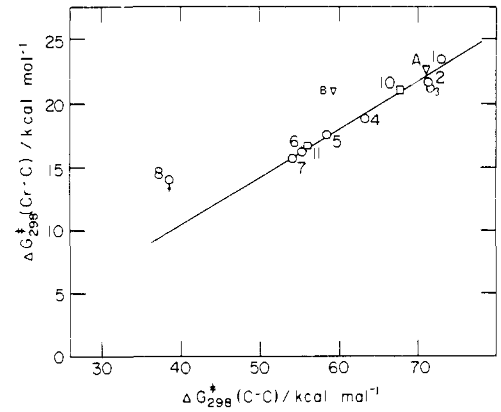

Figure 5. Plot showing a linear relationship between the activation free energies for the homolysis of the organochromium cations, $\Delta G^{\ddagger}_{298}$(Cr–C), and those for homolysis of the correspondingly substituted symmetrical ethanes $\Delta G^{\ddagger}_{298}$(C–C). Data and notation from Table VI.

values of $\Delta G^{\ddagger}_{298}$ for eq 18 vary from 34 to 79 kcal mol^{-1} or a factor $\sim 10^{32}$ in k_{18}. Rüchardt has shown[26] that this large variation in the homolysis rate constant can be accounted for by the steric requirements of the groups R^1, R^2, and R^3 alone.

From the available thermodynamic data we calculated the values of the activation free energies for the C–C bond homolysis in symmetrical ethanes at 298 K, $\Delta G^{\ddagger}_{298,C-C}$. These values are presented in Table VI, along with the values of $\Delta G^{\ddagger}_{298,H}$ for the homolysis of the organochromium complexes. In order to attempt a correlation between the two sets of data, it was necessary to assume that the steric effect of the OH group is identical with the steric effect of the group CH_2H. Similarly, the steric effects of groups OR are as for CH_2R groups, much as Rüchardt included CN groups as CH_3 groups.

The plot of $\Delta G^{\ddagger}_{298,C-C}$ for symmetrical ethanes vs. $\Delta G^{\ddagger}_{298,H}$ for the organochromium complexes is given in Figure 5, which shows that the data for complexes derived from both alcohols and ethers compare rather well with the data for symmetrical ethanes. Also included in the correlation are values for benzyl[3] and 2-propyl[27] complexes. While the latter fits the correlation extremely well, the former deviates somewhat from the line. In view of the fact that benzyl radical is the only nonaliphatic, resonance-stabilized radical in this study, a perfect correlation with the aliphatic radicals was not expected.

The slope of the line in Figure 5 (0.36) confirms the success of the correlation. On the basis of the fact that simultaneous structural variations occur on both of the ethane carbons of eq 18 while changes in the series of the organochromium complexes are only half as large ($Cr(H_2O)_5^{2+}$ being common to the entire series), one would predict a slope of 0.50. The experimentally found value of 0.36 is in good agreement with this prediction.

The results of the correlation indicate that for a series such as this in which substituents of widely different polar effects are not included, structural effects alone can account for the variation in reactivity.

Experimental Section

Organochromium complexes, including the previously unreported ones, were prepared from the reaction[2,6] of chromium(II) perchlorate and hydrogen peroxide in dilute aqueous perchloric acid solutions containing 0.01–1 M of the desired alcohol or ether, as solubility and other considerations permitted. Depending on the purpose of a given experiment, Cr^{2+} or H_2O_2 might be in excess, or the two might be in stoichiometric ratio (2:1 Cr^{2+}:H_2O_2).[28] The preparations and reactions were conducted under Cr^{2+}-scrubbed nitrogen.

Reactions were monitored by UV–vis spectrophotometry, most often employing the absorption maximum near 395 nm ($\epsilon \sim$ 200–700). Kinetics determinations of slower reactions were carried out by using a Cary 219 spectrophotometer. Faster reactions were monitored with a Durrum D110 stopped-flow spectrophotometer equipped with the D-132 Multimix accessory. The latter was essential for the shortest lived complexes, as it permitted mixing of the oxidizing scavenger in the third syringe with the organochromium complex which was produced upon mixing Cr^{2+}, H_2O_2, and the organic solute in the first two syringes. All of the data followed pseudo-first-order kinetics, from which rate constants were evaluated by using standard methods. Products were determined by using methods previously reported.[6] A Xenon Model 710C flash photolysis apparatus was used in the photochemical experiments, with the appropriate reagents contained in quartz vessels under a nitrogen atmosphere.

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Registry No. 1, 32108-95-5; **2**, 32108-94-4; **3**, 80572-83-4; **4**, 32108-93-3; **5**, 80572-84-5; **6**, 80572-85-6; **7**, 80572-86-7; **8**, 80572-87-8; **9**, 78402-17-2; **10**, 32108-97-7; **11**, 80572-88-9; **12**, 80572-89-0; $Co(NH_3)_5F^{2+}$, 15392-06-0; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5Br^{2+}$, 14970-15-1; H_2O_2, 7722-84-1; VO^{2+}, 20644-97-7; Cu^{2+}, 15158-11-9; Fe^{3+}, 20074-52-6.

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Kinetic and Thermodynamic Acidity of Hydrido Transition-Metal Complexes. 1. Periodic Trends in Group 6 Complexes and Substituent Effects in Osmium Complexes

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Abstract: Equilibrium acidities in acetonitrile have been measured for $(\eta^5\text{-}C_5H_5)M(CO)_3H$ (M = Cr, Mo, W) and *cis*-$Os(CO)_4(E)H$ (E = H, CH_3, $Os(CO)_4H$), and periodic trends and substituent effects have been assessed. Rates of proton transfer have been measured or estimated for the reactions of these complexes with their conjugate anions and with nitrogen bases such as morpholine and triethylamine. The rates of proton transfer to metal anions are much slower than those to nitrogen bases of comparable thermodynamic base strength.

While the importance of transition-metal hydrides in organometallic chemistry is manifest, remarkably little is known about their acid–base properties. Although Schunn remarked[2] in 1971 that "there is a definite need for the measurement of the acidity

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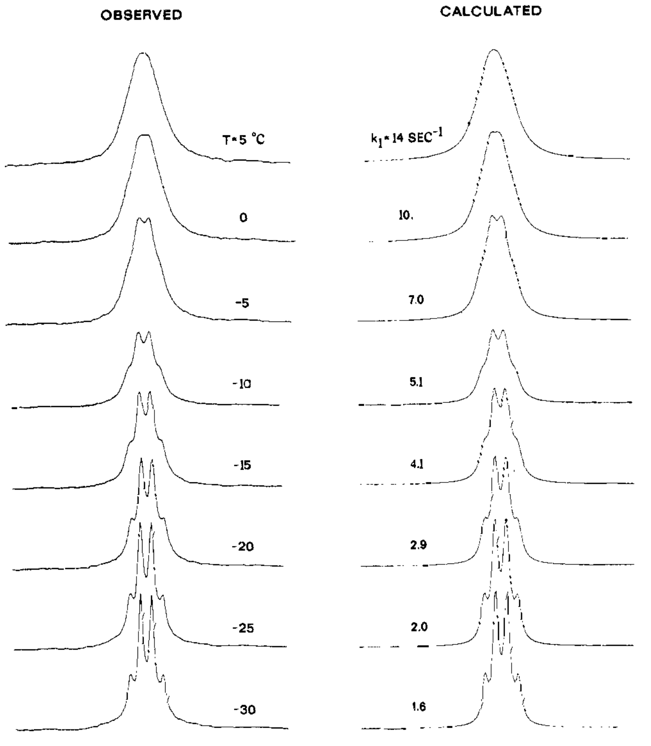

Figure 1. The hydride region 100-MHz ^1H NMR spectra observed for 0.31 M *cis*-$Os(CO)_4(CH_3)H$ and 1.20 M Et_3N in CD_3CN as a function of temperature and calculated for the exchange rates (with respect to *cis*-$Os(CO)_4(CH_3)H$) shown.

functions of a systematic series of metal hydrides under controlled, identical conditions", no such study has yet been performed for the common mononuclear hydrides.[3] Some individual equilibrium measurements can be found in the literature,[2-4] but they have typically been made under conditions convenient for the system at hand rather than under conditions that permit comparison with acid/base literature data. For example, the pK_a of $[(\eta^5\text{-}C_5H_5)_2ReH_2]^+$ has been measured in 60% dioxane/water.[4j]

Such equilibrium acidity data are needed for two principal reasons. First, they are related (after correction for solvation energies, electron affinities, and the ionization potential of hydrogen) to homolytic M–H bond energies. Second, they are required in order to identify situations where apparent reactions of metal hydride complexes actually result from their conjugate bases. It has been shown, for example, that the direction of addition of cobaloximes to olefins with electron-withdrawing substituents, as well as the stereochemistry of their addition to acetylenes, changes as the reactive species changes from a hydridocobaloxime to its conjugate anion (eq 1 and 2).[5-8]

$$HCo(dmgH)_2B + CH_2{=}CHX \rightarrow CH_3CHXCo(dmgH)_2B \qquad (1)$$

$$Co(dmgH)_2B^- + CH_2{=}CHX \xrightarrow{H^+} XCH_2CH_2Co(dmgH)_2B \qquad (2)$$

$$(B = \text{axial base})$$

Quantitative data on kinetic acidity are equally rare and equally essential. Scattered rate measurements have been reported on several systems under a variety of conditions,[3,4e,m,9] but there has been little systematic study of protonation and deprotonation rates, particularly for mononuclear hydrides.[3] Knowledge of proton-transfer rates in straightforward cases should help identify less obvious proton-transfer mechanisms. It should assist interpretation and prediction of relative protonation (and deprotonation) rates for metal sites vs. ligand sites. Finally, it should be of use in synthetic organometallic chemistry, where control of relative rates of proton-transfer processes and other reactions is often important. For example, in the synthesis of *cis*-$Os(CO)_4(H)CH_3$ by methylation of $[Os(CO)_4H]^-$ (eq 3), the use of methyl tosylate as CH_3X permits Os–Os proton transfer (eq 4) to compete with methylation, giving *cis*-$Os(CO)_4H_2$ and *cis*-$Os(CO)_4(CH_3)_2$ as byproducts; the use of the faster methyl fluorosulfonate as CH_3X in eq 3 eliminates this complication.[10]

$$[Os(CO)_4H]^- + CH_3X \rightarrow Os(CO)_4(H)CH_3 + X^- \qquad (3)$$

$$[Os(CO)_4H]^- + Os(CO)_4(H)CH_3 \rightarrow Os(CO)_4H_2 + [Os(CO)_4CH_3]^- \qquad (4)$$

$$[Os(CO)_4CH_3]^- + CH_3X \rightarrow Os(CO)_4(CH_3)_2 \qquad (5)$$

We have, therefore, begun a systematic investigation of the kinetic and thermodynamic acidity of hydrido transition-metal complexes under standard conditions. We have chosen acetonitrile as the solvent for these studies for the following reasons: (1) CH_3CN is a polar solvent ($\epsilon = 36$)[11a] in which almost all hydrido transition-metal complexes are soluble and in which their anions should undergo less ion pairing than in solvents such as THF; (2) CH_3CN has a low self-ionization constant ($K_{\text{autoprotolysis}} = 3 \times 10^{-29}$) and is thus suitable for experiments over a wide range of acid and base strengths;[11a] (3) there exists a fair body of thermodynamic acid/base data for organic compounds in this solvent.[11b,c] We now report our results for two series of compounds: $(\eta^5\text{-}C_5H_5)M(CO)_3H$, M = Cr, Mo, and W, and *cis*-$Os(CO)_4(E)(H)$, E = H, CH_3, and $Os(CO)_4H$. The former series allows the investigation of periodic trends, and the latter allows the investigation of substituent effects.

Experimental Section

General. All operations were performed under a nitrogen atmosphere or under vacuum by use of Schlenk or vacuum-line techniques. MCB reagent grade CH_3CN was predried over 3-Å molecular sieves and distilled under N_2 from P_2O_5 and then from CaH_2, and the middle fraction was collected and degassed by several freeze–pump–thaw cycles. $CH_3CN\text{-}d_3$ (Merck) was dried by vacuum transfer from P_2O_5. THF was distilled from sodium benzophenone ketyl. Et_3N, morpholine (mor), pyridine (py), and aniline (an) were dried over and then fractionally distilled from BaO. Tetramethylguanidine (TMG) was dried over and then bulb-to-bulb vacuum distilled from BaO. IR spectra were obtained with Perkin-Elmer 0.1-mm solution cells on a Beckman 4240 spectrophotometer. Variable-temperature NMR experiments were performed

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Table I. IR Spectra of Hydrido Transition-Metal Complexes and Their Anions

compound	solvent	νCO, cm^{-1} (abs)[a]	νMH, cm^{-1}
$(\eta^5\text{-}C_5H_5)W(CO)_3H$	CH_3CN	2008 (17.8), 1915 (34.2)	1845 w, br[c]
$K[(\eta^5\text{-}C_5H_5)W(CO)_3]$	CH_3CN	1887 (23.0), 1767 (34.5)	
	THF	1887 s, 1780 s, 1740 s	
$[Et_3NH][(\eta^5\text{-}C_5H_5)W(CO)_3]$	CH_3CN	1889 (27.2), 1768 (46.0)	
$(\eta^5\text{-}C_5H_5)Mo(CO)_3H$[b]	CH_3CN	2010 s, 1925 vs	1790 w, br[c]
$K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$	CH_3CN	1893 (25.4), 1770 (38.6)	
	THF	1893 s, 1782 s, 1740 s	
$[morH][(\eta^5\text{-}C_5H_5)Mo(CO)_3]$	CH_3CN	1892 (27.6), 1770 (44.0)	
$(\eta^5\text{-}C_5H_5)Cr(CO)_3H$	CH_3CN	1999 (17.5), 1917 (26.8)	1765 w, br
$[morH][(\eta^5\text{-}C_5H_5)Cr(CO)_3]$	CH_3CN	1888 (28.2), 1768 (42.7)	
$Os(CO)_4H_2$	CH_3CN	2132 w (1.1), 2060 sh, 2050 sh, 2038 vs (30)	1942 w, br
$K[Os(CO)_4H]$	THF	2010 m, 1975 sh, 1952 m, 1880 vs, 1850 m	
	CH_3CN	2006 m (7.6), 1975 sh, 1951 m (8.33), 1883 vs (39.1)	
$[Et_3NH][Os(CO)_4H]$	CH_3CN	2007 m, 1975 sh, 1950 m, 1883 vs	
$Os(CO)_4(CH_3)(H)$	CH_3CN	2135 s (1.88), 2063 s (16.0), 2040 vs (32.8), 2025 sh	1948 w, br
$[TMGH][Os(CO)_4CH_3]$	CH_3CN	1995 w, 1908 (21.0), 1880 (50.4)	
$Os_2(CO)_8H_2$	CH_3CN	2129 w (1.6), 2089 s (24), 2025 vs (37), 2029 s, 2012 sh	1954 w, br
$[TMGH][Os_2(CO)_8H]$	CH_3CN	2085 (5.4), 2077 sh, 2026 m, 1996 vs (47), 1935 m, 1905 sh, 1882 vs (31)	

[a] Abs is absorptivity (units, M^{-1}), measured in 0.1-mm NaCl cells at room temperature. [b] Abs could not be measured due to decomposition. [c] Assigned by comparison with values reported by Davison et al. (Davison, A. J.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* 1963, 1133) for CS_2 solution.

on a JEOL FX-100Q Fourier transform spectrometer equipped with a calibrated temperature controller. The uncertainty in temperature was ±1 °C between −45 and 20 °C.

Preparations. $(\eta^5\text{-}C_5H_5)M(CO)_3H$, M = Cr, Mo, and W, was prepared by literature methods[12] with H_3PO_4 serving as the proton source. ^1H NMR (CD_3CN): M = Cr, δ 5.01 (s, 5 H), −5.74 (s, 1 H); M = Mo, δ 5.52 (s, 5 H), −5.74 (s, 1 H); M = W, δ 5.60 (s, 5 H), −7.40 (m, $J(^{183}W\text{-}H)$ = 18.6 Hz, 1 H). $Os(CO)_4H_2$[13,14] and $Os(CO)_4(CH_3)(H)$[10,14] were prepared as previously reported. ^1H NMR (CD_3CN): $Os(CO)_4H_2$, δ −9.03 (s), $Os(CO)_4(CH_3)(H)$, δ −0.07 (d, J = 2.44 Hz, 3 H), −8.21 (q, J = 2.44 Hz, 1 H).

$(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ reacts with CH_3CN at 25 °C according to eq 6, the reverse of a reaction previously reported in the presence of excess

$$(\eta^5\text{-}C_5H_5)Mo(CO)_3H + 3CH_3CN \rightarrow Mo(CO)_3(CH_3CN)_3 + C_5H_6 \tag{6}$$

cyclopentadiene.[12d] This reaction was found to be sufficiently slow at 0 °C that experiments with $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ could be performed at that temperature.

Dihydridooctacarbonyldiosmium ($Os_2(CO)_8H_2$) was prepared by the controlled thermolysis of $Os(CO)_4H_2$.[15] In a typical reaction 0.386g (1.27 mmol) of $Os(CO)_4H_2$ and 3 mL of mesitylene were vacuum transferred into a 20-mL bulb on a high-vacuum line. The bulb was charged with 300 mm of CO and heated at 135 °C for 30 min. The resulting bright yellow solution was cooled, and the components volatile at room temperature (unreacted $Os(CO)_4H_2$ and solvent) were transferred to a second bulb, leaving behind a yellow residue. This process was repeated with the volatile components in the second bulb. The two residues were extracted with 5 mL of hexane each and the extracts combined. Solvent removal yielded a yellow oil from which the product (0.074g, 24%) was isolated by bulb-to-bulb distillation (40 °C, 0.005 mm). Its IR and NMR spectra agreed with those reported by Moss and Graham, who prepared $Os_2(CO)_8H_2$ from the high-pressure reaction of OsO_4 with H_2 and CO.[16] ^1H NMR (CD_3CN): δ −10.25 (s).

$K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Cr, Mo, and W) were prepared by the reaction of the corresponding hydrido transition-metal complexes with KH in THF.[17] KH gives anions cleanly and conveniently without producing side products which can interfere in acid/base studies. In a typical preparation, a solution of 0.24 g (0.96 mmol) of $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ in 4 mL of THF was added to a slurry of 0.034 g (0.86 mmol) of KH in 4 mL of THF. Gas evolution was immediate and vigorous, and the reaction was complete in several minutes. Solvent removal followed by hexane washing gave a quantitative yield of pure $K[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ as a tan powder. The IR spectra of the products in THF agreed with those previously reported.[18] ^1H NMR (CD_3CN): M = Cr, δ 4.42 (s); M = Mo, δ 5.06 (s); M = W, δ 5.08 (s).

$K[Os(CO)_4H]$ was prepared by the reaction of $Os(CO)_4H_2$ with KH. In a typical reaction, 0.18 g (0.60 mmol) of $Os(CO)_4H_2$ and 2 mL of THF were transferred onto 0.020 g (0.48 mmol) of KH on a high-vacuum line. Slow gas evolution continued for 1 h. After gas evolution had stopped, the solvent and excess $Os(CO)_4H_2$ were removed under vacuum, and the residue was washed with hexane, giving a quantitative yield of $K[Os(CO)_4H]$ as a pale yellow powder. The IR spectrum in THF agreed with that previously reported.[13,19] ^1H NMR (CD_3CN): δ −10.40 (s).

$[TMGH][Os(CO)_4(CH_3)]$ was prepared in situ by the addition of 10 equiv of TMG to a CH_3CN solution of $Os(CO)_4(CH_3)(H)$. IR peaks due to the starting material disappeared and new peaks at 1995 (w), 1908 (s), and 1880 (vs) cm^{-1} were observed. This spectrum is very similar to those of related $RFe(CO)_4^-$ compounds[20] and is assigned to $Os(CO)_4(CH_3)^-$. ^1H NMR (CD_3CN): δ −0.05 (s).

The reaction of $Os(CO)_4(CH_3)(H)$ with KH was attempted in the same manner as the $Os(CO)_4H_2$ reaction. Gas evolution was slow but detectable and IR peaks corresponding to $Os(CO)_4(CH_3)^-$ were transiently observed, but after 3 h, unreacted KH was still visible and the reaction mixture had turned deep yellow. The IR spectrum indicated the absence of the $Os(CO)_4(CH_3)^-$, and only a broad unassignable band at 1990 cm^{-1} and peaks due to $Os_3(CO)_{12}$ were observed.[21]

$[TMGH][Os_2(CO)_8H]$ was prepared in situ by the addition of a slight excess of TMG to a CH_3CN solution of $Os_2(CO)_8H_2$. The solution turned bright yellow, and the IR spectrum of the starting material was replaced by peaks at 2085 (w), 2077 (sh), 2026 (m), 1996 (vs), 1935 (m), 1905 (sh), 1882 (vs) cm^{-1}, which are assigned to $Os_2(CO)_8H^-$. Addition of CF_3COOH discharged the yellow color and the IR spectrum of $Os_2(CO)_8H_2$ reappeared quantitatively, confirming that the deprotonated material had in fact been $Os_2(CO)_8H^-$. ^1H NMR (CD_3CN): δ −10.65 (s).

The reaction of $Os_2(CO)_8H_2$ with KH was very slow, even at 40 °C. After 5 h, the IR spectrum indicated that the reaction was nearly complete, but decomposition reactions prevented isolation of the product.

IR Experiments—Absorptivities. Solutions of the salts formed by complete deprotonation of the hydrido metal complexes by sufficiently powerful nitrogen bases were prepared as described above for $[TMGH][Os_2(CO)_8H]$. Absorptivities for the ν_{CO} bands of these, the corresponding potassium salts, and the neutral hydrido metal complexes

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were obtained from the absorbances of solutions of known concentration (typically 0.003–0.05 M). These data are summarized in Table I. In representative cases, Beer's law was verified over the same concentration range.

As (η^5-C_5H_5)Mo(CO)$_3$H decomposed in CH_3CN at room temperature, it was impractical to measure the absorptivity of its carbonyl bands directly; the absorptivity at 2010 cm^{-1} was estimated as 17.6 M^{-1} by analogy to the virtually identical values measured for the corresponding bands of the Cr and W analogues.

Equilibrium Constants. Stock solutions of hydrido metal compounds L_nMH and appropriate nitrogen bases B were mixed to give solutions in which deprotonation was significant but not complete. Equilibrium constants K_{eq} (eq 7) were calculated under the assumption that only the primary acid/base reaction (eq 8) and the self-association of the base (eq 9) were significant. The effect of the latter equilibrium on K_{eq} was small

$$K_{eq} = [L_nM^-][BH^+]/([L_nMH][B]) \qquad (7)$$

$$L_nMH + B \rightleftharpoons L_nM^- + BH^+ \qquad K_{eq} \qquad (8)$$

$$BH^+ + B \rightleftharpoons BHB^+ \qquad K(BHB^+) \qquad (9)$$

in most cases. $[L_nMH]$ and $[M^-]$ were determined by IR; the absorptivities used for $[M^-]$ were those (given in Table I) determined when the hydrido complexes were completely deprotonated by strong nitrogen bases (except for Os(CO)$_4$H$^-$, for which the absorptivity of the potassium salt was used). $[BH^+]$ and [B] were calculated from the total concentration of base added, the known self-association constants,[11,22] and the extent of reaction according to eq 8 as determined by $[L_nMH]$ and $[M^-]$. Determinations of K_{eq} varied by an average of 13% over threefold changes in $[L_nMH]$ and [B]. The acid dissociation constants K_a of L_nMH were calculated from K_{eq} and the known[11] basicities of B.

NMR Rate Measurements. CD_3CN solutions of the exchanging species and an internal concentration and peak width standard, usually benzene, were sealed under vacuum in 5-mm NMR tubes. Excess line widths Δ were obtained by subtracting the line widths of the internal standard peaks from the measured line widths of the peaks of interest.

(η^5-C_5H_5)M(CO)$_3$H Proton-Transfer Rates. Second-order rate constants k^{MM} for the (η^5-C_5H_5)M(CO)$_3$H/K[(η^5-C_5H_5)M(CO)$_3$] proton exchanges were obtained from the NMR spectra of solutions (0.02–0.09 M) containing both the neutral hydrides MH and the anions M^-. The value of k^{MM} was calculated from the excess η^5-C_5H_5 line widths Δ and the concentrations by eq 10. When the η^5-C_5H_5 peaks of MH and M^-

$$k^{MM} = \pi\Delta(MH)/[M^-] = \pi\Delta(M^-)/[MH] \qquad (10)$$

overlapped significantly, the rate constants were obtained by comparison of the experimental spectra with spectra calculated by the dynamic NMR simulation program DNMR5.[23]

Forward and reverse rate constants for (η^5-C_5H_5)W(CO)$_3$H/morpholine proton transfer were obtained from the total exchange rate (the excess η^5-C_5H_5 line widths of (η^5-C_5H_5)W(CO)$_3$H and [morH][(η^5-C_5H_5)W(CO)$_3$]), corrected for the direct W–W exchange rate determined above, and the concentrations. The mor and morH$^+$ concentrations were calculated from the amount of morpholine originally added and the extent of the deprotonation reaction as determined by the integrated intensities of (η^5-C_5H_5)W(CO)$_3$H and [(η^5-C_5H_5)W(CO)$_3$]$^-$.

Os(CO)$_4$H$_2$/K[Os(CO)$_4$H] Proton-Exchange Rate. Spin–Lattice Relaxation Times. Solutions (~0.3 M) of Os(CO)$_4$H$_2$ and K[Os(CO)$_4$H] were sealed under vacuum in 5-mm cavity tubes. T_1 values were measured by the fast inversion-recovery method and the data analyzed by exponential curve fitting.[24]

Saturation transfer experiments[25,26] were performed on solutions containing both Os(CO)$_4$H$_2$ and K[Os(CO)$_4$H] (0.03–0.8 M) at 30 °C. In a typical experiment, the Os(CO)$_4$H$^-$ peak was irradiated for $5T_1$(Os(CO)$_4$H$_2$) and the integrated intensity of the Os(CO)$_4$H$_2$ peak, M_∞(Os(CO)$_4$H$_2$), was recorded. The irradiation frequency was then placed an equal frequency difference away from the Os(CO)$_4$H$_2$ peak, but in the direction opposite that of the Os(CO)$_4$H$^-$ peak, and the intensity of the Os(CO)$_4$H$_2$ peak, M_0(Os(CO)$_4$H$_2$), was recorded. These spectra were repeated several times to give average M_∞ and M_0 values, and the second-order rate constant k^{OsOs} was calculated by eq 11.

$$k^{OsOs} = \frac{2}{|Os(CO)_4H^-| \times T_1(Os(CO)_4H_2)}\left[\frac{M_0(Os(CO)_4H_2)}{M_\infty(Os(CO)_4H_2)} - 1\right] \qquad (11)$$

In an analogous manner, but without the statistical factor of 2,[27] k^{OsOs} was also obtained from the effect on the Os(CO)$_4$H$^-$ peak intensity of irradiating Os(CO)$_4$H$_2$.

Os(CO)$_4$(E)(H)/Et$_3$N Proton Transfer. For E = H and E = Os(CO)$_4$H, the forward and reverse second-order rate constants were obtained from the excess line widths of the neutral hydride and anion peaks and the Et$_3$N and Et$_3$NH$^+$ concentrations, which were calculated from the amount of Et$_3$N originally added and the extent of the deprotonation reaction as determined by the integrated intensities of Os(CO)$_4$(E)H and [Os(CO)$_4$E]$^-$. For E = CH$_3$, the forward rate constant was obtained from the collapse of J(CH$_3$–H) by comparison of the experimental spectra (Os–H region) to spectra simulated by DNMR5.[23]

Extrapolation of Rate Constants. Activation parameters were determined, and extrapolated rate constants obtained, by direct fitting of (k,T) data to the Eyring equation by nonlinear regression or, in cases where this was computationally inconvenient, by linear fitting of the data in logarithmic form. The standard deviation of k (25 °C) was calculated from the standard deviations and covariance of $\Delta H^\ddagger$ and $\Delta S^\ddagger$.[28]

Results

Equilibrium Acidities by Infrared Spectroscopy. We have found neutral nitrogen bases ideal for acid–base work with hydrido transition-metal complexes. They are volatile and easy to handle, and pK_a data, available for many of them in acetonitrile,[11] show that they cover a wide range of base strengths. Addition of weak nitrogen bases to acetonitrile solutions of the hydrido transition-metal complexes studied causes no change in their carbonyl region IR spectra whereas addition of strong nitrogen bases produces spectra identical (in all cases where both spectra are available) with those of the potassium salts of the corresponding anions. For example, aniline (pK_a(anH$^+$) = 10.6) does not affect the spectrum of (η^5-C_5H_5)Mo(CO)$_3$H whereas morpholine (pK_a(morH$^+$) = 16.6) converts its spectrum to that of [(η^5-C_5H_5)Mo(CO)$_3$]$^-$. Similarly, the carbonyl region IR spectrum of (η^5-C_5H_5)W(CO)$_3$H is unaffected by pyridine (pK_a(pyH$^+$) = 12.3) but converted to that of [(η^5-C_5H_5)W(CO)$_3$]$^-$ by triethylamine (pK_a(Et$_3$NH$^+$) = 18.5).

Treatment of these hydrido transition-metal complexes with bases of intermediate strength results in spectra attributable to mixtures of the original complex and the corresponding anion. For example, the treatment of (η^5-C_5H_5)W(CO)$_3$H with morpholine produces a carbonyl region IR spectrum reflecting the operation of eq 12. The IR spectra of such mixtures show no

$$(\eta^5\text{-}C_5H_5)W(CO)_3H + \text{mor} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [(\eta^5\text{-}C_5H_5)W(CO)_3]^- + \text{morH}^+ \qquad (12)$$

$$CH_3CN, 25\ °C$$

evidence (except for minor byproducts as discussed below in the case of Os(CO)$_4$(H)CH$_3$) for any species other than the hydrido complexes and the corresponding anions. These observations rule out other possible reactions of a nitrogen base such as carbonyl substitution, nucleophilic attack upon a carbonyl ligand, or formation of a strong hydrogen bond with the hydride ligand.

These observations do not rule out the formation of weakly hydrogen-bonded complexes M–H···N prior to deprotonation, as their carbonyl region IR spectra might differ little from those of the free hydrides. The ν(M–H) bands are potential probes of hydrogen bonding, but unfortunately they are so broad and weak in acetonitrile as to be of little use. However, the NMR spectra of such partially deprotonated mixtures show hydride ^{1}H NMR chemical shifts unchanged from those of the hydrido complexes prior to the addition of base. Even assuming rapid exchange between free and hydrogen-bonded hydride, these NMR results

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(27) Because only half of the protons in Os(CO)$_4$H$_2$ change their resonance frequency as proton transfer occurs, the first-order rate constant per Os(CO)$_4$H$_2$ is twice that per Os(CO)$_4$H$_2$ proton.

(28) The authors are grateful to Professor J. P. Hunt, Washington State University, for a copy of an unpublished manuscript by Dr. W. F. Siems which discusses the calculation of errors in extrapolated rate constants from the covariance of $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

Table II. Thermodynamic Acidity in Acetonitrile of Hydrido Transition-Metal Complexes[a]

hydrido complex	base (pK_a of BH^+)[b]	K_{eq}	pK_a of hydrido complex
$(\eta^5\text{-}C_5H_5)Cr(CO)_3H$	pyridine (12.3)	0.096 ± 0.006	13.3 ± 0.1
$(\eta^5\text{-}C_5H_5)Mo(CO)_3H$	pyridine (12.3)	0.028 ± 0.006 (0 °C)	13.9 ± 0.1[d]
$(\eta^5\text{-}C_5H_5)W(CO)_3H$	morpholine (16.6)	2.86 ± 0.18	16.1 ± 0.1
cis-$Os(CO)_4H_2$	Et_3N (18.5)	0.0048 ± 0.0005	20.8 ± 0.1
cis-$Os(CO)_4(CH_3)(H)$	TMG[c] (23.3)	2.0 ± 0.2 (0 °C)	23.0 ± 0.1[d]
$Os_2(CO)_8H_2$	Et_3N (18.5)	0.014 ± 0.002	20.4 ± 0.1

[a] At room temperature except where otherwise noted. [b] Data from ref 11. [c] TMG = tetramethylguanidine. [d] Estimated from K_{eq} at 0 °C and the pK_a data at 25 °C from ref 11.

imply either that the hydride ^1H chemical shifts change little upon formation of hydrogen bonds to the nitrogen base (and thus that the hydrogen bonds are very weak[29]) or that there is negligible formation of hydrogen-bonded complexes.

There is also no evidence for significant contact ion pair formation involving these transition-metal anions. The carbonyl region IR spectra of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ and analogous anions in CH_3CN (Table I) show only two bands, as expected for a free anion (or solvent-separated ion pair) C_{3v} symmetry and as assigned to free $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ in DMF.[18a] The situation with the anions $[Os(CO)_4E]^-$ (E = H, CH_3, $Os(CO)_4H$) is less clear. However, with reference to the IR spectra assigned to $[Fe(CO)_4H]^-$ in contact ion pairs and in symmetrical solvent environments,[30] $[TMGH][Os(CO)_4CH_3]$ in CH_3CN clearly shows the three-band pattern expected for free $[Os(CO)_4CH_3]^-$ in a symmetrical solvent environment, and $K[Os(CO)_4H]$ in THF clearly shows the more complex pattern expected when a contact ion pair has been formed. As the spectra of $[Et_3NH][Os(CO)_4H]$ and $K[Os(CO)_4H]$ in acetonitrile[31] are identical and quite different from the spectrum of $K[Os(CO)_4H]$ in THF, it seems unlikely that contact ion pair formation is appreciable in CH_3CN for $[Os(CO)_4H]^-$ and K^+ or $[Et_3NH]^+$. As there is neither evidence *for* significant hydrogen bonding nor evidence *for* contact ion pairs in these systems, we have evaluated our data on the assumption that the hydrido complexes and the corresponding free anions are the only organometallic species present.

Equilibrium constants for deprotonation of the transition-metal hydrides have been determined with nitrogen bases which produce only the partial deprotonation described above. The IR absorptivities for appropriate carbonyl bands of the metal anions in these mixtures were generally set equal to the absorptivities measured when the hydrido complexes were completely deprotonated by stronger nitrogen bases, in the belief that the latter values should be closer than those of the potassium salts to the absorptivities of the anions in the partially deprotonated mixtures. The K_{eq} results are given in Table II, as are the pK_a values calculated by the use of the known pK_a values for the conjugate acids of these bases in acetonitrile[11] and the known equilibrium constants[11,22] for the formation of complexes BHB^+ (as in eq 9) between these bases and their conjugate acids. We have seen no evidence for the formation of similar complexes $[L_nMHML_n]^-$ (which should have characteristic IR spectra) between the metal hydrides and their anions.

Table III. Second-Order Rate Constants for $(\eta^5\text{-}C_5H_5)M(CO)_3H/[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ Proton Exchange in CD_3CN

temp, °C	k, M^{-1} s^{-1} M = W[a,b]	 M = Mo[a,b]	 M = Cr[a,b]
−44			600
−40		78	900
−35	16	110	1400
−30	32	160	2150
−25	35	200	3000
−20	52	250	
−15	72	380	
−10	89	455	9000
−5	130		
0	162		
5	218		
10	280		
14	380		

[a] Combined results of two experiments. [b] $[(\eta^5\text{-}C_5H_5)M(CO)_3H]$ and $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ were 0.02–0.08 M.

As $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ reacts with CH_3CN at room temperature according to eq 6, K_{eq} for its deprotonation by py was determined at 0 °C. Similarly, as $Os(CO)_4(H)CH_3$ decomposes at room temperature in the presence of significant amounts of its conjugate anion $[Os(CO)_4CH_3]^-$,[21] K_{eq} for the deprotonation of *cis*-$Os(CO)_4(H)CH_3$ by TMG was determined at 0 °C. The IR spectrum of a small amount of the decomposition products was nevertheless observable during the determination.

$(\eta^5\text{-}C_5H_5)M(CO)_3H/K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ Proton Exchange (M = Cr, Mo, W). The ^1H NMR spectra of solutions (0.02–0.08 M) containing both $(\eta^5\text{-}C_5H_5)M(CO)_3H$ and $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ were observed between −40 and 20 °C. Sharp, separate $\eta^5\text{-}C_5H_5$ peaks for the metal hydride and anion (separated by about 50 Hz) were observed at low temperature; these broadened and coalesced as the temperatures or concentrations were raised. These line-shape changes were reversible and were not observed with separate solutions of $(\eta^5\text{-}C_5H_5)M(CO)_3H$ or $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$, and from them the second-order rate constants listed in Table III were calculated.

In the M = W system, the ^{183}W satellites of the W–H peak broadened and merged with the center peak, confirming that intermolecular W–W proton exchange was occurring. The rate constant at −20 °C (obtained by comparison of the experimental spectrum with spectra simulated with DNMR5[23]) from this satellite collapse agreed well with that calculated from the $\eta^5\text{-}C_5H_5$ line widths, confirming that the rates determined from the $\eta^5\text{-}C_5H_5$ line-shape changes were in fact rates of proton exchange. In the Cr and Mo cases, the M–H peak remained sharp, as expected for exchange between equivalent sites.

$(\eta^5\text{-}C_5H_5)W(CO)_3H$/Morpholine Proton Transfer. The NMR spectra of extremely dilute (0.003 M) solutions of $(\eta^5\text{-}C_5H_5)W(CO)_3H$ and morpholine exhibited separate $\eta^5\text{-}C_5H_5$ peaks for the neutral hydrido metal complex and $[morH][(\eta^5\text{-}C_5H_5)W(CO)_3]$ at low temperature. K_{eq} calculated from the integrated peak intensities between −20 and 0 °C for the equilibrium shown in eq 12 (2.8 ± 1) agreed within experimental error with the IR 25 °C value. The small temperature and concentration dependence of K_{eq} is consistent with our assumption that ion-pairing effects in these systems are not large.

As the temperature was raised at any given concentration, or as the concentrations were increased, the $\eta^5\text{-}C_5H_5$ peaks broadened and coalesced and the W–H peak broadened. The forward and reverse rates calculated from the $\eta^5\text{-}C_5H_5$ line-shape changes reflect the total rate of proton transfer. In the case of the forward reaction, k_{obsd} (eq 13) for $(\eta^5\text{-}C_5H_5)W(CO)_3H$ reflects the rate

$$k(\text{obsd}) = k_f[\text{mor}] + k^{ww}[(\eta^5\text{-}C_5H_5)W(CO)_3^-] \quad (13)$$

of proton transfer to morpholine (the forward reaction of equilibrium 12) and the rate of proton exchange with $(\eta^5\text{-}C_5H_5)W(CO)_3^-$. The self-exchange rate $k^{ww}[(\eta^5\text{-}C_5H_5)W(CO)_3^-]$, which here involves $morH^+$ as the counterion, was estimated from the

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(29) We are aware of only one case of the possible formation of a hydrogen bond by a transition-metal hydride, a long pairwise interaction between the hydrogen of a $[(\eta^5\text{-}C_5H_5)_2Mo(H)CO]$ cation and the carbonyl oxygen of an adjacent cation in $[(\eta^5\text{-}C_5H_5)_2Mo(H)CO][(\eta^5\text{-}C_5H_5)Mo(CO)_3]$. The length and the fact that the solid-state $\nu(CO)$ of the cation does not differ from that in solution make it clear that the interaction is quite weak: Adams, M. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1979**, *18*, 3020.

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(31) The three strong bands of the observed spectrum agree well with those expected for a symmetrical solvent environment.[30] The weak shoulder at 1975 cm^{-1} may result from vibrational coupling of $\nu(M\text{-}H)$ with $\nu(CO)$.

Table IV. Forward and Reverse Second-Order Rate Constants for $(\eta^5\text{-}C_5H_5)W(CO)_3H$/Morpholine Proton Transfer in CD_3CN

temp, °C	$10^{-3}k_f$, $M^{-1}\,s^{-1}$	$10^{-3}k_r$, $M^{-1}\,s^{-1}$
−20	2.7	1.1
−16	4.5	1.7
−10	7.3	3.3
−8	10	3.9
−5	12	5.4
0	16	6.7
5	22	

[a] Combined results of two experiments. [b] $[(\eta^5\text{-}C_5H_5)W(CO)_3H]$ = 0.005–0.009 M; [morpholine] = 0.002–0.003 M.

Table V. ^1H Spin-Lattice Relaxation Times for Hydrido Osmium Compounds[a]

temp, °C	T_1, s	
	$Os(CO)_4H_2$	$K[Os(CO)_4H]$
−14	18.4	
0	22.7	
15	25.5	
30	34.6	240

[a] 0.3 M in CD_3CN.

rate measured above for the potassium salt. If ion pairing is negligible as assumed, k^{ww} should be the same in both systems; in any case the self-exchange rate is small relative to the W–N proton-transfer rate. The calculated forward and reverse second-order constants for proton transfer to morpholine, k_f and k_r, are listed in Table IV.

The spectra of morpholine and morpholineH^+ were averaged even at −30 °C. At 0 °C, the NH/NH_2^+ peak appeared as a broad hump at δ 7.5.[32] This assignment was confirmed by the spectrum of a solution containing the same concentrations of mor and morH^+ (prepared from appropriate quantities of morpholine and $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, which is completely deprotonated by this base).

$Os(CO)_4(E)H/K[Os(CO)_4E]$ (E = H, CH_3, $Os(CO)_4H$) Proton Exchange. The hydride-region ^1H NMR peaks of mixtures of $Os(CO)_4(E)H$ and $K[Os(CO)_4E]$ (E = H, $Os(CO)_4H$) exhibited no significant broadening over the natural line width (even, in the case of $Os(CO)_4H_2/[Os(CO)_4H]^-$, up to 75 °C), showing that proton transfer in these systems is very slow. It proved impossible to perform the corresponding experiment with $Os(CO)_4(CH_3)H$ and $K[Os(CO)_4CH_3]$ because of the instability of $Os(CO)_4(CH_3)H$ in the presence of significant amounts of its conjugate anion.[21]

Although the first two experiments above provided upper limits for their respective proton-exchange rates, it proved feasible to obtain a value for the rate in the case of $Os(CO)_4H_2/K[Os(CO)_4H]$. The spin–lattice relaxation times for these compounds (Table V) are quite long (as expected especially in the case of $[Os(CO)_4H]^-$, which lacks any possibility of intramolecular dipole–dipole relaxation), and so saturation transfer methods[25,26] can be used for the measurement of this slow proton-exchange rate. At 30 °C with suitable concentrations, we observed transfer of saturation in both directions, i.e., irradiation of the ^1H resonance of $Os(CO)_4H_2$ resulted in a decrease in the intensity of the $[Os(CO)_4H]^-$ signal and irradiation of the $[Os(CO)_4H]^-$ resonance produced a decrease in the intensity of the $Os(CO)_4H_2$ signal. For example, in one experiment (0.75 M $Os(CO)_4H_2$, 0.29 M $K[Os(CO)_4H]$) k^{OsOs} was determined as 0.058 $M^{-1}\,s^{-1}$ from the irradiation of $[Os(CO)_4H]^-$ and as 0.037 $M^{-1}\,s^{-1}$ from the irradiation of $Os(CO)_4H_2$ (a result which is less accurate because of the long $Os(CO)_4H^-$ T_1).

Table VI. Second-Order Rate Constants for $Os(CO)_4(E)(H)/Et_3N$ Proton Transfer in CD_3CN

temp, °C	E = H[a,b] k_f, $M^{-1}\,s^{-1}$	E = H[a,b] k_r, $M^{-1}\,s^{-1}$	E = CH_3[a,b] k_f, $M^{-1}\,s^{-1}$	E = $Os(CO)_4H$[a,b] k_f, $M^{-1}\,s^{-1}$	E = $Os(CO)_4H$[a,b] k_r, $M^{-1}\,s^{-1}$
−40	12	240			
−35	18	360			
−30	27	790	1.2		
−25	41		1.6		
−20	52		2.3	.6	59
−15			3.2		
−10	100		4.6	1.4	140
−5	130		5.8	2.1	210
0	160		8.0	2.5	280
5	200		11.7	3.8	
10	250		17.0	4.2	
15				6.5	

[a] $[Os(CO)_4(E)(H)]$ = 0.1–0.3 M; $[Et_3N]$ = 0.2–1.6 M. [b] Combined results of two experiments.

In addition to the variation between the exchange rate constants obtained from the two different irradiation positions in any one experiment, there was a variation of 30% among the average rate constants obtained in different experiments. (0.57 M $Os(CO)_4H_2$ and 0.084 M $K[Os(CO)_4H]$ gave an average k^{OsOs} of 0.080 $M^{-1}\,s^{-1}$; 0.034 M $Os(CO)_4H_2$ and 0.086 M $K[Os(CO)_4H]$ gave a k^{OsOs} of 0.096 $M^{-1}\,s^{-1}$.) There are a number of possible explanations for this. The values for T_1 in the absence of exchange were measured in separate experiments on solutions of pure materials and may not be accurate under the conditions of the saturation-transfer experiment. In particular, such long T_1 values as 240 s for $K[Os(CO)_4H]$ could vary substantially with concentration. It should also be pointed out that a proton-transfer reaction as slow as this one is extremely susceptible to adventitious catalysis. The proton-transfer rate data for $Os(CO)_4H_2/Et_3N$ (to be presented in the next section) show that as little as 10^{-6} M of a base with the kinetic basicity of Et_3N could produce the observed 30% variation in rate. Although it can be argued that the lowest measured rate constant thus represents an upper limit, the average value from three experiments is reported in Table VII.

It is conceivable that the variation measured in $Os(CO)_4H_2/K[Os(CO)_4H]$ proton-exchange rate constants is real and not the result of experimental error. Although we believe ion-pairing effects to be small in these systems, they may be significant at the high concentration (much higher than that used in any other experiments in this work) of $K[Os(CO)_4H]$ used in the experiment that gave the slowest rate.

$Os(CO)_4(E)(H)/Et_3N$ Proton Transfer (E = H, CH_3, $Os(CO)_4H$). The ^1H spectra of solutions containing $Os(CO)_4(E)H$ (E = H, $Os(CO)_4H$) (0.1–0.3 M) and Et_3N (0.2–1.6 M) exhibited separate Os–H resonances for $Os(CO)_4(E)H$ and $[Et_3NH][Os(CO)_4E]$ at low temperatures, with the former being both sharper and more intense. In the case of E = H, it was possible to obtain good measurements of K_{eq} for eq 14 (0.04, −40 °C; 0.014, −20

$$Os(CO)_4(E)(H) + Et_3N \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Os(CO)_4(E)]^- + Et_3NH^+ \quad (14)$$

°C), which showed that it increased significantly over the 25 °C IR value with decreasing temperature;[33,34] in the case of E =

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[32] As the chemical shift difference between the averaged NH resonance of mor/morH^+ and the hydride resonance of $(\eta^5\text{-}C_5H_5)W(CO)_3H$ is much larger than that between the $\eta^5\text{-}C_5H_5$ resonances of $(\eta^5\text{-}C_5H_5)W(CO)_3H$ and $(\eta^5\text{-}C_5H_5)W(CO)_3^-$, the former resonances only broaden at temperatures where the latter coalesce.

[33] This increase contrasts with the close agreement observed earlier in the $(\eta^5\text{-}C_5H_5)W(CO)_3H$/morpholine system between the IR K_{eq} at 25 °C and the NMR values measured below 0 °C. Such disagreement may reflect small ion-pairing effects at the higher concentrations used in the NMR experiments, but it is more likely to reflect temperature dependence of K_{eq}. In cases where a neutral acid and base react to generate charged species (and $\Delta S^\circ < 0$), entropy considerations should shift the equilibrium toward the charged species at lower temperatures. It is interesting to note that K_{eq} for the $(\eta^5\text{-}C_5H_5)W(CO)_3H$/morpholine equilibrium (for which ΔS^* and presumably ΔS° as well are near zero) is temperature independent while K_{eq} for the $Os(CO)_4H_2/Et_3N$ equilibrium (for which $\Delta S^* \ll 0$) increases with decreasing temperature. Such temperature-dependent equilibria have been observed previously in organometallic systems.[34]

Table VII. Proton-Transfer Rate Constants and Activation Parameters in CD_3CN

HA	B	ΔpK_a[a]	k, 25 °C, $M^{-1}\ s^{-1}$[b-d]	$\Delta H^{\ddagger}$, kcal mol^{-1}[b,d]	$\Delta S^{\ddagger}$, cal $deg^{-1}\ mol^{-1}$[b,d]
$(\eta^5\text{-}C_5H_5)Cr(CO)_3H$	$(\eta^5\text{-}C_5H_5)Cr(CO)_3^-$	0	$7.4\ (2) \times 10^4$	8.8 (1)	−7 (1)
$(\eta^5\text{-}C_5H_5)Mo(CO)_3H$	$(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$	0	$2.4\ (2) \times 10^3$	6.8 (4)	−20 (1)
$(\eta^5\text{-}C_5H_5)Mo(CO)_3H$	$(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$	0	$5.1\ (3) \times 10^3$[e]	6.1 (1)[e]	−21 (1)[e]
$(\eta^5\text{-}C_5H_5)W(CO)_3H$	$(\eta^5\text{-}C_5H_5)W(CO)_3^-$	0	$6.4\ (2) \times 10^2$	8.1 (3)	−19 (1)
$(\eta^5\text{-}C_5H_5)W(CO)_3H$	morpholine	−0.5	$1.0\ (1) \times 10^5$[f]	11.3 (6)[f]	2 (2)[f]
$morH^+$	$(\eta^5\text{-}C_5H_5)W(CO)_3^-$	0.5	$5.6\ (10) \times 10^4$[g] $(3.6 \times 10^4$[h]$)$	12.4 (8)[g]	5 (3)[g]
$Os(CO)_4H_2$	$Os(CO)_4H^-$	0	$7.5\ (21) \times 10^{-2}$[i]		
$Os(CO)_4H_2$	Et_3N	2.3	$4.8\ (1) \times 10^2$	6.5 (2)	−24 (1)
Et_3NH^+	$Os(CO)_4H^-$	−2.3	$1\ (1) \times 10^5$[j] $(1.0 \times 10^5$[h]$)$	13 (2)[j]	7 (10)[j]
$Os_2(CO)_8H_2$	$Os_2(CO)_8H^-$	0	<7[k]		
$Os_2(CO)_8H_2$	Et_3N	1.9	$1.2\ (1) \times 10^1$	9.1 (5)	−23 (2)
Et_3NH^+	$Os_2(CO)_8H^-$	−1.9	$1.6\ (3) \times 10^3$[g] $(0.8 \times 10^3$[h]$)$	10.4 (8)[g]	−9 (3)[g]
$Os(CO)_4(CH_3)(H)$	Et_3N	4.5	$3.4\ (2) \times 10^1$	8.5 (2)	−23 (1)

[a] $\Delta pK_a = pK_a\ (HA) - pK_a\ (BH^+)$. [b] k(25 °C) extrapolated and activation parameters calculated from data obtained over at least a 30 °C range unless noted otherwise. [c] Second-order rate constant for the reaction $HA + B \rightarrow A^- + HB^+$. [d] Value in parentheses is uncertainty (standard deviation) in least significant digit. [e] THF-d_8 solvent. [f] From data obtained between −20 and 5 °C. [g] From data obtained between −20 and 0 °C. [h] Calculated from $k_{forward}$ and K_{eq}. [i] 30 °C. [j] From data obtained between −40 and −30 °C. [k] Upper limit from lack of peak broadening.

$Os(CO)_4H$, the best estimates for K_{eq} (0.010 ± 0.05 from −20 °C to −10 °C) showed only minor deviations from the 25 °C IR value.

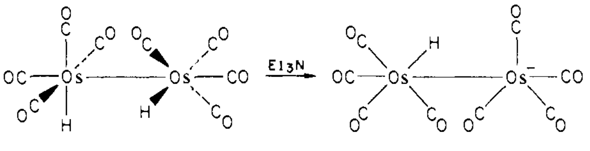
As the temperature was raised at any given concentration or as the concentrations were increased, the Os–H peaks broadened and coalesced. As direct Os–Os proton exchange had been found to be too slow to produce line broadening, the forward and reverse second-order rate constants for Os–N proton transfer, k_f and k_r, were calculated directly from these line-shape changes. The results are given in Table VI.

The ^1H NMR spectra of solutions containing $Os(CO)_4(CH_3)(H)$ (0.2 M) and Et_3N (1–2 M) exhibited only peaks due to the neutral metal hydride, consistent with the conclusion from the IR studies that equilibrium 14 (for E = CH_3) lies far to the left (K_{eq} (calcd) = 3×10^{-5}). However, as the temperature or the Et_3N concentration was raised, both the Os–H quartet and the Os–CH_3 doublet broadened and both collapsed at the same temperature to sharp singlets. These line-shape changes were reversible and were not observed in the absence of Et_3N and are thus due to the forward reaction in eq 14. The line shapes for the collapsing Os–H quartet were compared (as shown in Figure 1) to the line shapes calculated for various rates of proton transfer.[35] Despite our inability to measure it directly, the rate of proton exchange between $Os(CO)_4(CH_3)(H)$ and $[Os(CO)_4(CH_3)]^-$ is undoubtedly very slow, so the rates of proton transfer thereby obtained are Os–N proton-transfer rates. The second-order rate constants k_f obtained after division by $[Et_3N]$ are given in Table VI. Because of the low concentration of $[Os(CO)_4(CH_3)]^-$, no information about k_r was obtained.

Discussion

The pK_a data in Table II show that many hydrido transition-metal complexes are surprisingly strong acids in CH_3CN. For example, the pK_a values of $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$ and $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$ fall between that of CH_3SO_3H (pK_a = 10.0 in CH_3CN[11]) and that of 2,4-dinitrophenol (pK_a = 16.0 in CH_3CN[11]). Even the least acidic hydrido transition-metal complex studied ($Os(CO)_4(CH_3)H$) has a pK_a comparable to those of simple carboxylic acids (the pK_a of CH_3CO_2H is 22.3 in CH_3CN[11]), calling into question the common practice[12a,b] of using acetic acid to protonate transition-metal anions. (Relative acid strengths may of course be different in other solvents such as THF.)

Comparison of the pK_a values for the three $(\eta^5\text{-}C_5H_5)M(CO)_3H$ offers quantitative support for the general belief[36-38] that basicity increases down a column in the periodic table, although the change between Cr and Mo is much less than that between Mo and W. Similarly, comparison of the pK_a values for the three $Os(CO)_4(E)H$ shows the effect of substituents on thermodynamic acidity. A methyl substituent on an osmium hydride decreases its acidity by 2.2 pK_a units, an inductive effect comparable with the change of 1.9 pK_a units observed between NH_4^+ and $CH_3NH_3^+$ in CH_3CN.[11] An $Os(CO)_4H$ substituent on an osmium hydride increases its acidity by 0.4 pK_a unit, presumably because of increased delocalization of negative charge in the $[Os_2(CO)_8H]^-$ anion, although the latter does not appear to have a symmetric structure.[39-42]



$Os_2(CO)_8H_2$ $[Os_2(CO)_8H]^-$ (15)

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(35) The spectra shown in Figure 1 are strikingly reminiscent of those obtained for the collapse upon proton transfer of the methyl quartet of $CH_3NH_3^+$ in the classic work of Grunwald, E.; Loewenstein, A.; Meiboom, S. *J. Chem. Phys.* **1957**, *27*, 641.

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(39) It is apparent from its lack of an IR band in the bridging carbonyl region that $[HOs_2(CO)_8]^-$ does not have the same structure (two bridging carbonyls and one bridging hydride) as that found in the solid state and in THF solution for $[HFe_2(CO)_8]^-$.[40] The structure drawn, reminiscent of that suggested[41] for $[(OC)_5CrFe(CO)_4]^{2-}$, is supported by (a) the ^1H chemical shift, which is more consistent with a terminal hydride than with a bridging one,[42] and (b) the range of over 200 cm^{-1} in the carbonyl-region IR spectrum, which is more consistent with one formally neutral and one formally negatively charged $Os(CO)_4$ unit than with a completely delocalized structure.

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The activation parameters for all of the proton-transfer reactions and the extrapolated values of the rate constants at 25 °C are given in Table VII. As measurement of the reverse rates was generally possible over only a limited temperature range, the activation parameters and extrapolated values for k_r (i.e., for morH$^+$/[(η^5-C_5H_5)W(CO)$_3$]$^-$, Et_3NH^+/[Os(CO)$_4$H]$^-$, and Et_3NH^+/[$Os_2(CO)_8H$]$^-$) are considerably less certain than are the corresponding quantities for k_f. Nevertheless, the extrapolated k_r agree reasonably well with the values calculated from the corresponding extrapolated 25 °C k_f and the IR-measured (Table II) 25 °C K_{eq}.

Although there are a number of exceptions, many of the reactions in Table VII have large negative entropies of activation (about −20 cal deg^{-1} mol^{-1}). Similar results have been reported in studies of proton-transfer reactions between organic molecules in acetonitrile. $\Delta S^{\ddagger}$ for the reaction of (4-nitrophenyl)nitromethane with Et_3N, n-Bu_3N, and TMG in that solvent ranges from −22 to −27 cal deg^{-1} mol^{-1}.[43] The small solvent effect (a factor of two between CD_3CN and THF-d_8) upon the rate of (η^5-C_5H_5)Mo(CO)$_3$H/[(η^5-C_5H_5)Mo(CO)$_3$]$^-$ proton exchange suggests that proton-transfer reactions of this sort may be comparatively insensitive to the degree of ion pairing.

The metal–metal proton-exchange rates decrease down the periodic table, Cr > Mo > W—the pattern observed for almost all reactions of transition-metal complexes. In general, the proton-transfer rates vary a great deal with the nature of the receiving base even when the differences in thermodynamic base strength are comparatively small. For example, although [(η^5-C_5H_5)W(CO)$_3$]$^-$ is only a slightly weaker base (0.5 pK_a unit) than morpholine, the rate of proton transfer to [(η^5-C_5H_5)W(CO)$_3$]$^-$ from (η^5-C_5H_5)W(CO)$_3$H is 160 times slower than the rate of proton transfer to morpholine from (η^5-C_5H_5)W(CO)$_3$H. Similarly, [Os(CO)$_4$H]$^-$ is a somewhat stronger base (2.3 pK_a units) than triethylamine, but the rate of proton transfer to [Os(CO)$_4$H]$^-$ from Os(CO)$_4$H$_2$ is over 6×10^3 times slower than the rate of proton transfer to Et_3N from Os(CO)$_4$H$_2$. It appears that metal–metal proton transfer is slower than metal–nitrogen or nitrogen–metal proton transfer for comparable values of ΔpK_a.

All of the rate constants are small in comparison with those for other proton-transfer reactions in acetonitrile. For example, the rate constant for proton transfer from protonated methyl red (pK_a = 10.2) to picrate ion (the pK_a of picric acid is 11.0) is 5.1×10^9 M^{-1} s^{-1} at 25 °C.[44] The rate constants in Table VII are, however, the same order of magnitude as those for the deprotonation of the carbon acid (4-nitrophenyl)nitromethane by Et_3N, n-Bu_3N, and TMG.[43] The deprotonation of hydrido transition-metal complexes is thus a slow process, comparable in rate to the slow deprotonations observed for many carbon acids rather than to the fast deprotonations characteristic of oxygen and nitrogen acids.[45] A similar conclusion has been reached by Walker et al., who noted that the rate constants for deprotonation of the (mostly polynuclear) hydrides they studied in methanol were "remarkably small for a base as strong as methoxide ion" and comparable with those for the deprotonation of carbon acids such as nitroparaffins.[3]

The deprotonation of hydrido transition-metal complexes, like the deprotonation of carbon acids, is accompanied by substantial electronic changes which have no counterpart in the deprotonation of oxygen or nitrogen acids. Deprotonation of the hydrido metal complexes we have studied is possible only because the resulting negative charge is delocalized onto π-acceptor ligands, as is reflected in the considerable decrease (well over 100 cm^{-1} in mononuclear cases) in carbonyl stretching frequencies between the neutral hydrides in Table I and the corresponding anions. In contrast, deprotonation of oxygen or nitrogen acids generates a negative charge which largely remains on these more electronegative atoms.

The electronic changes that occur upon deprotonation of hydrido transition-metal complexes are reflected in structural changes. Whereas deprotonation of an oxygen or a nitrogen acid leaves a stereochemically active lone pair, deprotonation of a metal hydride effects a formal reduction as the pair of electrons in the M–H bond is transformed into a stereochemically inactive pair of d electrons. For example, the initially octahedral[46] d^6 Os(CO)$_4$(E)H complexes become d^8 and approximately trigonal bipyramidal upon deprotonation (as seen in the structures of the corresponding iron anions [Fe(CO)$_4$H]$^{-}$[47] and [Fe(CO)$_4$C$_3$H$_7$]$^{-}$[48]). Similarly, the (η^5-C_5H_5)M(CO)$_3$H complexes change from a d^4 configuration and a "four-legged piano stool" geometry (which is a general feature of (η^5-C_5H_5)M(CO)$_3$X systems and is supported by NMR results for (η^5-C_5H_5)W(CO)$_3$H[49,50]) to a d^6 configuration and a "three-legged piano stool" geometry of approximately C_{3v} symmetry (as seen in the [(η^5-C_5H_5)Mo(CO)$_3$]$^-$ anion[18a,29]). The necessity for such structural and electronic rearrangements results in a barrier to the removal of protons from transition metals and presumably results in an even bigger barrier to the exchange of protons between transition metals.

The rate of deprotonation of the dinuclear $Os_2(CO)_8H_2$ is not only 40 times slower than that of the slightly less acidic (ΔpK_a = 0.4) Os(CO)$_4$H$_2$ but even 3 times slower than that of the much less acidic (ΔpK_a = 2.6) Os(CO)$_4$(CH$_3$)H. Although this slowness may simply reflect steric hindrance, it is possible that the same additional delocalization that decreases the pK_a of $Os_2(CO)_8H_2$ below that of Os(CO)$_4$H$_2$ contributes to the decreased rate by increasing the electronic rearrangement that must occur upon deprotonation.

A better understanding of the details of metal proton-transfer reactions will require a more detailed examination of the relationship between kinetic and thermodynamic acidity in such systems. The present data cover too wide a range of structural differences to permit the construction of meaningful Brønsted plots[45] of ln k vs. ΔpK_a, although comparison of the Et_3N deprotonation rates of Os(CO)$_4$H$_2$ and Os(CO)$_4$(CH$_3$)H (which arguably differ more for thermodynamic than for steric reasons) suggests that the slope (α) of such a plot may be about 0.5. Future work with additional nitrogen bases will allow the construction of such plots.

A Caveat. In view of the comparative ease with which transition-metal complexes undergo one-electron oxidation and reduction, it is possible that reactions which appear to be proton transfers may actually be the result of one-electron transfer followed by hydrogen atom transfer. For example, the fact that measurements of the Os(CO)$_4$H$_2$/[Os(CO)$_4$H]$^-$ "proton-transfer" rate were not as reproducible as our other measurements, considered in light of recent reports that the hydrido anion (η^5-C_5H_5)V(CO)$_3$H$^-$ can serve as a one-electron reducing agent[51] and that hydrido iron carbonyl anions readily undergo one-electron oxidation,[52] suggests the mechanism of reactions 16 and 17 as a

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plausible alternative to proton transfer.

$$Os(CO)_4H_2 + [Os(CO)_4H]^- \xrightarrow[\text{transfer}]{e^-} Os(CO)_4H_2^{-\cdot} + Os(CO)_4H\cdot \quad (16)$$

$$Os(CO)_4H_2^{-\cdot} + Os(CO)_4H\cdot \xrightarrow[\text{transfer}]{H\cdot} [Os(CO)_4H]^- + Os(CO)_4H_2 \quad (17)$$

Conclusions

On the basis of the systems thus far examined, three generalizations may be proposed: (1) Both thermodynamic and kinetic acidity decrease down a column in the periodic table. (2) The rate of deprotonation of a hydrido transition-metal complex is slow compared with that of an oxygen or nitrogen acid and comparable with that of a carbon acid. (3) The rate of proton transfer from a hydrido transition-metal complex to its conjugate anion is much slower than that to a nitrogen base of comparable thermodynamic base strength.

Future work will test the validity of these generalizations for other types of hydrido transition-metal complexes.

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Registry No. $(\eta^5\text{-}C_5H_5)W(CO)_3H$, 12128-26-6; $K[[\eta^5\text{-}C_5H_5)W(CO)_3]$, 62866-03-9; $[Et_3NH][(\eta^5\text{-}C_5H_5)W(CO)_3]$, 80462-63-1; $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, 12176-06-6; $K[(\eta^5\text{-}C_5H_6)Mo(CO)_3]$, 62866-01-7; $[morH][(\eta^5\text{-}C_5H_5)Mo(CO)_3]$, 80462-65-3; $(\eta^5\text{-}C_5H_5)Cr(CO)_3H$, 36495-37-1; $K[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$, 69661-90-1; $[morH][(\eta^5\text{-}C_5H_5)Cr(CO)_3]$, 80462-67-5; $Os(CO)_4H_2$, 18972-42-4; $K[Os(CO)_4H]$, 80462-68-6; $[Et_3NH][Os(CO)_4H]$, 80462-70-0; $Os(CO)_4(CH_3)(H)$, 22639-03-8; $[TMGH][Os(CO)_4CH_3]$, 80462-42-6; $Os_2(CO)_8H_2$, 2565-05-6; $[TMGH][Os_2(CO)_8H]$, 80462-44-8; morpholine, 110-91-8; Et_3N, 121-44-8.

Reductive Coupling of Coordinated Alkyl Isocyanides in Seven-Coordinate Molybdenum(II) and Tungsten(II) Complexes. Removal of the Coupled Ligand as an Oxamide[1,2]

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Abstract: The synthesis of a variety of $[M(CNR)_4\{(CNHR)_2\}X]^+$ complexes ($M = Mo$, $R = t\text{-}C_4H_9$, $X = Cl, Br, I, CN$; $M = Mo$, $R = c\text{-}C_6H_{11}$, $X = I$; $M = W$, $R = t\text{-}C_4H_9$, $X = I$) is described. The bright red complexes contain the coordinated RHNCCNHR ligand, formally regarded as an (*N,N'*-dialkyldiamino)acetylene, derived by reductive coupling of two isocyanide ligands in the seven-coordinate $[M(CNR)_6X]^+$ cations. When zinc is used as the reducing agent in a refluxing protic solvent such as wet THF or ethanol, the products were isolated in good to excellent (>90%) yields. Small amounts (~7%) of $[Mo(CN\text{-}t\text{-}C_4H_9)_4\{(CNH\text{-}t\text{-}C_4H_9)_2\}I]^+$ were also obtained in homogeneous reactions of the trityl radical or of the photochemically generated benzophenone diradical with $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]^+$ in ethanol at room temperature. Although $[Mo(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$ yields mainly $[Mo(CN\text{-}t\text{-}C_4H_9)_4\{(CNH\text{-}t\text{-}C_4H_9)_2\}(CN)]^+$ when subjected to the reductive coupling reaction conditions, the desired blue cation $[Mo(CN\text{-}t\text{-}C_4H_9)_5\{(CNH\text{-}t\text{-}C_4H_9)_2\}]^{2+}$ was prepared by addition of *tert*-butyl isocyanide to $[Mo(CN\text{-}t\text{-}C_4H_9)_4\{(CNH\text{-}t\text{-}C_4H_9)_2\}I]^+$. Proton and ^{13}C NMR studies of the blue complex showed that, although the four *tert*-butyl isocyanide ligands cis to the acetylene are equivalent at room temperature, the fifth (trans) ligand is not in rapid exchange with the others. The mixed ligand $[Mo(CNCH_3)_4\{(CNH\text{-}t\text{-}C_4H_9)_2\}I]^+$ complex was prepared by addition of methyl isocyanide to $[Mo(CN\text{-}t\text{-}C_4H_9)_4\{(CNH\text{-}t\text{-}C_4H_9)_2\}I]^+$ under mild conditions. The coupled acetylene ligand could be removed with its C–C bond intact by oxidation, which produced the corresponding *N,N*-dialkyl oxamide. The best yields (~40%) were achieved by using hydrogen peroxide as the oxidant. Bonding interactions between the metal and coupled ligand are qualitatively discussed and used to rationalize trends in the structural and spectroscopic properties of the $[Mo(CN\text{-}t\text{-}C_4H_9)_4\{(CNH\text{-}t\text{-}C_4H_9)_2\}X]^+$, $X = Cl, Br, I, CN$, and $[Mo(CN\text{-}t\text{-}C_4H_9)_5\{(CNH\text{-}t\text{-}C_4H_9)_2\}]^{2+}$ cations. Mechanistic aspects of the coupling reaction are briefly considered.

Compounds of the group 6 transition metals of the general formula $[M(CNR)_7]^{2+}$, $[M(CNR)_6X]^+$ (R = alkyl, X = Cl, Br, I, CN, $SnCl_3$; R = aryl, X = I), and $M(CNR)_5X_2$ comprise a well-studied[2–12] class. These complexes have close interligand contacts which could give rise to ligand migration or coupling reactions. Reductive coupling of two isocyanide ligands was found to occur in the reaction of $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]^+$ with zinc.[13] In particular, a brilliant red crystalline material was obtained, the nature of which was revealed by X-ray crystallography. The complex turned out to be $[Mo(CN\text{-}t\text{-}C_4H_9)_4\{(CNH\text{-}t\text{-}C_4H_9)_2\}I]I$,

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[1] Part 15 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 14 see ref 2.

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