mmol) of zirconocene dichloride in 100 mL of tetrahydrofurane. After being stirred overnight the red solution was stripped. The resulting orange residue was extracted twice with 150 mL of pentane. The combined extracts were cooled to -15 °C. The obtained first crystal fraction was very impure. Subsequent crystallization of the same solution at -15 °C resulted in small orange crystals of **24**. Concentration of the mother liquor to about 200 mL followed by crystallization at -30 °C yielded another orange crystal portion of **24**. After the combined fractions of **24** were dried in vacuo, 2.9 g (43%) of product remained. Anal. Calcd for $C_{23}H_{21}ClZr$: C, 65.15; H, 4.96. Found: C, 65.79; H, 5.28. ^1H NMR (C_6D_6) δ 6.7–7.2 (m, 10 H, Ph), 5.62 (s, 10 H, Cp), 3.35 (s, 1 H, C*H*Ph$_2$). ^{13}C NMR (CD_2Cl_2) δ 150.5 (s, q-Ph), 128.6, 128.7 (d each, 158, *o*- and *m*-Ph), 123.5 (d, 162, *p*-Ph), 114.6 (d, 175, Cp), 80.1 (d, 116, *C*HPh$_2$). IR (KBr) ν (cm^{-1}) 2810 (CPh$_2$-H). MS *m/e* 422 (M$^+$).

Preparation of Benzhydrylzirconocene Methoxide (25). A solution of 0.65 g (3.9 mmol) of diphenylmethane in 50 mL of tetrahydrofurane was slowly treated at room temperature with 2.4 mL (3.9 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. After the mixture was stirred for 1 h the resulting red solution was transferred slowly into a stirred solution of 1.05 g (3.65 mmol) of methoxyzirconocene chloride in 30 mL of tetrahydrofurane. After the mixture was stirred for an additional 2 h the orange solution was stripped. The resulting yellow residue was extracted with 100 mL of pentane. The pentane solution was filtered over a G4-frit and stripped. The resulting yellow oil consisted of a mixture of **25** and diphenylmethane. Because of similar solubilities no further purification took place upon attempted recrystallization. ^1H NMR (C_6D_6) δ 6.9–7.2 (m, 10 H, Ph), 5.56 (s, 10 H, Cp), 3.80 (s, 1 H, C*H*Ph$_2$), 3.65 (s, 3 H, CH$_3$). ^{13}C NMR (C_6D_6) δ 152.0 (s, q-Ph), 128.3 (d, 155, *m*-Ph), 128.2 (d, 156, *o*-Ph), 122.6 (d, 158, *p*-Ph), 112.1 (d, 172, Cp), 67.6 (d, 118, *C*HPh$_2$), 61.8 (q, 140, OCH$_3$).

Reaction of Cp$_2$Zr(Cl)CPh$_2$OCH$_3$ (8) with [Cp$_2$Zr(H)Cl]$_x$ (3). [Cp$_2$Zr(H)Cl]$_x$ (**3**) (15 mg, 0.06 mmol) was placed in a 5-mm NMR tube and suspended with a solution of 25 mg (0.06 mmol) of Cp$_2$Zr-(Cl)CPh$_2$OCH$_3$ (**8**) in 0.5 mL of deuterated benzene. The NMR tube was sealed and heated at 55 °C with constant agitation for 7 h. The progress of the reaction was controlled by ^1H NMR. The products were identified by comparison of their ^1H NMR signals with those of authentic

samples. A mixture of the products zirconocene dichloride (**6**) (20%), methoxyzirconocene chloride (**9**) (30%), benzhydrylzirconocene chloride (**24**) (30%), and benzhydrylzirconocene methoxide (**25**) (20%) was obtained after 7 h. ^1H NMR (C_6D_6) δ 5.89 (**6**), 5.92/3.65 (**9**), 6.9–7.2/5.62/3.35 (**24**), 6.9–7.2/5.56/3.80/3.65 (**25**).

Reaction of Cp$_2$Zr(Cl)CPh$_2$OCH$_3$ (8) with (Cp$_2$ZrH$_2$)$_x$ (4). (Cp$_2$ZrH$_2$)$_x$ (**4**) (15 mg, 0.07 mmol) was placed in a 5-mm NMR tube and suspended with a solution of 25 mg (0.06 mmol) of Cp$_2$Zr(Cl)-CPh$_2$OCH$_3$ (**8**) in 0.5 mL of deuterated benzene. The NMR tube was sealed and thermolyzed at 55 °C with constant agitation for 2 h. The analysis was carried out as described above for the analogous reaction between **8** and **3**. Eventually, a mixture of zirconocene dichloride (**6**) (5%), methoxyzirconocene chloride (**9**) (30%), benzhydrylzirconocene chloride (**24**) (30%), and benzhydrylzirconocene methoxide (**25**) (30%) was obtained besides several unidentified products (5%).

Reaction of μ-(CH$_2$=O)(Cp$_2$ZrCl)$_2$ (1) with [Cp$_2$Zr(H)Cl]$_x$ (3). [Cp$_2$Zr(H)Cl]$_x$ (**3**) (15 mg, 0.06 mmol) was placed in a 5-mm NMR tube and suspended with a solution of 30 mg (0.06 mmol) of **1** in 0.5 mL of deuterated benzene. The NMR tube was sealed and thermolyzed at 55 °C for 14 h as described above. A clean mixture of μ-O-(Cp$_2$ZrCl)$_2$ (**29**) (50%) and Cp$_2$Zr(Cl)CH$_3$ (**23**) (50%) was obtained. ^1H NMR (C_6D_6) δ 6.02 (s, 20 H, Cp, **29**), 5.76 (s, 10 H, Cp, **23**), 0.42 (s, 3 H, CH$_3$, **23**).

Kinetic and Thermodynamic Acidity of Hydrido Transition-Metal Complexes. 3. Thermodynamic Acidity of Common Mononuclear Carbonyl Hydrides

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Abstract: The pK_a values of the common mononuclear carbonyl hydrides have been determined in acetonitrile by IR measurement of the position of deprotonation equilibria with various nitrogen bases and potassium phenolate. The resulting values cover a range of about 20 pK_a units, from 8.3 for HCo(CO)$_4$ to 26.6 for CpW(CO)$_2$(PMe$_3$)H. Hydrides with η^5-C$_5$Me$_5$ ligands are appreciably weaker acids than the corresponding hydrides with η^5-C$_5$H$_5$ ligands (e.g., the pK_a of (η^5-C$_5$Me$_5$)Fe(CO)$_2$H is 26.3, while that of (η^5-C$_5$H$_5$)Fe(CO)$_2$H is 19.4). The acidities of the group 8 carbonyl hydrides H$_2$M(CO)$_4$ decrease in the order Fe > Ru > Os.

Despite the 1971 comment[1] that "there is a definite need for the measurement of the acidity functions of a systematic series of metal hydrides under controlled, identical conditions", few such measurements have been made until recently. Early German workers carefully determined the pK_a of a few carbonyl hydrides in H$_2$O,[2] but the scope of this approach is limited by the low solubility of transition-metal hydrides in that solvent (and

sometimes by their reactivity with it). Using polarographic and IR techniques, Vlcek and co-workers[3] attempted the *qualitative* determination of the relative thermodynamic acidities in THF of several common carbonyl hydrides and published a preliminary report; however, all measurements in THF are complicated by the tendency of carbonylmetallate anions to form ion pairs in that solvent.[4] More recently, Walker, Ford, and Pearson[5] determined

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the equilibrium extent of deprotonation of several carbonyl hydrides by methoxide ion in methanol; although good results were obtained with polynuclear hydrides, for mononuclear hydrides (e.g., $H_2Os(CO)_4$) the deprotonation equilibrium was complicated by ion pairing equilibria involving the carbonylmetallate anions, methoxide ion, and alkali metal cations.

We believe that acetonitrile is the ideal solvent for the systematic study of metal hydride acidities, and we have already employed it to study the thermodynamic and kinetic acidities of certain osmium hydrides and of the group 6 hydrides.[6] Acetonitrile solvates cations very effectively,[7] and for that and other reasons it is much less conducive to the formation of ion pairs than is THF or MeOH.[4] (We have never, with any carbonylmetallate anion, seen any IR evidence for contact ion pair formation in CH_3CN.) Furthermore, transition-metal hydrides are generally much more soluble in acetonitrile than in water. Good acidity data for organic acids[7,8a,b] and protonated amines[7,8c] are available in CH_3CN. Finally, unlike relatively basic solvents such as H_2O which exert a leveling effect on strong acids, acetonitrile as a solvent is a sufficiently weak base to differentiate among the acid strengths of strong proton donors (H_2SO_4, HNO_3, and HCl are all weak acids in CH_3CN[9]).

We now report the measurement of the pK_a values in CH_3CN of the remaining common mononuclear carbonyl hydrides, including $HCo(CO)_4$ and its derivatives.

Experimental Section

General. All manipulations were performed in an inert atmosphere (N_2) with high vacuum line, Schlenk, or inert atmosphere box techniques. Hexane and toluene were distilled from Na- or K/benzophenone, followed by vacuum transfer from "titanocene".[10] THF, tetraglyme (under vacuum), glyme, and diglyme were distilled from Na- or K/benzophenone.

For early experiments involving the less acidic hydrides, acetonitrile was, as in our previous work,[6] purified by distillation under N_2 from P_4O_{10} onto CaH_2, then distillation from CaH_2, and finally vacuum transfer; for the more acidic (e.g., cobalt) hydrides, where deprotonation by basic impurities was sometimes observed, more elaborate purification procedures—discussed in a separate section below—were employed. The CD_3CN used as an NMR solvent was always purified by vacuum transfer from P_4O_{10}.

Aniline, *p*-(trifluoromethyl)aniline, morpholine, triethylamine, pyrrolidine, and tetramethylguanidine (TMG) were predried over, and then fractionally distilled from, barium oxide. 2,4-Dichloroaniline, *p*-cyanoaniline, *p*-toluidine, and *p*-anisidine were recrystallized from ethanol and dried in vacuo for 6 h at 40 °C. Trifluoroacetic acid was distilled from a small amount of P_4O_{10} prior to use. $Co_2(CO)_8$ was sublimed at 25 °C under vacuum prior to use.

Infrared spectra were recorded on a Perkin-Elmer PE983 spectrometer using CaF_2 solution cells. ^1H NMR spectra were recorded on either an IBM WP-200-SY or an IBM WP-270-SY spectrometer; ^{31}P NMR spectra were recorded on the WP-200 instrument.

Materials. The following compounds were prepared by literature methods: $NaCo(CO)_3PPh_3\cdot2THF$,[11] $NaCo(CO)_3P(OPh)_3\cdot2THF$,[11] $[PPN][HFe(CO)_4]$,[4a] $Cp*Fe(CO)_2K$,[12] $CpW(CO)_2(PMe_3)H$,[13] $NaM(CO)_5$,[14] $HM(CO)_5$[15] (M = Mn, Re), $Cp_2Ru_2(CO)_4$,[16] $Cp*Mo(CO)_3H$

($Cp* = \eta^5\text{-}C_5Me_5$),[17] $K[M(CO)_2Cp]$ (M = Fe, Ru),[18] and $Na_2Ru(CO)_4$.[19] $[Co(CH_3CN)_6][Co(CO)_4]_2$: Several reports indicated that strongly coordinating solvents promoted the disproportionation of $Co_2(CO)_8$ to $Co(B)_6^{2+}$ and $Co(CO)_4^-$.[20] Dissolving $Co_2(CO)_8$ in CH_3CN resulted in a rapid evolution of gas (CO) and a color change from red-brown to pink-orange $[Co(CH_3CN)_6]^{2+}$. The salt decomposed upon removal of solvent and so was prepared and used in situ.

Evaluation of Solvent Purification Techniques. $HCo(CO)_4$ was generated by the method described in the next section in acetonitrile purified by each of several procedures,[21] and the extent of deprotonation by basic impurities was measured by IR spectroscopy; the same IR cell (path length, 0.06 mm, see below) was used for all measurements in each set of experiments. In the first set of experiments, Fischer reagent grade CH_3CN was purified by the following methods: (a) successive distillation from alkaline $KMnO_4$ and $KHSO_4$, fractional distillation from CaH_2, and vacuum transfer from P_4O_{10}; (b) distillation from $CuSO_4$ followed by vacuum transfer from P_4O_{10}; and (c) distillation from $CuSO_4$ followed by distillation from CaH_2. The resulting acetonitrile was degassed by several freeze–pump–thaw cycles and stored under vacuum. Solutions 31 mM in $HCo(CO)_4$ showed 17% deprotonation in CH_3CN purified by method a, 24% deprotonation in CH_3CN purified by method b, and 17% deprotonation in CH_3CN purified by method c. Subsequent experiments with cobalt hydrides were therefore carried out with acetonitrile purified by procedure a.

In the second set of experiments, the CH_3CN used was (d) Fischer reagent grade CH_3CN distilled from CaH_2; (e) Fischer CH_3CN distilled from $CuSO_4$, then fractionally distilled from CaH_2; (f) Fischer CH_3CN distilled from alkaline $KMnO_4$, then fractionally distilled from CaH_2; (g) Fischer CH_3CN distilled successively from alkaline $KMnO_4$, $KHSO_4$, and $CuSO_4$, then fractionally distilled from CaH_2; (h) Fischer CH_3CN distilled successively from alkaline $KMnO_4$, $KHSO_4$, $CuSO_4$, and P_4O_{10}; (i) Fischer CH_3CN distilled from $CuSO_4$, passed through a column of Woelm N-Super I alumina, and fractionally distilled from alumina; (j) Burdick and Jackson "distilled in glass" CH_3CN distilled from CaH_2; and (k) Burdick and Jackson CH_3CN distilled from $CuSO_4$, passed through a column of alumina, and fractionally distilled from alumina. Solutions ca. 60 mM in $HCo(CO)_4$ (and therefore less susceptible to deprotonation by impurities than the solutions employed in the first set of experiments) showed the following extents of deprotonation in CH_3CN purified by the various techniques: (d) 16%; (e) 11%; (f) 14%; (g) 11%; (h) 12%; (i) 10%; (j) 10%; and (k) 9%.

$HCo(CO)_4$. An orange-pink solution of $[Co(CH_3CN)_6][Co(CO)_4]_2$ obtained by the dissolution of $Co_2(CO)_8$ in CH_3CN was frozen at −196 °C. A limiting amount of HCl was then added ($HCl:[Co(CH_3CN)_6][Co(CO)_4]_2 \leq 2.0$). This method assures complete reaction and hence the absence of HCl from the product. The frozen mixture was then allowed to warm to 0 °C with a concomitant color change from orange-pink to royal blue ($CoCl_2$). The $HCo(CO)_4$ and CH_3CN were then removed by vacuum transfer. Solutions 0.001–1.0 M in $HCo(CO)_4$ were obtained by this technique. In general, the concentration of the $HCo(CO)_4$ solution thus prepared was 6–15% below theoretical (see below).[22]

$HCo(CO)_3PPh_3$. A modification of the procedure used by Hieber[11] was employed. Because of the limited thermal stability of the product, all manipulations were performed rapidly at −78 °C and, once isolated, the product was used immediately. $NaCo(CO)_3PPh_3\cdot2THF$ (75 mg, 0.15 mmol) was dissolved in THF (6 mL) and the solution frozen at −196 °C. CF_3COOH (0.23 mmol) was then added by vacuum transfer and the mixture warmed to room temperature with rapid stirring. The THF was removed in vacuo to afford a yellow waxy residue which was triturated

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Hydrido Transition-Metal Complexes

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Table I. IR Spectra of Mononuclear Transition-Metal Hydrides and Their Conjugate Bases in Acetonitrile

compound	ν_{CO}, cm^{-1} (molar absorptivity, M^{-1} cm^{-1})
HCo(CO)$_4$	2117.3 (388), 2053.6 (1980), 2023.1 (5240)
[Co(CH$_3$CN)$_6$][Co(CO)$_4$]$_2$	1892.4 (8160)
H$_2$Fe(CO)$_4$	2119.3 w, 2050.0 sh, 2042.8 sh, 2034.5 (4300)
[PPN][HFe(CO)$_4$]	2003.1 w, 1913.6 (2520), 1881.4 (7090)
HCo(CO)$_3$P(OPh)$_3$	2074.8 w, 2021.5 w, 1996.1 (2860)
NaCo(CO)$_3$P(OPh)$_3$	1960.5 (1480), 1872.0 (5220)
HMn(CO)$_5$	2012.3 (6260)
[HNEt$_3$][Mn(CO)$_5$]	1910.4 (3540), 1863.5 (5450)
HCo(CO)$_3$PPh$_3$	2050 w, 1970.7 (2850)
[HNEt$_3$][Co(CO)$_3$PPh$_3$]	1927.2 (991), 1838.4 (3640)
H$_2$Ru(CO)$_4$	2138.9 w, 2085.3 sh, 2071.6 sh, 2051.0 (4420)
[TMGH][HRu(CO)$_4$]	2013.0 w, 1935.3 (3009), 1889.5 (6480)
Cp*Mo(CO)$_3$H	2009.3 (2086), 1918.3 (3167)
[TMGH][Cp*Mo(CO)$_3$]	1881.1 (1915), 1762.0 (2152)
CpFe(CO)$_2$H	2013.4 (1430), 1949.2 (1520)
CpFe(CO)$_2$K	1862.2 (2230), 1787.1 (2470)
CpRu(CO)$_2$H	2023.6 (1880), 1958.3 (2230)
CpRu(CO)$_2$K	1855.2 (2160), 1800.5 (2320)
HRe(CO)$_5$	2012.3 (7630)
NaRe(CO)$_5$	1917.5 (6420), 1862.4 (9240)
Cp*Fe(CO)$_2$H	1992.0 (2630), 1929.2 (2810)
Cp*Fe(CO)$_2$K	1840.5 (2750), 1768.4 (2710)
CpW(CO)$_2$(PMe$_3$)H	1917.5 (2500), 1830.0 (2380)
CpW(CO)$_2$(PMe$_3$)K	1762.5 (2120), 1682.4 (1800)

with hexane (5 mL). The hexane was removed in vacuo and the solid residue triturated with toluene (5 mL). The mixture was filtered at −78 °C to remove the CF$_3$COONa, and the toluene was again removed in vacuo to afford a yellow-cream colored solid which was used immediately.

[HNEt$_3$][Co(CO)$_3$PPh$_3$]. HCo(CO)$_3$PPh$_3$ (7.5 mg, 0.019 mmol) was dissolved in CH$_3$CN (1.2 mL) and the solution frozen at −196 °C. NEt$_3$ (0.035 mmol) was added by vacuum transfer and the mixture warmed to room temperature with stirring. The product was not isolated but generated and used in situ.

HCo(CO)$_3$P(OPh)$_3$. A modification of the procedure used by Hieber[11] was employed. Because of the *very* limited thermal stability of the product and its high solubility in hydrocarbon solvents, HCo(CO)$_3$P-(OPh)$_3$ was prepared in situ. NaCo(CO)$_3$P(OPh)$_3$·2THF (7.2 mg, 0.012 mmol) was dissolved in CH$_3$CN (1.5 mL) and the solution frozen at −196 °C. HCl (0.21 mmol) was then added by vacuum transfer and the mixture warmed to 0 °C with rapid stirring. The solution became cloudy as NaCl precipitated. Removal of solvent in vacuo afforded a white solid (HCo(CO)$_3$P(OPh)$_3$ and NaCl).

Acetonitrile Solutions of Hydrides Not Isolated. In many cases hydrides were more stable in dilute acetonitrile solution than when pure. These stable CH$_3$CN hydride solutions were obtained by acidification of CH$_3$CN solutions of the anion; the CH$_3$CN and hydride were then removed from the salt, usually by vacuum transfer. **CpM(CO)$_2$H (M = Fe,[23] Ru):** The potassium anion was dissolved in CH$_3$CN and acidified with a limiting amount of HCl or CF$_3$COOH (i.e., CpM(CO)$_2$K:HCl < 1). **H$_2$Fe(CO)$_4$:** [PPN][HFe(CO)$_4$] (53 mg, 6.4 mmol) was dissolved in CH$_3$CN (0.42 mL) and treated with a twofold excess of H$_2$SO$_4$ (98%) at −196 °C. The mixture was warmed to −25 °C and stirred for 10 min. **H$_2$Ru(CO)$_4$:** Na$_2$Ru(CO)$_4$[19] (8.0 mg, 0.031 mmol) was dissolved in CH$_3$CN (0.55 mL) and treated with a threefold excess of H$_2$SO$_4$ (98%) at −196 °C. The mixture was warmed to −25 °C and stirred for 10 min. The ^{1}H NMR spectrum (δ −7.9) and IR spectrum (Table I) of the H$_2$Ru(CO)$_4$ obtained in acetonitrile by vacuum transfer were in acceptable agreement with these reported for H$_2$Ru(CO)$_4$ in other media.[19,24] **Cp*Fe(CO)$_2$H:** Cp*Fe(CO)$_2$K (5.4 mg, 0.018 mmol) was dissolved in CH$_3$CN (2.3 mL) and the solution frozen at −196 °C. HCl (0.020 mmol) was added by vacuum transfer and the mixture warmed to room temperature with stirring. In this case separation of the CH$_3$CN and hydride by vacuum transfer was not feasible, and the solution of the hydride thus generated was used for further work. Removal of the

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CH$_3$CN in vacuo, and dissolution of the residue in C$_6$D$_6$, gave a solution with a ^{1}H NMR spectrum identical with that reported[25] for Cp*Fe-(CO)$_2$H.

Behavior of HCo(CO)$_4$ in CH$_3$CN. A small and variable amount of deprotonation (evidenced by formation of Co(CO)$_4^-$) was observed in the IR spectra of freshly prepared CH$_3$CN solutions of HCo(CO)$_4$. Typical values for the extent of this deprotonation were 6–22%, depending upon the HCo(CO)$_4$ concentration. The extent of deprotonation was smaller at higher concentrations of HCo(CO)$_4$, suggesting the presence of a small amount of basic impurity in the IR cell or solvent (and not the formation of Co(CO)$_4^-$ by the decomposition of HCo(CO)$_4$, i.e., HCo(CO)$_4 \rightarrow$ H$_2$ + [Co(CH$_3$CN)$_6$][Co(CO)$_4$]$_2$). For this reason, a short path length solution cell (CaF$_2$, 0.06 mm) with Teflon spacers was employed, and the concentration of HCo(CO)$_4$ was kept as high as practical during pK_a measurements.

The total cobalt concentration in these solutions was determined by allowing them to decompose to H$_2$ and [Co(CH$_3$CN)$_6$][Co(CO)$_4$]$_2$ and using the known absorptivity of Co(CO)$_4^-$. These total cobalt concentrations were typically 6–15% below theoretical (see above). The HCo(CO)$_4$ concentration was computed by subtracting the initial Co-(CO)$_4^-$ concentration (resulting from deprotonation by small amounts of impurities, as discussed above) from the total cobalt concentration and used to determine the absorptivity of HCo(CO)$_4$.

IR Experiments—Absorptivities. Solutions of isolable hydridometal compounds (HCo(CO)$_3$PPh$_3$, HMn(CO)$_5$, HRe(CO)$_5$, Cp*Mo(CO)$_3$H, CpW(CO)$_2$(PMe$_3$)H) and anionic salts ([Co(CH$_3$CN)$_6$][Co(CO)$_4$]$_2$, NaCo(CO)$_3$P(OPh)$_3$, NaCo(CO)$_3$PPh$_3$, CpFe(CO)$_2$K, CpRu(CO)$_2$K, NaRe(CO)$_5$, [PPN]HFe(CO)$_4$, Cp*Fe(CO)$_2$K, CpW(CO)$_2$PMe$_3$K) were prepared by dissolving a known weight of the compound in a known volume of CH$_3$CN. Solutions of [baseH$^+$][M$^-$] ([HNEt$_3$][Co-(CO)$_3$PPh$_3$], [HNEt$_3$][Mn(CO)$_5$], and [TMGH][Mo(CO)$_3$Cp*]), in which the base was chosen so as to deprotonate the hydride complex completely, were prepared by addition of a slight excess of the base to a solution containing the hydride in known concentration. In cases where it would have been very difficult to isolate the hydride (HCo(CO)$_3$-P(OPh)$_3$, CpFe(CO)$_2$H, CpRu(CO)$_2$H, H$_2$Fe(CO)$_4$, H$_2$Ru(CO)$_4$, Cp*Fe(CO)$_2$H), solutions of known concentrations were prepared by acidification, with an excess of an acid known to protonate the anion completely (see above), of a CH$_3$CN solution containing a known concentration of the corresponding metal anion.

The absorptivities of the ν_{CO} bands of the metal hydride complexes and their corresponding anions are given in Table I. A 0.099 mm CaF$_2$ solution cell was used in all cases except for HCo(CO)$_4$ and [Co(CH$_3$-CN)$_6$][Co(CO)$_4$]$_2$ (for which, as mentioned above, a cell with a path length of 0.06 mm was used). Complete Beer's law plots were done for HMn(CO)$_5$ and [Et$_3$NH][Mn(CO)$_5$]. For all other hydride compounds and metal anions, absorptivities were measured at two or three different concentrations.

Equilibrium Constants. As in our previous work,[6] the pK_a of the transition-metal hydride complexes (MH) was determined by treating hydride solutions with an appropriate base (B) of known pK_a (BH$^+$), effecting a partial deprotonation and establishing the equilibrium shown in eq 1. In general, the solutions were prepared at room temperature and

$$MH + B \rightleftharpoons M^- + BH^+ \qquad K_{eq} \qquad (1)$$
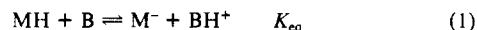
transferred by syringe into N$_2$-filled IR cells. Solutions containing H$_2$Fe(CO)$_4$ were prepared at −23 °C and transferred into room temperature IR cells; solutions containing the extremely unstable HCo(CO)$_4$ and H$_2$Ru(CO)$_4$ were injected into the IR cell immediately after thawing.

[MH] and [M$^-$] were determined by IR, and, in cases (Et$_3$N, PhNH$_2$ and derivatives,[26] and TMG[27,28]) where the self-association constant K_f (eq 2) was known[8c,29] to be effectively zero, [BH$^+$] was assumed equal

$$B + BH^+ \rightleftharpoons BHB^+ \qquad K_f = \frac{[BHB^+]}{[B^-][BH]} \qquad (2)$$
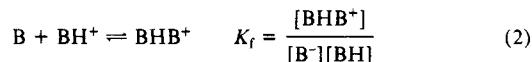
to [M$^-$] and [B] was calculated by subtracting [BH$^+$] from the total

(25) (a) Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1983**, 430. (b) Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 1094.

(26) The K_f values for aniline and *p*-toluidine are reported as 0.[7,8c,29] Therefore, the K_f values for other substituted anilines are assumed to be negligible.

(27) No K_f value for TMG has been reported, although a pK_a value for TMGH$^+$ in CH$_3$CN has been given.[28] The only pK_a values in this work arising from the use of TMG (those of HRe(CO)$_5$ and Cp*Fe(CO)$_2$H) were calculated on the assumption that the K_f was zero then confirmed by the use of other bases (Et$_3$N for HRe(CO)$_5$, and KOPh for Cp*Fe(CO)$_2$H).

(28) Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23.

(29) Coetzee, J. F.; Padmanabhan, G. R.; Cunningham, G. P. *Talanta* **1964**, *11*, 93.

concentration of base initially added. When K_{eq} for deprotonation of HCo(CO)$_4$ by p-CF$_3$C$_6$H$_4$NH$_2$ was determined, [BH$^+$] was calculated by correcting the measured [Co(CO)$_4^-$] for the [Co(CO)$_4^-$] formed in an otherwise identical control experiment without p-CF$_3$C$_6$H$_4$NH$_2$ (i.e., for anion arising from deprotonation by impurities); K_{eq} was then calculated from this [p-CF$_3$C$_6$H$_4$NH$_3^+$], the remaining [p-CF$_3$C$_6$H$_4$NH$_2$], and the measured [HCo(CO)$_4$] and [Co(CO)$_4^-$]—a procedure which assures that the impurities are much stronger bases than p-CF$_3$C$_6$H$_4$NH$_2$, so that p-CF$_3$C$_6$H$_4$NH$_3^+$ is the only species present capable of protonating Co(CO)$_4^-$.

In cases (all amine bases other than Et$_3$N, PhNH$_2$ and its derivatives,[26] and TMG[27,28]) where the known[8c,29] value of K_f indicated that eq 2 had to be taken into account, [BH$^+$] was calculated according to eq 3[30] from [M$^-$] and the total concentration of base initially added; [BHB$^+$]

$$[BH^+]^2 + \left\{[B]_{total} - 2[M^-] + \frac{1}{K_f}\right\}[BH^+] - \frac{[M^-]}{K_f} = 0 \quad (3)$$

was then calculated from [M$^-$] and [BH$^+$], and [B] was calculated from [B]$_{total}$, [BHB$^+$], and [BH$^+$]. When, as in the case of CpRu(CO)$_2$H, the acid–base equilibrium was established by protonation of the metal anion with the hydrochloride of the base, [B] was calculated from [MH] and [A]$_{total}$, the total concentration of hydrochloride initially added, according to eq 4.[30] When phenolate ion was used as a base, as its association with

$$[B]^2 + \left\{[A]_{total} - 2[MH] + \frac{1}{K_f}\right\}[B] - \frac{[MH]}{K_f} = 0 \quad (4)$$

phenol according to eq 5 was known to be significant,[31] the cubic expression in eq 6[32] was used to calculate [PhOH] = [BH$^+$] and thence [PhO$^-$] = [B].

$$PhO^- + 2PhOH \rightleftharpoons [PhO(PhOH)_2]^-$$
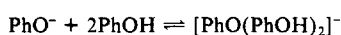
$$K_{assoc} = \frac{[PhO(PhOH)_2^-]}{[PhO^-][PhOH]^2} \quad (5)$$

$$[PhOH]^3 + \{2[PhO^-]_{total} - 3[M^-]\}[PhOH]^2 + \frac{[PhOH]}{K_{assoc}} - \frac{[M^-]}{K_{assoc}} = 0 \quad (6)$$

The resulting values of [M$^-$], [M], [BH$^+$], and [B] were then used to calculate K_{eq} for eq 1, and the pK_a of the metal hydride was then calculated according to eq 7 from K_{eq} and the known[7,8c,28,31] pK_a of BH$^+$.

$$pK_a(MH) = pK_a(BH^+) + pK_{eq} \quad (7)$$

Determination of the pK_a in Acetonitrile of the Protonated Form of Substituted Anilines. These values were determined by the potentiometric method of Coetzee and Padmanabhan,[8c] using the cell design of Kolthoff and Thomas.[33] The electrode was calibrated with buffer solutions of picric acid and tetra-n-butylammonium picrate, taking the pK_a of picric acid as 11.0.[34] These measurements are described in greater detail in a separate publication.[35] The pK_a found for 2,4-dichloroanilinium perchlorate was 8.0, that for p-cyanoanilinium perchlorate was 7.6, that for p-anisidinium perchlorate was 11.3, and that for p-(trifluoromethyl)anilinium perchlorate was 8.6; the literature values[7,8c,28] for anilinium perchlorate and p-toluidinium perchlorate were successfully reproduced as 10.5 and 11.1, respectively.

NMR Determination of the pK_a in CH$_3$CN of HCo(CO)$_4$. Four separate solutions of [Co(CD$_3$CN)$_6$][Co(CO)$_4$]$_2$ in CD$_3$CN were prepared by reacting a known amount of Co$_2$(CO)$_8$ with 0.40 mL of CD$_3$CN. A slight excess of H$_2$SO$_4$ was added to each of the solutions at –196 °C, and they were slowly warmed to 0 °C; solvent and hydride were then quickly vacuum transferred into NMR tubes. Each of the four tubes

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(30) [B](total) = [B] + [BH$^+$] + 2 [BHB$^+$], and, if we start with HM and B only, [M$^-$] = [BH$^+$] + [BHB$^+$]; if we substitute [BHB$^+$] = K_f[B][BH$^+$] from eq 2, solve both equations for B, and set the resulting expressions equal to each other, we obtain eq 3. If we start with M$^-$ and BH$^+$ (= A) only, then [MH] = [B] + [BHB$^+$], while [A](total) = [B] + [BH$^+$] + 2[BHB$^+$]; if we substitute [BHB$^+$] = K_f[B][BH$^+$], solve both equations for B, and set the resulting expressions equal to each other, we obtain eq 4.

(31) Coetzee, J. F.; Padmanabhan, G. R. *J. Phys. Chem.* **1965**, *69*, 3193.

(32) [PhO$^-$](total) = [PhO$^-$] + [PhOH] + 3[PhO(PhOH)$_2^-$], and, if we start from MH and PhO$^-$ only, [PhO$^-$](total) = [M$^-$] + [PhO$^-$] + [PhO(PhOH)$_2^-$]. If we substitute [PhO(PhOH)$_2^-$] = K(assoc)[PhOH]^2[PhO$^-$] from eq 5, solve both equations for [PhO$^-$], and set the resulting expressions equal to each other, we obtain eq 6.

(33) Kolthoff, I. M.; Thomas, F. G. *J. Phys. Chem.* **1965**, *69*, 3049.

(34) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 4428. This paper contains numerous references to previous incorrect measurements of the pK_a of picric acid in acetonitrile.

(35) Edidin, R. T.; Sullivan, J. M.; Norton, J. R., submitted for publication.

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contained an equal and known amount of an internal standard, neopentane; two of the tubes also contained carefully measured amounts of 2,4-dichloroaniline and p-cyanoaniline. After all four tubes were frozen and sealed under vacuum, the ^{1}H NMR spectra of the two tubes that contained no base were used to determine the amount of HCo(CO)$_4$ lost during acidification and vacuum transfer (9% and 11%). The pK_{eq} for the deprotonation of HCo(CO)$_4$ by 2,4-dichloroaniline was estimated as 0.54 from the additional decrease in the integrated intensity of the hydride resonance in the tube containing 2,4-dichloroaniline; substitution of this pK_{eq} value into eq 7 gave 8.5 as an estimate for the pK_a of HCo(CO)$_4$. Similarly, the pK_{eq} for the deprotonation of HCo(CO)$_4$ by p-cyanoaniline was estimated as 0.85 from the additional decrease in the integrated intensity of the hydride resonance in the tube containing p-cyanoaniline; substitution of this pK_{eq} value into eq 7 also gave 8.5 as an estimate for the pK_a of HCo(CO)$_4$. All spectra were obtained at –30 °C, where the rate of proton transfer was slow, with 30-s intervals between pulses in order to ensure accurate integrations. For both 2,4-dichloroaniline and p-cyanoaniline, the extent of deprotonation calculated from the integrated intensity of the hydride resonance was confirmed by the excess of the integrated intensity of the NH$_2$/NH$_3^+$ peak over that expected for unprotonated ArNH$_2$.

The Spectrophotometric Titration of 2,4-Dichloroaniline with HCl in Acetonitrile. A 7.25×10^{-3} M solution of 2,4-dichloroaniline was titrated with a 0.25 M solution of HCl. The equilibrium concentration of 2,4-dichloroaniline was monitored at 305 nm (ϵ = 2050 M^{-1} cm^{-1}). The equilibrium concentration of the protonated form (ϵ = 0 at 305 nm) was calculated from mass balance. The equilibrium concentration of HCl was estimated by subtracting twice the concentration of protonated 2,4-dichloroaniline from the concentration of HCl initially added, and the log of the product $K_{HCl}K_{10}$ (where K_{10} is the equilibrium constant for the Cl$^-$/HCl homoconjugation equilibrium shown as eq 10 in the Results section below) was then estimated as 6.6 by the use of eq 8 of Kolthoff, Bruckenstein, and Chantooni[9] along with our value of the pK_a of 2,4-dichloroanilinium ion.

Results

The pK_a values determined in CH$_3$CN for transition-metal hydrides by measurement of K_{eq} in eq 1 with bases of known strength (amines and potassium phenolate) are given in Table II. In all cases but HCo(CO)$_3$P(OPh)$_3$ and HRe(CO)$_5$ (see below), no carbonyl-containing species other than the hydride complex and its conjugate anion have been observed in these experiments. In particular, no associated species of the type [L$_n$MHML$_n$]$^-$ has been seen. As found in our previous work,[6] the carbonylmetallate anions generally show the IR spectra expected for symmetrical solvent environments.

Anomalous behavior is observed with HCo(CO)$_3$P(OPh)$_3$ and HRe(CO)$_5$. Acetonitrile solutions of HCo(CO)$_3$P(OPh)$_3$ display three ν_{CO} bands, although only two would be expected from the local C_{3v} symmetry. The ^{1}H NMR spectrum of a CD$_3$CN solution of HCo(CO)$_3$P(OPh)$_3$ does not exhibit the characteristic high-field doublet of the hydride ligand resonance split by phosphorus[36] but rather a broad singlet at δ –11.02. A single resonance is also observed in the ^{31}P spectrum (δ 163.9). Addition of neat P(OPh)$_3$ (1 equiv) to a solution of HCo(CO)$_3$P(OPh)$_3$ results in a single resonance (δ 158.5) upfield from the phosphorus resonance of the hydride complex and downfield from that (δ 128.0) of free P-(OPh)$_3$. These results suggest that the equilibrium in eq 8 operates rapidly on the ^{31}P NMR time scale in CH$_3$CN. The "extra" IR

$$HCo(CO)_3P(OPh)_3 \underset{CH_3CN}{\rightleftharpoons} HCo(CO)_3(CH_3CN) + P(OPh)_3 \quad (8)$$
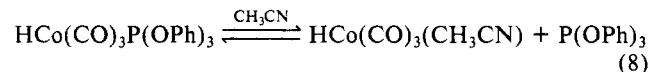
band at 2021.5 cm^{-1} is plausibly assigned to HCo(CO)$_3$-(CH$_3$CN).[37] Equilibrium studies of eq 8 were not attempted, and the pK_a value reported for HCo(CO)$_3$P(OPh)$_3$ is therefore that of the HCo(CO)$_3$P(OPh)$_3$/HCo(CO)$_3$(CH$_3$CN) mixture

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(36) A toluene-d_8 solution of HCo(CO)$_3$P(OPh)$_3$ does display a doublet ($^2J_{PH}$ = 19.6 Hz) at δ –7.23 in the ^{1}H NMR spectrum. For ^{1}H NMR data of other phosphite complexes of this type see ref 2d. Kinetic data have been reported which suggest that the isoelectronic HFe(CO)$_3$P(OMe)$_3^-$ undergoes similar reversible phosphite dissociation (although the P–H coupling constant remains observable in THF): Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83.

(37) For a discussion of HCo(CO)$_3$ see: (a) Sweany, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 3739; (b) Warner, P.; Ault, B. S.; Orchin, M. *J. Organomet. Chem.* **1978**, *162*, 189.

Table II. Thermodynamic Acidity of Transition-Metal Hydrides in Acetonitrile

hydride	base (pK_a(BH$^+$), K_f^a)^b	K_{eq}^c	pK_a(MH)^c
HCo(CO)$_4$	p-(trifluoromethyl)aniline (8.6,^{d} 0^e)	2.2 (5) (ca. −20 °C)^f	8.3 (2)^{g,h}
HCo(CO)$_3$P(OPh)$_3$	anisidine (11.3,^{d} 0^e)	0.96^i	11.3^{h,i}
H$_2$Fe(CO)$_4$	aniline (10.56, 0)	0.16 (2) (ca. −20 °C)^f	11.4 (1)^h
CpCr(CO)$_3$H^j	pyridine (12.3, 3.98)	0.096 (6)	13.3 (1)
CpMo(CO)$_3$H^j	pyridine (12.3, 3.98)	0.028 (6) (ca. 0 °C)^f	13.9 (1)
HMn(CO)$_5$	morpholine (16.6, 10)	34.0 (10)	15.1 (1)
HCo(CO)$_3$PPh$_3$	morpholine (16.6, 10)	13.2 (14)	15.4 (2)^h
CpW(CO)$_3$H^j	morpholine (16.6, 10)	2.86 (18)	16.1 (1)
Cp*Mo(CO)$_3$H^k	morpholine (16.6, 10)	0.31 (3)	17.1 (1)
H$_2$Ru(CO)$_4$	morpholine (16.6, 10)	0.008 (2) (ca. −20 °C)^f	18.7 (2)^h
CpFe(CO)$_2$H	NEt$_3$ (18.5, 0)	0.119 (12)	19.4 (1)
CpRu(CO)$_2$H	pyrrolidine (19.6, 32)	0.246 (12)	20.2 (1)
H$_2$Os(CO)$_4^j$	NEt$_3$ (18.5, 0)	0.0048 (5)	20.8 (1)
HRe(CO)$_5$	NEt$_3$ (18.5, 0)	0.0024 (10)	21.1 (3)^n
	TMG^l (23.3, 0)^m	176	
Cp*Fe(CO)$_2$H^k	potassium phenolate (26.6, 6.3 × 10^5)^o	2.09 (16)	26.3 (2)^p
	TMG^l (23.3, 0)^m	9.0 × 10^{-4}	
CpW(CO)$_2$(PMe$_3$)H^q	potassium phenolate (26.6, 6.3 × 10^5)^o	0.90 (5)	26.6 (2)

^{a} As defined in eq 2. ^{b} Data taken from ref 7, 8c, and 29 unless otherwise noted. ^{c} At 25 °C unless otherwise noted. Values in parentheses are uncertainties in the least significant digit. ^{d} Measured by potentiometry as in ref 8c. ^{e} See footnote 26. ^{f} The solutions were made up at lower temperatures but injected into room temperature IR cells for the determination of K_{eq}; see text. ^{g} Confirmed (see text) by approximate ^{1}H NMR measurements at low temperature of the position of the deprotonation equilibria with 2,4-Cl$_2$C$_6$H$_3$NH$_2$ and p-NCC$_6$H$_4$NH$_2$. ^{h} Estimated from K_{eq} at lower temperatures and BH$^+$ pK_a values from 25 °C. ^{i} The pK_a is that of the HCo(CO)$_3$P(OPh)$_3$/HCo(CO)$_3$(CH$_3$CN) mixture rather than that of pure HCo(CO)$_3$P(OPh)$_3$. Equilibrium studies of phosphite dissociation were not attempted. ^{j} Previously reported (ref 6). ^{k} Cp* = η^5-C$_5$Me$_5$. ^{l} TMG = tetramethylguanidine. ^{m} See footnotes 27 and 28. ^{n} Average of the values estimated from the Et$_3$N data and from the TMG data. ^{o} See ref 31. Note that the second figure in parentheses is K_{assoc}, as defined in eq 5, rather than K_f. ^{p} Average of the values calculated from the PhO$^-$ data and from the TMG data. ^{q} Interconversion of the cis and trans isomers is sufficiently rapid to permit treatment of both as a single species in these experiments; see ref 13.

rather than that of pure HCo(CO)$_3$P(OPh)$_3$.

Although IR spectra of acetonitrile solutions of HRe(CO)$_5$ and NaRe(CO)$_5$ show no irregularities, addition of base (Et$_3$N or TMG) to solutions of HRe(CO)$_5$ results not only in simple deprotonation and formation of Re(CO)$_5^-$ but also in the formation of other carbonyl-containing species,[38] presumably polynuclear carbonyl anions. It has been assumed that these polynuclear anions are much less basic than Re(CO)$_5^-$ (Walker, Pearson, and Ford[5] have found that polynuclear anions are generally less basic than mononuclear ones) and that their concentration is negligible relative to that of the base, Et$_3$N or TMG, initially added. K_{eq} for HRe(CO)$_5$ has been estimated from knowledge of [HRe(CO)$_5$] and [Re(CO)$_5^-$] (both of which are available from the IR measurements) and of the total concentration of initially added base and from the assumption that [BH$^+$] is approximately equal to [Re(CO)$_5^-$].

As HCo(CO)$_4$, H$_2$Ru(CO)$_4$, and H$_2$Fe(CO)$_4$ decompose rapidly at room temperature in solution, the equilibrium constants K_{eq} for these species have been determined at lower temperatures. When the proton-transfer rate has proved slow enough, IR measurements of [HM] and [M$^-$] have been checked by ^{1}H NMR. For example, the equilibrium constant for deprotonation of HCo(CO)$_4$ has been determined by monitoring the decrease in intensity (vs. an internal standard) of its hydride resonance in the presence of appropriate aniline bases, 2,4-Cl$_2$C$_6$H$_3$NH$_2$ and p-NCC$_6$H$_4$NH$_2$, at low temperatures. The pK_a values of the protonated forms 2,4-Cl$_2$C$_6$H$_3$NH$_3^+$ and p-NCC$_6$H$_4$NH$_3^+$ have been determined by potentiometry and the HCo(CO)$_4$ pK_a values calculated from these numbers agree with the HCo(CO)$_4$ pK_a calculated from the IR data.

The pK_a value thereby determined for HCo(CO)$_4$ (8.3) suggested comparison with the several reported values of the pK_a of HCl in CH$_3$CN (8.94,[9] 8.1,[39] and 6.2[40]), as we had observed experimentally that HCl completely protonated Co(CO)$_4^-$ (eq 9). We therefore briefly investigated the acidity of HCl in CH$_3$CN, by spectrophotometric titration of HCl with 2,4-dichloroaniline.

The situation is complicated by the Cl$^-$/HCl homoconjugation equilibrium shown in eq 10, and it is possible to determine only the product $K_{HCl}K_{10}$ from such data alone (using the procedure

$$HCl + Co(CO)_4^- \rightarrow HCo(CO)_4 \qquad (9)$$

of Kolthoff, Bruckenstein, and Chantooni[9,41]). The use of a value of K_{10} derived from conductometric data[39] gave an estimate of the pK_a of HCl as 8.9.

$$Cl^- + HCl \xrightleftharpoons{K_{10}} HCl_2^- \qquad (10)$$
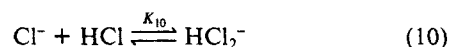
Solvent purity is very important in obtaining reliable thermodynamic acidity data, especially when dealing with very acidic species. Except for HCo(CO)$_4$, all of the hydrides examined in this study showed no IR evidence for deprotonation when dissolved in CH$_3$CN purified by any reasonable method. However, the IR spectrum of freshly prepared solutions of HCo(CO)$_4$ showed some Co(CO)$_4^-$; the fraction of HCo(CO)$_4$ deprotonated depended upon the method of acetonitrile purification and decreased at higher concentrations. These results suggested that the deprotonation was due to impurities, either in the solvent or in the IR cell. We therefore carried out two separate sets of experiments, each at constant concentration and in the same IR cell, measuring the extent of deprotonation of HCo(CO)$_4$ in the CH$_3$CN resulting from the different purification procedures described in the Experimental Section. The most effective purification procedures were (a) distillation from alkaline KMnO$_4$, followed by distillation from KHSO$_4$, fractional distillation from CaH$_2$, and vacuum transfer from P$_4$O$_{10}$ and (k) distillation from CuSO$_4$, passage through a column of highly activated alumina, and distillation from that alumina. In order to minimize the effects of basic impurities in the acetonitrile, high concentrations of hydride complex were employed in the measurement of absorptivity values and equilibrium constants.

Discussion

The thermodynamic acidities tabulated in Table II cover a range of about 20 pK_a units, from the very acidic HCo(CO)$_4$ to the weakly acidic CpW(CO)$_2$(PMe$_3$)H. However, in a solvent like acetonitrile *relative* pK_a values are more meaningful than *absolute*

(38) In addition to carbonyl bands for HRe(CO)$_5$ and Re(CO)$_5^-$, bands at 1988.7 (sh) and 1970.4 (s) cm^{-1} were also observed. These additional bands accounted for 50% of the total area in the carbonyl region.

(39) Janz, G. J.; Danyluk, S. *J. Am. Chem. Soc.* **1959,** *81,* 3854. Reference 9 gives values of K_{HCl} and K_{10} based on the data herein and a description of the procedure used to extract them.

(40) Desbarres, J. *Bull. Chim. Fr.* **1962,** 2103.

(41) The equilibrium value of [HCl] was estimated as [HCl](total initially added) − [BH$^+$].

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ones. All of the literature values[7,8c,28] we have employed for the pK_a of the protonated nitrogen bases and the values we have measured for p-$CH_3OC_6H_4NH_2$, p-$CF_3C_6H_4NH_2$, 2,4-$Cl_2C_6H_3NH_2$, and p-$NCC_6H_4NH_2$ (we have also duplicated the literature values[7,8c,28] for p-$CH_3C_6H_4NH_2$ and for aniline itself) are based on the well-established pK_a of picric acid and on the relationship between hydrogen ion activity and glass electrode potential established by Kolthoff and co-workers in the course of their picric acid pK_a determination.[34] However, these nitrogen base measurements (our own as well as the ones in the literature[8c,28]) have required extrapolation of the (H⁺ activity)/(glass electrode response) relation beyond the concentration range in which it was calibrated,[8c] and thus these measurements have an uncertainty in their absolute values which exceeds the uncertainty in their relative values. Furthermore, despite the impressive number of separate methods by which Kolthoff and co-workers checked their 1965 value of the picric acid pK_a in CH_3CN,[34] the number of different values previously reported suggests that some uncertainty remains in the present value and therefore that some uncertainty remains in the absolute values of the derived nitrogen base and metal hydride pK_a's. The uncertainties in our *relative* pK_a values (because they are all derived from this same picric acid standard) are obviously smaller, and only these are shown in Table II.

Additional uncertainty as to the significance of the *absolute* pK_a values in acetonitrile arises from the direct or indirect dependence of much equilibrium constant data in that solvent upon spectrophotometrically measured equilibrium constants for the protonation of indicator bases with perchloric acid.[9] Evaluation of the latter rests upon the assumption, strongly supported by the success of the spectrophotometric data treatment[9] as well as by other evidence,[42] that $HClO_4$ is completely dissociated in CH_3CN—although occasional statements to the contrary can be found in the literature.[43] Fundamentally, it is difficult to establish the activity coefficient of hydrogen ions in a solvent where (because there is at most one strong acid, perchloric) the concentration of hydrogen ions is not unambiguously known from stoichiometric considerations.

It is obvious that some of the transition-metal hydrides in Table II (e.g., $HCo(CO)_4$) are quite acidic, although it is misleading to compare them quantitatively to literature values for the pK_a of mineral acids in CH_3CN because the latter (or, more precisely, all spectrophotometric measurements of the latter) were determined[9] by methods which involved the use of an old value of the picric acid pK_a.[34] For HCl, as mentioned above, the literature contains three values: 6.2 from work which is internally inconsistent on the question of whether or not $HClO_4$ is completely dissociated,[40,43] 8.1 from the analysis of Kolthoff and co-workers of conductometric data measured by others,[39] and 8.94 from work by Kolthoff and co-workers which depends upon an obsolete value of the picric acid pK_a.[9] There is no obvious problem with the conductometric result, and, if one assumes that the value of K_{10} extracted by Kolthoff from the conductometric data[9,39] is correct, the value of the product $K_{10}K_{HCl}$ reported by Kolthoff and approximately redetermined in this work gives a pK_a for HCl of 8.9—all of which implies a pK_a for HCl somewhere between 8 and 9. In any case the combination of complexation by Cl⁻ with HCl (eq 10) and by Cl⁻ with Co^{2+} easily explains why the equilibrium in reaction 9 lies to the right, and it seems reasonable to conclude that the acid strengths of $HCo(CO)_4$ and HCl in acetonitrile are about equal.

These results make the advantages of the weakly basic acetonitrile as a solvent for strong acids quite evident. $HCo(CO)_4$,[2a] HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4 are, because of the solvent "levelling effect", indistinguishably strong in water but

have appreciably different pK_a values in acetonitrile. If one assumes that the literature[9] pK_a values for mineral acids are at least *relatively* accurate, one can see that $HCo(CO)_4$ is a much weaker acid than perchloric, a somewhat weaker acid than HI, HBr, and H_2SO_4, and comparable in acid strength to HCl and HNO_3. $HCo(CO)_4$ is nevertheless an appreciably stronger acid than CH_3SO_3H ($pK_a = 10.0$)[26] and 2,4,6-trinitrophenol ($pK_a = 11.0$)[34] and definitely stronger than all other transition-metal hydrides we have examined.

All of the transition-metal hydrides in Table II show significant acid strength. The pK_a of $Cp^*Mo(CO)_3H$ compares with that of o-hydroxybenzoic acid ($pK_a = 16.7$),[44] and the pK_a's of the least acidic hydride complexes studied, $Cp^*Fe(CO)_2H$ and $CpW(CO)_2(PMe_3)H$, are comparable to that of phenol ($pK_a = 26.6$).[31] It is worth noting that, because phenolate ion is the strongest base stable in acetonitrile solution,[31] the methods described in this paper will not be directly applicable to the measurement of the pK_a of transition-metal hydrides significantly less acidic than $CpW(CO)_2(PMe_3)H$.

A number of periodic trends are evident from the data in Table II. As we have previously reported for Cr, Mo, and W,[6] acidity generally decreases down a column. For example, moving from iron ($H_2Fe(CO)_4$) to ruthenium ($H_2Ru(CO)_4$) results in a decrease in acidity of 7.3 pK_a units, and moving from ruthenium to osmium ($H_2Os(CO)_4$)[6] results in a further decrease of 2.1 pK_a units. Likewise, moving from manganese ($HMn(CO)_5$) to rhenium ($HRe(CO)_5$) results in a decrease of 6.0 pK_a units. Exceptions to this generalization include $HM(P(OMe)_3)_4^+$ (M = Ni, Pd, and Pt)[5d] and perhaps $HM(CO)_4$ (M = Co, Rh, and Ir[45,46]).

It appears that acidity generally increases from left to right across a transition series ($HMn(CO)_5 \rightarrow H_2Fe(CO)_4 \rightarrow HCo(CO)_4$). This increase appears to be much greater for the first-row transition series than for the third-row, as evidenced by the negligible difference between $HRe(CO)_5$ and $H_2Os(CO)_4$ (0.3 pK_a units). The pK_a values of the six-coordinate $CpFe(CO)_2H$ and $CpRu(CO)_2H$ are much greater (19.4 and 20.2, respectively) than the pK_a values of the seven-coordinate $CpM(CO)_3H$ (M = Cr, Mo, W),[6] for reasons explained by Bursten and Gatter.[47]

Table II also offers considerable information on substituent effects. The pK_a's of $CpMo(CO)_3H$ and $(\eta^5$-$C_5Me_5)Mo(CO)_3H$ confirm a recent prediction,[17] based on qualitative observations in THF, that the pK_a of the C_5Me_5 compound would exceed that of the Cp compound by at least 3.0 units (the measured ΔpK_a is 3.2). In another system ($CpFe(CO)_2H$-$Cp^*Fe(CO)_2H$), this difference in acidity is much more pronounced (6.9 pK_a units). Substitution of a triphenyl phosphite ligand for CO in $HCo(CO)_4$ results in a decrease in acidity of 3 pK_a units, whereas substitution by triphenylphosphine decreases the acidity by 7 pK_a units—supporting the traditional belief that net electron-withdrawing ability increases in the order $PR_3 < P(OR)_3 < CO$. Replacement of a CO ligand by trimethylphosphine in $CpW(CO)_3H$ not surprisingly results in a much larger decrease in acidity ($\Delta pK_a = 10.5$) than the substitution of Ph_3P on $HCo(CO)_4$.

In the comparatively few cases where accurate pK_a values have been measured in other solvents, the reported trends are reproduced in CH_3CN. For example, the reported pK_a values for $HCo(CO)_3P(OPh)_3$ (4.95) and $HCo(CO)_3PPh_3$ (6.96) in water[2d] and the observation that $HCo(CO)_4$ itself is completely dissociated in water[2a] agree with the order of pK_a values for $HCo(CO)_4$, $HCo(CO)_3P(OPh)_3$, and $HCo(CO)_3PPh_3$ in Table II. Similarly, the reported aqueous pK_a of $HMn(CO)_5$ (7.1)[2b] is near that of $HCo(CO)_3PPh_3$, and the reported aqueous pK_a of $H_2Fe(CO)_4$ (4.00)[2c] is near that of $HCo(CO)_3P(OPh)_3$; both trends are reproduced in the Table II CH_3CN data. In general, the pK_a values

(42) Coetzee, J. F.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1957**, *79*, 6110.

(43) In tabulating this work in his review,[7] Coetzee listed the pK_a of $HClO_4$ as "<2". Desbarres[40] began with the assumption that perchloric acid was completely dissociated but listed the pH of half-deprotonation as pH 1.9—a result which has recently (Hillery, P. S.; Cohen, L. A. *J. Am. Chem. Soc.* **1983**, *105*, 2760) been cited as the basis for a statement that the pK_a of $HClO_4$ in CH_3CN is 6.7 (a statement for which no justification is apparent).

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(46) (a) Imyanitov, N. S.; Rudkovskii, D. M. *J. Appl. Chem. USSR* **1967**, *40*, 1948; *Kinet. Catal.* **1967**, *8*, 1051. (b) Imjanitow, N. S. *Hung. J. Ind. Chem.* **1975**, *3*, 331. We thank Dr. Leonard Kaplan for bringing these references to our attention.

(47) Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 2554; *Organometallics* **1984**, *3*, 941.

measured for hydride complexes in acetonitrile are ca. 7.5 pK_a units higher than those measured in H_2O.

The acidity of $CpCr(CO)_3H$ in MeOH (pK_a = 6.4, by extrapolation from measurements in 70:30 MeOH/H_2O) has been found to be greater than that of $H_2Fe(CO)_4$ (pK_a = 6.8),[5c,d] a reversal of the acidity order obtained in acetonitrile. In general, the pK_a values measured for hydride complexes in acetonitrile are ca. 6.7 pK_a units greater than those measured in MeOH.

Lastly, these acetonitrile acidity measurements agree with the small amount of reported gas-phase data. Stevens and Beauchamp, using ion cyclotron resonance spectroscopy,[48] have reported that $HCo(CO)_4$ is far more acidic than either $H_2Fe(CO)_4$ or $HMn(CO)_5$ (it is not clear which of the latter two compounds is the more acidic). Recent theoretical work calculates a larger total protonation energy,[49] and a smaller LUMO/HOMO energy difference,[50] for $Mn(CO)_5^-$ than for $Co(CO)_4^-$. Modified extended-Hückel theory calculates that ΔH for gas-phase proton transfer onto H_2O increases in the order $HCo(CO)_4 < H_2Fe(CO)_4$

< $HMn(CO)_5$,[51] in agreement with the order of acidities in CH_3CN in Table II. It seems likely that *differential* solvation effects have little effect on the acidity of transition-metal hydride in solution.

(48) Stevens, A. E.; Beauchamp, J. L., private communication.
(49) Ziegler, T. *Organometallics* 1985, *4*, 675.
(50) Bursten, B. E.; Gatter, M. G. *Organometallics* 1984, *3*, 895.

(51) McKinney, R. J.; Pensak, D. A. *Inorg. Chem.* 1979, *18*, 3413.

Picosecond Spectroscopic Studies of (d8-d8) Binuclear Rhodium and Iridium Complexes: A Comparison of 1B2 and 3B2 Reactivity in Bis(1,5-cyclooctadiene)bis(μ-pyrazolyl)diiridium(I)

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Abstract: Picosecond transient kinetics and difference spectra have been recorded for the singlet and triplet ($d\sigma^*p\sigma$) excited states in the d8-d8 dimers $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) and $[Ir(\mu-pz)(COD)]_2$ (pz = pyrazolyl, COD = 1,5-cyclooctadiene). The singlet excited state in the rhodium dimer (τ = 820 ps) displays a strong transient absorption feature maximizing at 440 nm that is not present in the spectrum of the triplet excited state. This intense absorption feature, characteristic of a $^1(d\sigma^*p\sigma)$ electronic configuration, is assigned to a $^1(d\sigma^*p\sigma) \rightarrow {}^1(p\sigma^2)$ excitation. The singlet excited state lifetime of the iridium dimer in cyclohexane is less than 20 ps. Though the solvent 1,2-dichloroethane (DCE) quenches luminescence from both singlet and triplet excited states in $[Ir(\mu-pz)(COD)]_2$ and oxidatively adds to the dimer upon steady-state illumination, picosecond spectroscopy finds *no* evidence for any chemical reactivity of the very short-lived singlet excited state. The quenching of $[Ir(\mu-pz)(COD)]_2$ singlet luminescence in DCE appears to result from enhanced singlet $\rightarrow$ triplet intersystem crossing in DCE relative to that in cyclohexane. Also, the invariance of triplet yield in these two solvents indicates that the efficiency of intersystem crossing is near unity.

Considerable spectroscopic work on d8-d8 binuclear complexes of rhodium, iridium, and platinum has shown that the lowest energy singlet and triplet excited states can be described by a $d\sigma^*p\sigma$ electronic configuration.[1] This configuration leads to $^{1,3}A_{2u}$ excited states in tetragonal (local D_{4h} symmetry) complexes such as $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) and to $^{1,3}B_2$ states in the lower symmetry (local C_{2v}) "A-frame" complexes exemplified by $[Ir(\mu-pz)(COD)]_2$ (Ir2) (pz = pyrazolyl, COD = 1,5-cyclooctadiene). Luminescence from both singlet and triplet excited states has been reported for these complexes, as well as for a number of related molecules. The Ir2 complex has

adjacent vacant coordination sites at the metal centers that afford the opportunity for multielectron redox reactions. Recently, Caspar and Gray have reported net photochemical, two-electron reduction of substrates whose initial, one-electron-transfer products are unstable.[2] Prior studies have shown that d8-d8 species with both D_{4h} and C_{2v} symmetries are powerful one-electron photoreductants.[1d,3] In all the above studies, the long-lived (hundreds

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