(13) Only one As-Me 90-MHz ^{1}H NMR signal (at τ 8.26 in CH_2Cl_2) is seen down to −90 °C. From the coalescence behavior in the lower two-temperature ranges of the ^{13}C NMR spectra, estimates for $\Delta G^{\ddagger}$ of 8.4 and 11.9 kcal/mol may be calculated. These values correspond to values for the respective exchange rates at −90 °C of 360 and 0.02 s^{-1}. Thus, the expected pair of As-Me signals would be in the slow-exchange regime with respect to the intermediate process and above coalescence with respect to the lowest energy process, as long as $\Delta\nu \lesssim 160$ Hz. For comparison, separate 90-MHz As-Me signals are observed for $Ir_4(CO)_9(diars)(PPh_2Me)$ at τ 8.03 and 8.42 ($\Delta\nu = 31$ Hz) and for $Ir_4(CO)_8(diars)(PMe_3)_2$ at τ 8.06 and 8.57 ($\Delta\nu = 46$ Hz). See Stuntz G. F. Ph.D. Thesis, University of Illinois, 1978.

(14) Lawson, R. J.; Shapley, J. R. *Inorg. Chem.* **1978,** *17,* 772.

(15) Canziani, F.; Chini, P., personal communication.

(16) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1973,** *12,* 531.

(17) A. P. Sloan Foundation Fellow, 1978–1980; Camille and Henry Dreyfus Teacher-Scholar, 1978–1983.

John R. Shapley,*[17] Gordon F. Stuntz
Department of Chemistry, University of Illinois
Urbana, Illinois 61801

Melvyn Rowen Churchill,* John P. Hutchinson
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

Received July 16, 1979

Rates of Deprotonation and pK_a Values of Transition Metal Carbonyl Hydrides

Sir:

There has been much recent interest in the synthesis, properties, and reactions of metal carbonyl hydride clusters,[1] accentuated by the probable roles of such species in homogeneous catalysis.[2] One long known property of metal hydrides is the ability to act as a Brønsted acid in solution. Nonetheless, virtually no quantitative information is available regarding either the equilibrium acidities (pK_a values) or the kinetics of deprotonation–protonation steps for these cluster species. In fact, very few rate studies have been reported for the deprotonation of transition metal hydrides in general.[3] Described here are kinetic and equilibrium deprotonation–protonation data for several tetranuclear group 8 metal hydride clusters of the general formulae $H_4M_4(CO)_{12}$ and $H_2M_4(CO)_{13}$ and of two mononuclear analogues $H_2M(CO)_4$. To our knowledge, this represents the first report of quantitative rate data for the deprotonation of a metal carbonyl hydride cluster or of any neutral transition metal hydride complex.

A typical example is

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

Rates were determined in a Durrum-Gibson D110 stopped-flow spectrophotometer. The metal complex concentration was in the range of 1×10^{-5} to 1×10^{-4} M and the concentration of sodium methoxide, always being in excess, varied from 1×10^{-4} to 5×10^{-2} M. Optical density changes in the region of 300–400 nm were monitored. Reactions were found to be first order for several half-lives, and plots of k_{obsd} vs. the base concentration were linear with a nonzero intercept. The slope gives k_1; the intercept gives k_{-1}. Extrapolation of the optical density back to zero time gave readings expected for the neutral hydride, except for $H_2Fe(CO)_4$. The final optical densities were those of the monoanions, where these were known. Any decomposition reactions were much slower than the reactions studied.

The equilibrium constant for reaction 1 is given by

$$K = k_1/k_{-1} = K_a/K_s \qquad (2)$$

where K_a is the acid ionization constant of the hydride and K_s is the ion product of methanol (1.96×10^{-17} at 25 °C[4]). The rate constants obtained and the pK_a values (−log K_a) calculated by the kinetics method are summarized in Table I. The validity of the kinetics method to obtain the pK_a values is confirmed by agreement with the values independently determined by a buffer/indicator method[6] for $H_4Ru_4(CO)_{12}$ and $H_4Os_4(CO)_{12}$.

Table I. Rate and Equilibrium Data for Some Carbonyl Hydrides in Methanol at 25 °C

compd	k_1, M^{-1} s^{-1} [a]	k_{-1}, s^{-1} [a]	pK_a [b]	pK_a [c]
$H_4Ru_4(CO)_{12}$	6.2×10^3	0.08	11.7	11.9
$H_4FeRu_3(CO)_{12}$	8.6×10^3	4.4	13.4	
$H_2Ru_4(CO)_{13}$	5.3×10^2	4.8	14.7	
$H_2FeRu_3(CO)_{13}$	7.7×10^2	3.1	14.3	
$H_2Os(CO)_4$	8.2×10^4	10.2	12.8	
$H_4Os_4(CO)_{12}$	2.3×10^3	0.05	12.0	12.3
$H_2Fe(CO)_4$	1.3×10^6	72	(12.4)	pK_1 = 6.8 [d] pK_2 = 15 [d]

[a] Average experimental uncertainty ±10%. [b] From pK_a = −log (k_1K_s/k_{-1}). [c] From buffer/indicator or emf methods.[6] [d] From ref 5.

The reaction of $H_2Fe(CO)_4$ with methoxide was much more rapid than for the other hydrides studied. Extrapolation of the optical density back to zero time did not give the spectrum of $H_2Fe(CO)_4$. Furthermore the pK_a (12.6) calculated from the rates does not agree with either pK_1 (6.77) or pK_2 (≥15) for $H_2Fe(CO)_4$ in methanol.[5] It is likely that the changes observed in the stopped flow are a mixture of the first and second steps and the measured rates represent only upper limits for the first step. Because of the much lower acidity of all the other hydrides in Table I, it is unlikely that appreciable formation of dianion occurs in these cases.

The greater acidity of $H_2Fe(CO)_4$ compared with $H_2Os(CO)_4$ has been noted previously, although the difference of 6.2 pK_a units is somewhat less than has been estimated.[7] There is a general trend for the heavier metal hydrides to be less acidic than their lighter metal analogues.[8]

The results for the polynuclear hydrides are somewhat surprising since these contain only bridging hydride ligands, rather than the terminal hydrides of $H_2Os(CO)_4$ and $H_2Fe(CO)_4$. It had been suggested that bridging hydrides would be quite inert kinetically;[9] however, our data show only a modest lability difference between $H_4Os_4(CO)_{12}$ and $H_2Os(CO)_4$ and, although less labile, the polynuclear species is actually the more acidic. Similar greater acidity of bridging hydrides over terminal hydrides is seen for polynuclear boron hydrides[10] and the rhenium carbonyl hydrides $HRe(CO)_5$ and $H_3Re_3(CO)_{12}$.[11]

The values of k_1 are remarkably small for a base as strong as methoxide ion. Rates of proton removal from the ruthenium and osmium hydrides are quite comparable with rates of reaction of nitroparaffins with hydroxide ion.[12] Presumably slow rates are the result of the substantial structural and electronic rearrangements which accompany removal of the proton. Another noteworthy feature of the rate data is the slow protonation rates for $H_3Ru_4(CO)_{12}^-$ and $H_3Os_4(CO)_{12}^-$ relative to the other tetranuclear anions (Table I). It is tempting to suggest that these slow reactions reflect a structural rearrangement concomitant with protonation such as has been reported for $Fe_4(CO)_{13}^{2-}$.[1b] However, X-ray diffraction studies show that the carbonyl and ruthenium frameworks (in the solid phase) are qualitatively the same for $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$[13] as for $H_4Ru_4(CO)_{12}$.[14] An important difference may be the presence of two conformers for the anion in solution.[9] One of these apparently has three hydrides bridging the Ru–Ru bonds forming one triangular face.[13]

0002-7863/79/1501-7428$01.00/0

Similar bridging is not found in the parent $H_4Ru_4(CO)_{12}$; thus, if this were the favored conformation in methanol solution for the $H_3Ru_4(CO)_{12}^-$ and $H_3Os_4(CO)_{12}^-$ anions, the unusually slow back-reaction may reflect this added conformational change.

Acknowledgments. This work was supported in part by a contract (No. DE-AS03-76SF0034) with the Department of Energy, Office of Basic Energy Sciences (with P.C.F.), and in part by a grant (No. CH77-27417) from the National Science Foundation (to R.G.P.). The platinum group metals were provided on a loan from Matthey Bishop, Inc.

References and Notes

(1) For reviews see: (a) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979,** *25*, 145–222. (b) Chini, P.; Heaton, B. T. *Top. Curr. Chem.* **1977,** *71*, 1–70.

(2) (a) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977,** *99*, 252. (b) Ungermann, C.; Landis, V.; Moya, S. A.; Cohen, H.; Walker, H.; Pearson, R. G.; Ford, P. C. *Ibid.* **1979,** *101*, 5922. (c) Kang, H.; Mauldin, C. H.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *Ibid.* **1977,** *99*, 8323–8325. (d) Falbe, J. *J. Organomet. Chem.* **1975,** *94*, 213–227. (e) Vaglio, G. A.; Osella, D.; Valle, M. *Trans. Met. Chem.* **1977,** *2*, 94.

(3) (a) Tolman, C. A. *J. Am. Chem. Soc.* **1970,** *92*, 4217. (b) Venerable, G. D., II; Halpern, J. *Ibid.* **1971,** *93*, 217. (c) Louw, W. J. *J. Chem. Soc., Chem. Commun.* **1977,** 845.

(4) Koskikallio, J. *Suom. Kemistil. B* **1957,** *30*, 111, 115.

(5) Hieber, W.; Hübel, W. B. *Z. Elektrochem.* **1953,** *57*, 235. This work shows that in methanol $H_2Fe(CO)_4$ is 465 times stronger than acetic acid, for which $pK_a = 9.60$ in methanol.[6] The estimate of pK_2 for $H_2Fe(CO)_4$ follows from the lack of a second break in the titration curve (Hieber and Hübel), and the fact that salts such as $Na_2Fe(CO)_4$ can be prepared in alcohols.

(6) Kolthoff, J. M.; Guss, L. S. *J. Am. Chem. Soc.* **1939,** *61*, 330.

(7) Evans, J.; Okrasinski, S. J.; Pribula, A. J.; Norton, J. R. *J. Am. Chem. Soc.* **1976,** *98*, 4000.

(8) (a) Nakamura, A.; Otsuka, S. *J. Mol. Catal.* **1976,** *1*, 285–307. (b) Lokshin, B. V.; Parinski, A. A. *J. Organomet. Chem.* **1973,** *55*, 315. (c) Harris, D. C.; Gray, H. B. *Inorg. Chem.* **1975,** *14*, 1215–1217.

(9) Koepke, J. W.; Johnson, J. R.; Knox, S. A. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975,** *97*, 3947–3952. The very slow reaction of $H_4Ru_4(CO)_{12}$ with KOH observed in this work may be due to the insolubility of the complex.

(10) Muetterties, E. L. "Boron Hydride Chemistry"; Academic Press: New York, 1975; pp 82, 117, 356, 376.

(11) Kaesz, H. D. *Chem. Br.* **1973,** *9*, 344–352.

(12) Maron, S. H.; La Mer, V. K. *J. Am. Chem. Soc.* **1938,** *60*, 2588–259.

(13) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc.* **1978,** 920–921.

(14) Wilson, R. D.; Wu, S. M.; Love, R. A.; Bau, R. *Inorg. Chem.* **1978,** *17*, 1271–1280.

Howard W. Walker, Charles T. Kresge
Peter C. Ford,* R. G. Pearson*
Department of Chemistry, University of California
Santa Barbara, California 93106

Received August 16, 1979

Palladium Catalyzed Hydrolysis of Tertiary Amines with Water

Sir:

Although catalytic hydrolysis of tertiary amines is principally of importance with respect to biological deamination processes[1-2] and energy-transfer systems for solar energy conversion,[3] there has been no report on catalytic hydrolysis with metal catalysts. We report a novel palladium catalyzed hydrolysis of tertiary amines, which is superior in certain cases to current procedures that require stoichiometric amount of oxidants.[4] The reaction involves insertion of palladium coordinated to the nitrogen lone pair into the carbon–hydrogen bond adjacent to nitrogen, giving iminium ion (**1**) and enamine complexes (**2**). The key step is the activation of hydrogen at saturated carbon to which much attention has been devoted recently.[5-8]

$$R^1CH_2NR^2R^3 + H_2O \xrightarrow{\text{cat.}} R^1CHO + R^2R^3NH + H_2$$

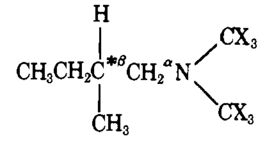
When a mixture of tributylamine (2 mmol), hydrochloric acid (0.7 mmol), palladium black (0.8 mmol), and 2,4-dinitrophenylhydrazine (2 mmol) in water (40 mmol) was heated with stirring under argon for 40 h at 200 °C, dibutylamine and the 2,4-dinitrophenylhydrazone of butanal were obtained in 98 and 92% yields, respectively.[9] The catalytic hydrolysis of tertiary amines proceeded generally and efficiently with palladium catalysts.[10,11] Examples of this simple reaction system for the hydrolysis of tertiary amines using palladium black and hydrochloric acid catalysts[12] are shown in Table I. The carbon–nitrogen bond of a tertiary amine is cleaved more readily in the order methine > methylene > methyl. Typically, hydrolysis of nicotine gave the relatively unstable pseudooxynicotine[13] exclusively in 85% isolated yield.

Table I. The Hydrolysis of Tertiary Amines with Water[a]

		product,[b] % yield[c,d]	
tertiary amines	convn, %	secondary amines	carbonyl compounds
tributylamine	30	dibutylamine, 97	butanal, 98[e]
N-hexylpyrrolidine	61	pyrrolidine, 98	hexanal, 89[e]
N-cyclohexylhexamethylenimine	25	hexamethylenimine (90)	cyclohexanone (95)
N-cyclopentylmorpholine	50	morpholine (85)	cyclopentanone (90)
N,*N*-dimethyl-α-methylbenzylamine	30	dimethylamine	acetophenone (80)
nicotine	67	pseudooxynicotine (85)	

[a] A mixture of an amine (2 mmol), HCl (0.7 mmol), palladium black (0.8 mmol), and water (40 mmol) was allowed to react with stirring at 200 °C for 40 h. [b] Identified by IR, ^1H NMR spectroscopy, and elemental analysis. [c] GLC yield based on the amine. [d] Isolated yield in parentheses. [e] Yield of 2,4-dinitrophenylhydrazone.

Catalysis of the hydrolysis of a tertiary amine by a proton exhibits a rate increase unless the proton is in excess of the amine, indicating that coordination of palladium to the lone pair of nitrogen competes with protonation. When optically active (*S*)-(+)-*N*,*N*-dimethyl-2-methylbutylamine (**3a**), ($[\alpha]^{23}_{D}$ 7.50°, 2.0 mmol) was treated with palladium in deuterium oxide (40 mmol) in the presence of CH_3CO_2D (0.7 mmol) at 190 °C for 14 h, the recovered amine lost its optical activity completely. The ^1H NMR analysis of recovered **3a** showed that α-methylene, β-methine, and methyl groups were 63, 80, and 25% deuterated, respectively. Further when (*S*)-(+)-*N*,*N*-di(trideuteriomethyl)-2-methylbutylamine (**3b**) alone was treated with palladium catalyst at 200 °C for 16 h, deuterium distribution took place but with retention of the optical activity;[7] the α-methlene, β-methine, and methyl groups of the recovered amine were 34, 17, and 67% deuterated, respectively. A ^{13}C NMR study[14] showed that the deuterium incorporation into the alkyl chain was limited to the α and β positions of the tertiary amines under both amine exchange and hydrolysis conditions.[15]



3a, X = H
b, X = D

A mechanism that may explain the above results is shown in Scheme I. The mechanism requires initial coordination of the nitrogen lone pair to metal followed by metal insertion into the adjacent carbon–hydrogen bond to form **5**,[7,8] which comes to rapid equilibrium with the iminium ion (**1**)[16-18] and the enamine intermediate (**2**). In the absence of proton, the interconversions **5** ⇌ **1** and **5** ⇌ **2** ⇌ **6** proceed rapidly without losing the optical activity at the β position of **3**. The exclusive