ vs. $[NaOCH_3]$ shows the former to be nearly constant with a value of $\sim 4.0 \pm 0.5$ over the range 0.0–0.2 M in sodium methoxide concentration. This relative constancy is consistent with a common deprotonation mechanism despite the curvatures in the rate plots and with the view that these curvatures are due to the equilibrium formation of relatively inactive Na^+,OCH_3^- ion pairs or larger aggregates.

Discussion

pK_a Values. Taking advantage of the relatively slow rates of deprotonation (see below) allows determination of pK_a values of the $H_xM_y(CO)_z$ species studied here by measuring kinetics for the forward and reverse reactions (eq 4) in anhydrous methanol. In some cases, equilibria could also be checked by buffer/indicator methods; however, the instability of initially formed species under the reaction conditions prevented this method in several circumstances. The data in Table I indicate that the iron triad metal carbonyl hydrides investigated here are each weak acids in methanol with dissociation constants (pK_a's 11.0–15.2) somewhat larger than the autoionization constant of the solvent ($pK_s = 16.7$). By comparison acetic acid ($pK_a = 9.6$),[24] ammonium ion NH_4^+ ($pK_a = 10.8$)[25] and $H_2Fe(CO)_4$ ($pK_a = 6.9$, vide supra) are somewhat more acidic in methanol under comparable conditions.

Among the tetranuclear carbonyls, the tetrahydrides $H_4M_4(CO)_{12}$ each displayed pK_a values about 12, with little difference between the cases where M_4 is Ru_4, Os_4, or Ru_3Fe. For each of these clusters, the protons removed originate from an edge bridging position. The substitution of the trimethyl phosphite ligand for CO in the H_4Ru_4 clusters make these species less acidic, the first phosphite substitution decreasing K_a by 3 orders of magnitude, subsequent substitutions decreasing the acidity to the point where significant deprotonation was immeasurable in 0.01 M methoxide solutions. This effect is consistent with the greater σ donor, poorer π acceptor character of $P(OCH_3)_3$ relative to CO,[33] an effect which apparently is transmitted to all the bridging hydride positions despite the fact that not all the edge bridging hydrides are in positions adjacent to the substituted ligand. The two $H_2M_4(CO)_{13}$ complexes investigated are each somewhat more acidic than their $H_4M_4(CO)_{12}$ analogues. Given that structural studies have shown that the tridecacarbonyl clusters have two bridging carbonyls[35] while the dodecacarbonyl analogues have none,[36] the increased activity of the former species is consistent with the widely held perception that bridging carbonyls are more electron withdrawing than are terminal carbonyls.[37]

More dramatic differences are seen between the acidities of the bridging hydrides of the pseudotetrahedral $H_4Os_4(CO)_{12}$ cluster and those of the terminal hydrides of the open chain trinuclear complex $H_2Os_3(CO)_{12}$ and of the mononuclear $H_2Os(CO)_4$ species. These limited data imply that for analogous complexes of the same element, bridging hydrides will be more acidic than are terminal hydrides, a trend which has been noted previously with polynuclear boron hydrides[38] and with the rhenium carbonyl hydrides $HRe(CO)_5$ and $H_3Re_3(CO)_{12}$.[39] It is clear, however, that a greater body of data must be accumulated under comparable conditions in order to extend this generalization to other transition-metal hydrides. For example, the relative instability of the iron cluster $H_4Fe_4(CO)_{12}$ and of mononuclear $H_2Ru(CO)_4$ prevented our measurements of pK_a values for an iron–iron bridging hydride and for a terminal ruthenium hydride. However, in the context of the above discussion, one would argue that $H_4Fe_4(CO)_{12}$ should be very acidic with a pK_a less than 6.9 in methanol while that of $H_2Ru(CO)_4$ should be greater than that of $H_4Ru_4(CO)_{12}$ (11.7).

Recent studies by Norton[12] in acetonitrile solution have established pK_a's (values in parentheses) in that medium for the terminal osmium hydrides $H_2Os(CO)_4$ (20.8), $Os(CO)_4(CH_3)H$ (23.0), and $H_2Os_2(CO)_8$ (20.4), as well as for the series $(\eta^5\text{-}C_5H_5)M(CO)_3H$, M = Cr (13.3), Mo (13.9), or W (16.1). In acetonitrile, the acidity of $H_2Os(CO)_4$ is greater than that of acetic acid ($pK_a = 22.3$); however, it is notable that both of these acids are considerably poorer acids in this solvent than in the more ionizing methanolic and aqueous solvents. (The solvent-induced change in the order in the strengths of the two acids can be largely attributed in the dramatic increase in the acetic acid pK_a on going to the non-hydrogen bonding solvent.) Similarly the $(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Cr, Mo, W) hydrides are much stronger acids (pK_a's 5.39, 6.19, and 8.00, respectively) in 70/30 methanol/water[40] than in acetonitrile.

The differences recorded in the pK_a's of the mononuclear and dinuclear dihydrides $H_2Os(CO)_4$ and $H_2Os_2(CO)_8$ in acetonitrile[12] are quite close to the differences reported here for the mono- and trinuclear species $H_2Os(CO)_4$ and $H_2Os_3(CO)_{12}$ in methanol. In each case the polynuclear complex is more acidic by about half a pK_a unit, consistent with the ability of the larger species to delocalize the anionic charge created when the substrate is deprotonated.

The pK_a values measured for the series $(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Cr, Mo, W) in acetonitrile and in methanol/water reinforce the conclusion drawn from the $H_2M(CO)_4$ (M = Fe, Os) pK_a's that analogous transition-metal hydrides become less acidic as one procedes down a column of the periodic chart.[1] Supporting evidence of this tendency is drawn from the qualitative observations that $(\eta^5\text{-}C_5H_5)_2MoH_2$ is more acidic than the tungsten analogue by several pK_a units in aqueous dioxane[41] and that the gas-phase proton affinities[42] of the following series fall into the orders noted: $M(CO)_6$ (Cr < Mo $\simeq$ W), $M(CO)_5CH_3$ (Mn < Re), $(\eta^5\text{-}C_5H_5)_2M$ (Fe < Ru), and $(\eta^5\text{-}C_5H_5)M(CO)_2$ (Co < Rh). However, it should also be noted that qualitative studies by Vidal and Walker[43] have been interpreted to indicate the order of acidities $HRh(CO)_4 > HCo(CO)_4 > HIr(CO)_4$ in a mixed tetraglyme–toluene (6:1) solvent.

Rates for Deprotonation/Protonation. Examination of Table I indicates that the deprotonation rates of these metal carbonyl hydrides, while considerably more rapid than once suggested,[7] are slow relative to many acids of similar pK_a's in reaction with a base as strong as methoxide. The corollary is that protonation of the conjugate base $H_{x-1}M_y(CO)_z^-$ by solvent is also comparatively slow. Few direct comparisons in methanol appear to be available; however, in aqueous solution, nitrogen acids such as NH_4^+ ($pK_a = 9.3$) and oxygen acids such as phenol ($pK_a = 10.0$) react with hydroxide ion (eq 13) with second-order rate constants (k_f) in excess of 10^{10} M^{-1} s^{-1}.[44]

$$HA + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^- + H_2O \tag{13}$$

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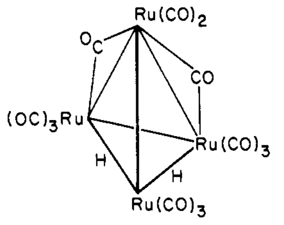
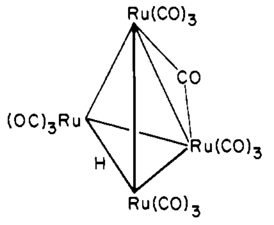
Correspondingly, the reaction of the conjugate base (NH_3 or $C_6H_5O^-$) with H_2O occurs with rate constants k_r about 10^6 s^{-1}. In methanol, rates for symmetrical proton transfer between benzoic acid and its conjugate base displays a bimolecular rate constant of 10^8 M^{-1} s^{-1} (25 °C).[45] Similarly, the proton exchange rate constant between CH_3O^- and CH_3OH in anhydrous methanol is 7×10^8 M^{-1} s^{-1} (25 °C) less than an order of magnitude smaller than that for analogous exchange between OH^- and H_2O in water.[46] The significantly slower deprotonation/protonation rates for the metal hydrides studied here are more reminiscent of the slow proton transfer reactions between carbon acids and hydroxide ion. For example, the rate constants k_f for AH = CH_3NO_2 (pK_a = 10.2) and AH = $H_2C(COCH_3)_2$ (pK_a = 9) are but 25 and 4×10^4 M^{-1} s^{-1}, respectively,[47] in each case many orders of magnitude slower than for the nitrogen and oxygen acids of comparable strength. The accepted rationale for these differences is that proton transfer from the carbon acids involves considerably more electronic and structural rearrangement than for the oxygen and nitrogen acids.

Several factors can be envisioned as possibly responsible for the relatively low rates of proton transfer from (and to) the metal hydrides (and anions) studied here. One might be structural changes in the substrate itself between the conjugate acid and base forms. Such changes have been noted between the $Fe_4(CO)_{13}^{2-}$ ion and its protonated forms.[48] Given the pseudooctahedral structure of $H_2M(CO)_4$ and the pseudo-trigonal-bipyramidal structure[10] of the $HM(CO)_4^-$ anions (axial H), such structural changes certainly are the result of some of the protonation/deprotonation reactions described here. Similarly, the deprotonation of $H_2Ru_4(CO)_{13}$ which has two edge-bridging CO's (structure A) would give the anion $HRu_4(CO)_{13}^-$ having but one edge-bridging CO (B).[49] The changes in carbonyl and ruthenium frameworks between the prototype cluster tetrahydride $H_4Ru_4(CO)_{12}$ and its conjugate base salt [PPN][$H_3Ru_4(CO)_{12}$] are smaller,[50] although in solution the cluster anions do exist in two different conformers determined by the positions of the bridging hydrides (see Results).



A



B

Equally significant are the electronic perturbations of the cluster upon deprotonation. These are reflected in the shift of the envelope of infrared CO stretching bands to lower frequency upon deprotonation of $H_4Ru_4(CO)_{12}$ indicating delocalization of the resultant negative charge to all metal centers and their coordinated carbonyls.[7] (A similar observation was made by Jordan and Norton.)[12] One reason for the extent of these shifts can be related to the nature of the coordinated hydrogen. Calculations based upon photoelectron spectra of metal carbonyl hydrides (e.g., $H_2Fe(CO)_4$) have concluded that the coordinated hydrogens are indeed hydridic,[51] that is, carry partial negative charge. Thus, the removal of the hydrogen as a proton must encompass much greater electronic changes than the comparable reaction when the hydrogen is bonded to oxygen or nitrogen, in which case the hydrogen is protonic in nature.

The hydridic character of the metal hydrogen has another feature perhaps even more important to the reaction dynamics of proton transfer. Hydrogen bonding between the metal-coordinated hydrogen and the oxygen of the solvent would be expected to be minimal or nonexistent, and the ability of the solvent methanol molecules to act as proton transfer mediators would be significantly decreased. Such mediation, while not absolutely essential for rapid proton transfer reactions, is generally considered to be the rule in protonic solvents.[47] More importantly, proton transfer via hydrogen bonding minimizes the extent of structural changes in the solvent sheath required during the proton transfer event.

Another structural feature of the metal carbonyl hydrides is the relatively protected positions occupied by the hydrogens. Space-filling models suggest considerable steric crowding might be expected in the transition states of proton transfers to methoxide (or from methanol to the anion). If such is the case, one might predict terminal hydrides to be more accessible than bridging hydrides. In this context, it is notable that although the osmium terminal hydride $H_2Os_3(CO)_{12}$ is less acidic than the bridging hydride analogue $H_4Os_4(CO)_{12}$, the rates of deprotonation by methoxide are the same and the decreased acidity of the former species is due entirely to its larger value for k_{-1}. Protonation of $HOs_3(CO)_{12}^-$ is a factor of 500 times faster than that of $H_3Os_4(CO)_{12}^-$. Similarly, protonation of $HOs(CO)_4^-$ is faster than for the tetranuclear cluster anion, but in this case the contribution to the overall pK_a differences is smaller.

The kinetic isotope effects may also be indicative of mechanistic differences in the reactions of bridging and terminal hydrides. The $k_1(H)/k_1(D)$ ratio (~4) for the methoxide deprotonation of osmium tetracarbonyl dihydride are approximately what would be expected for the relative slow deprotonation of a nitroalkane by a base as strong as methoxide.[52] The magnitude of the effect suggests substantial bond breaking of the Os–H(D) bond at the transition state. In contrast the $k_1(H)/k_1(D)$ ratio is essentially unity (perhaps even slightly less than unity) for the tetrahydride tetraruthenium cluster. Since the $k_1(D)$ value for this experiment was necessarily measured in CH_3OD solvent, the very small kinetic isotope effect may represent the product of the positive primary (and secondary) effects expected from perdeuteration of the cluster and an inverse solvent isotope effect.[53] However, the latter effect was found to be rather small (~0.7) in the deprotonations of nitroalkanes in D_2O,[47] suggesting that the expected primary isotope effect in the present case should be relatively small ($<\sim 2$) to give the overall ratio of about unity. A small primary kinetic isotope effect might reflect the smaller zero-point energy differences given the lower vibrational frequencies seen for bridging vs. terminal hydrides. However, an attractive but speculative alternative explanation would be that the deprotonation step for bridging hydrides involves a greater energetic contribution from distortion of the carbonyl ligands to allow access by the methoxide ion.

In summary, the following qualitative trends can be drawn from the above discussion. pK_a values determined both by kinetics methods and from buffer/indicator experiments indicate that bridging hydrides are more acidic than are terminal hydrides and that lighter metal hydrides are more acidic than are homologous heavier metal complexes. With regard to substituent effects, replacement of two hydrides of a $H_4M_4(CO)_{12}$ cluster by a CO (and the consequential structural changes) leads to increased acidity of the remaining hydrides while replacement of CO's by trimethyl phosphite significantly decreases the acidity of the resulting complex. For all the complexes studied, the rates of deprotonation by methoxide and of reprotonation of the conjugate bases by methanol are orders of magnitude slower than the rates seen for similar reactions of nitrogen and oxygen acids having analogous pK_a values and are much more like those found for carbon acids such as the nitroalkanes. Notably, the lability

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differences between terminal and bridging sites, while suggesting steric contributions to the overall reactivities, in no way accounts for the overall sluggishness of these reactions. Other structural and electronic factors of substrate and solvent must play the dominant roles in explaining these features.

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Registry No. CH_3O^-, 3315-60-4; CH_3OH, 67-56-1; $H_4Ru_4(CO)_{11}[P(OMe)_3]$, 34438-92-1; $H_4Ru_4(CO)_{10}[P(OMe)_3]_2$, 84254-45-5; $H_4Ru_4(CO)_9[P(OMe)_3]_3$, 34438-94-3; $H_4OS_4(CO)_{12}$, 12375-04-1; $H_4FeRu_3(CO)_{12}$, 11064-20-3; $H_2Ru_4(CO)_{13}$, 12110-32-6; $H_2FeRu_3(CO)_{13}$, 12375-24-5; $H_2Os_3(CO)_{12}$, 62863-43-8; $H_2Os(CO)_4$, 22372-70-9; $H_2Ru(CO)_4$, 42781-58-8; deuterium, 7782-39-0.

Crystal, Molecular, and Electronic Structures of Tetrasulfur Dinitride, S_4N_2

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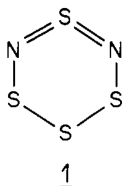
Abstract: A simple method for obtaining high-purity S_4N_2 crystals is described. The crystal and molecular structure of S_4N_2 at −100 (5) °C has been determined by X-ray diffraction. Crystals of S_4N_2 are tetragonal, space group $P4_2nm$, $a = b = 11.146$ (4) Å, $c = 3.773$ (1) Å, $V = 468.7$ Å^3, and $Z = 4$. The refined structure ($R = 0.021$) shows the molecule to be a six-membered ring with the nitrogen atoms in the 1,3-positions. The molecule adopts a half-chair conformation with the central sulfur of the trisulfide unit lifted out of the plane of the remaining five atoms, producing a dihedral angle of 54.9°. Of the two types of S–N bonds, those linking the N–S–N moiety to the S_3 unit are considerably longer (1.676 (4) Å) than those within the N–S–N group (1.561 (4) Å). The S–S bonds (2.061 (2) Å) are as expected for an S–S single bond. MNDO and ab initio Hartree–Fock–Slater SCF calculations on a variety of model S_4N_2 structures show that the observed conformation is preferred by 6–10 kcal mol^{-1} (depending on the computational method) over a planar structure. The electronic structure and bonding are discussed on the basis of the HFS calculations on the crystal structure geometry and a related planar model. For the latter it is possible to assign 10 π-electron distributions formed by the weak interaction of two allyl-type fragments, S_3 and NSN. The strong visible absorptions observed for S_4N_2 (at 455 and 377 nm) are assigned to HOMO (π^*-type) → LUMO (π^*-type) and HOMO − 1 (π^*-type) → LUMO (π^*-type) excitations. The vibrational spectra of $S_4{}^{14}N_2$ and $S_4{}^{15}N_2$ are reported.

Of the known binary compounds of sulfur and nitrogen,[2] tetrasulfur dinitride, S_4N_2, has proven the most difficult to characterize structurally. Although the compound can be prepared by a variety of methods,[3] its low melting point (23 °C) and susceptibility to rapid thermal decomposition upon melting has made its manipulation an onerous task. The compound was first isolated in 1898 by Muthman and Clever, and their proposed formula, N_2S_5, serves to illustrate the susceptibility of the molecule toward disproportionation (hence their high sulfur content).[4] The correct composition "NS_2" was established in 1925,[5] but the molecular formula was not reported until 1951.[6] Twenty years later Nelson and Heal concluded, on the basis of mass, vibrational, and ^{14}N spectral data and dipole moment measurements that the most likely molecular structure was the six-membered ring **1**.[7]



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However, they could make no conclusive assignment regarding ring conformation. In 1972 Jolly pointed out that the most stable geometry should be one in which the central atom of the trisulfide sequence is tilted out of the plane of the remaining five atoms.[8] Subsequent CNDO/2 calculations by Adkins and Turner refuted this suggestion,[9] but more recent ab initio calculations have shown a preference for the nonplanar conformation.[10]

We have recently developed a simple method for preparing S_4N_2 and purifying it by crystallization from diethyl ether. The ready availability of this material has enabled us to determine its low-temperature crystal and molecular structure.[11] In order to probe the reasons for the observed solid state geometry, we have carried out ab initio Hartree–Fock–Slater (HFS) and MNDO molecular orbital calculations on a variety of model S_4N_2 structures. In addition we have examined in detail the nature of the electronic excitations responsible for the UV–visible absorptions of the molecule. The vibrational spectra of $S_4{}^{14}N_2$ and $S_4{}^{15}N_2$ in a variety of phases have also been measured, and these spectra are discussed in relation to the structure of the molecule.

Experimental Section

Preparation of S_4N_2. In a typical reaction, a solution of 25 mL of S_2Cl_2 in 75 mL of carbon disulfide was added dropwise (20 min) to a 1-L Erlenmeyer flask containing 200 mL of carbon disulfide and 200 mL of 12 M NH_4OH. During the course of the addition the reaction mixture

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