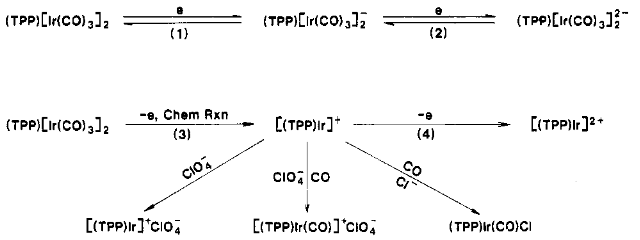

Figure 5. Overall mechanism for the oxidation and reduction of (TPP)$[Ir(CO)_3]_2$. Numbers 1–4 correspond to processes in the cyclic voltammograms illustrated in Figure 1. The possible solvation of $[(TPP)Ir]^+$ is omitted for clarity.

Overall Reaction Scheme for (TPP)$[Ir(CO)_3]_2$. The overall reaction scheme of (TPP)$[Ir(CO)_3]_2$ in PhCN and CH_2Cl_2 is summarized in Figure 5. (TPP)$[Ir(CO)_3]_2$ can undergo two consecutive reductions at the porphyrin π-ring system to form an anion radical and a dianion. This electron-transfer mechanism is supported by the electrochemical and spectroelectrochemical data as well as by the ESR spectra recorded after bulk solution electrolysis.

The first oxidation of (TPP)$[Ir(CO)_3]_2$ is followed by a chemical reaction to generate $[(TPP)Ir]^+ClO_4^-$ in PhCN, 0.2 M TBAP. Similar types of reactions have been reported for (TPP)$[Rh(CO)_2]_2$[17] which, upon oxidation, generates a transient Rh^{II}–Rh^{I} complex followed by an intramolecular electron transfer to form $[(TPP)Rh]^+ClO_4^-$ and elemental rhodium metal. The formation of $[(TPP)Ir]^+ClO_4^-$ following the one-electron oxidation of (TPP)$[Ir(CO)_3]_2$ would also require the transfer of a second electron, presumably from the second iridium atom. However, iridium metal was not clearly isolated in the present study, and positive identification of the second electron source has not been made.

In summary, the electrochemical properties of (TPP)$[Ir(CO)_3]_2$ are almost identical with the properties of (TPP)$[Rh(CO)_2]_2$. The first reduction of both binuclear complexes reversibly occurs at the porphyrin π-ring system. The values of $E_{1/2}$ are similar and occur at −0.99 V for (TPP)$[Ir(CO)_3]_2$ and −1.04 V for (TPP)$[Rh(CO)_2]_2$ in benzonitrile. The first oxidation of both binuclear complexes is irreversible and occurs at $E_p = 0.92$ V for (TPP)$[Ir(CO)_3]_2$ and $E_p = 0.84$ V for (TPP)$[Rh(CO)_2]_2$ in benzonitrile at a scan rate of 0.1 V/s.[17] The electrooxidation of each compound involves the overall conversion of a metal(I) to a metal(III) ion and the ultimate formation of $[(P)M]^+$. However, unlike (TPP)$[Rh(CO)_2]_2$ which can be reversibly oxidized at low temperature or fast scan rates, the chemical reaction or reactions following electron abstraction from (TPP)$[Ir(CO)_3]_2$ are extremely rapid and in no case could reversible electrooxidations be obtained.

Acknowledgment. The support of the National Science Foundation (Grant No. CHE-8215507) is greatly acknowledged.

Registry No. (TPP)$[IR(CO)_3]_2$, 114763-61-0; $[IR(CO)_3Cl]_2$, 34135-21-2; (TPP)H_2, 917-23-7; (TPP)$[IR(CO)_3]_2^-$, 114763-62-1; (TPP)$[IR(CO)_3]^{2-}$, 114789-56-9; $[(TPP)Ir]^+$, 114763-63-2; $[(TPP)Ir]^{2+}$, 114763-64-3.

Kinetic and Thermodynamic Acidity of Hydrido Transition-Metal Complexes. 5. Sensitivity of Thermodynamic Acidity to Ligand Variation and Hydride Bonding Mode

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The pK_a values of $CpRe(CO)_2H_2$, $(\eta^3\text{-}C_6H_9)Mn(CO)_3$, $(\eta^6\text{-}C_6H_6)Mn(CO)_2H$, $HMn(CO)_4(PPh_3)$, $HMn(CO)_4(PEtPh_2)$, $(\mu\text{-}H)_2Fe_3(CO)_9(\mu_3\text{-}P\text{-}t\text{-}Bu)$, $(\mu\text{-}H)_2Fe_3(CO)_9(\mu_3\text{-}P\text{-}p\text{-}C_6H_5OCH_3)$, $(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}SC_6H_{11})$, $H_4Ru_4(CO)_{11}(P(OCH_3)_3)$, and $H_4Ru_4(CO)_{10}(P(OCH_3)_3)_2$ have been determined in acetonitrile by IR measurement of the position of deprotonation equilibria with various nitrogen bases and sodium phenolate. The acidity of transition-metal hydrides appears more sensitive to the nature of the ancillary ligands than to the identity of the metal center.

We have reported the thermodynamic acidity of common mononuclear transition-metal hydrides in acetonitrile.[1] These results have enabled us to quantify periodic trends and some substituent effects. Our work has been carried out in acetonitrile for several reasons: it dissolves most metal hydrides without decomposition and solvates cations effectively; it minimizes ion pairing; and, as it is both a weak acid and a weak base, a large range of pK_a values can be measured in it.

We have now extended our initial studies to compounds containing other types of hydride ligands, e.g., to agostic and edge-bridging hydrides. We have also investigated the sensitivity of hydride pK_a values to small changes in the nature of ancillary phosphine ligands.

We have examined the edge-bridging hydrides in the $H_4Ru_4(CO)_{12-x}(P(OCH_3)_3)_x$ of tetranuclear ruthenium hydride clusters because Pearson and Ford[2] had previously studied their thermodynamic and kinetic acidities in

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(2) (a) Walker, H. W.; Kresge, C. T.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 7428. (b) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.*, **1983**, *105*, 1179.

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methanol solution and we wanted acetonitrile values with which to compare their results. Finally, we have measured the pK_a of $CpRe(CO)_2H_2$ in acetonitrile; in 1984 Bursten[3] had predicted that such seven-coordinate complexes would be more acidic than their six-coordinate analogues.

Experimental Section

General Data. All manipulations were performed under an inert atmosphere (N_2) using high vacuum line, Schlenk, or inert-atmosphere box techniques. Acetonitrile was purified by a combination of steps that our previous work had shown were effective:[1] it was distilled from $CuSO_4$ and then from alkaline $KMnO_4$; it was then passed through a column of Woelm N-Super 1 alumina and finally vacuum transferred from P_4O_{10}. The CD_3CN used as an NMR solvent was purified by vacuum transfer from P_4O_{10}. Methanol was dried by reflux over, and distillation from, calcium hydride.

Aniline, pyridine, morpholine, triethylamine, pyrrolidine, and tetramethylguanidine were predried over, and then fractionally distilled from, barium oxide. Sodium phenolate was generated from phenol and sodium hydride in THF.

Infrared spectra were recorded on a Perkin-Elmer PE983 spectrophotometer using 0.01-cm CaF_2 solution cells. ^1H NMR spectra were recorded on either an IBM WP-200-SY or an IBM WP-270-SY spectrometer.

Materials. The following compounds were prepared by literature methods: $CpRe(CO)_2H_2$ (**1**),[4] $HMn(CO)_4(PEtPh_2)$,[5] $H_4Ru_4(CO)_{12}$ (**7a**),[6] and $[PPN][H_3Ru_4(CO)_{12}]$.[7a] Samples of both $(\eta^3\text{-}C_6H_9)Mn(CO)_3$ (**2**)[8] and $(\eta^6\text{-}C_6H_6)Mn(CO)_2H$ (**3**) were generously provided by M. Brookhart and S. K. Noh. Samples of $(\mu\text{-}H)_2Fe_3(CO)_9(\mu_3\text{-}P\text{-}p\text{-}C_6H_4OCH_3)$ (**4**), $(\mu\text{-}H)_2Fe_3(CO)_9(\mu_3\text{-}P\text{-}t\text{-}Bu)$ (**5**), and $(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}S\text{-}C_6H_{11})$ (**6**) were generously provided by G. Huttner.[10]

Synthesis of $H_4Ru_4(CO)_{12-x}(P(OCH_3)_3)_x$ (x = 1, 2). The preparation of these compounds was carried out by using a modified form of the reported method.[11] $H_4Ru_4(CO)_{12}$ (**7a**, 200–300 mg, 0.27–0.40 mmol) was treated with an equimolar amount of $P(OCH_3)_3$ (0.03–0.05 mL) in refluxing heptane. The reaction was monitored by IR. When an absorption at 2097 cm^{-1}, indicating formation of the monosubstituted cluster (x = 1), appeared in the IR spectrum (ca. 15 min), the solution was cooled and solvent was removed in vacuo. (Longer reaction times resulted in loss of product and formation of more highly substituted (x = 2–4) species.) Products were separated by chromatography on SiO_2. Elution with hexanes removed starting material; elution with 1:1 hexanes/dichloromethane removed the trimethyl phosphite substituted clusters in order of increasing ligand substitution. The mono- (**7b**) and disubstituted (**7c**) products were isolated in pure form in 10–20% yield and identified by comparison of their IR and ^1H NMR spectra with those in the literature.[11]

Synthesis of $[((C_6H_5)_3P)_2N][H_3Ru_4(CO)_{11}(P(OCH_3)_3)]$. In a typical preparation, $H_4Ru_4(CO)_{11}(P(OCH_3)_3)$ (**7b**, 20 mg, 0.02 mmol) was combined with an equimolar amount of sodium phenolate under N_2. Tetrahydrofuran (10 mL) was introduced by vacuum transfer, and the resulting orange solution was stirred at room temperature for 30 min. An equimolar amount of $[((C_6H_5)_3P)_2N]Cl$ was added by syringe as a THF solution. After the solution was stirred for 1 h at room temperature, the solvent was removed in vacuo. The crude product was redissolved in a minimum volume of methylene chloride and precipitated by slow addition of excess heptane at 0 °C. The resulting red-orange microcrystalline solid was washed with cold heptane and dried in vacuo to give a variable yield of the product. The observed spectra agreed with those observed during deprotonation studies (see below) of the parent compound: ^1H NMR (CD_3CN) δ 7.56 (m, PPN^+), 3.57 (d, $P(OCH_3)_3$), −17.33 (br s, $(\mu\text{-}H)_3$); IR, see Table I; vis (CH_3OH) λ_{max} 343.2 nm; vis (CH_2Cl_2) λ_{max} 345.6 nm.

Reaction of 7a with $NaC_8H_{11}N_2O_3$ in CH_3OH. $H_4Ru_4(CO)_{12}$ (**7a**, 5.5 mg, 0.0074 mmol) and sodium veronalate (29.1 mg, 0.14 mmol) were placed in a 25-mL bulb under nitrogen. Dry methanol (3.5 mL) was added by syringe with stirring under nitrogen. Because $H_4Ru_4(CO)_{12}$ has limited solubility in methanol, the initial solution was a pale yellow slurry. As the reaction progressed, the solution became more homogeneous and darker orange in color. After 2.5 h, the IR spectrum (0.1-mm CaF_2 solution cell under nitrogen) showed the soluble monoanion $[H_3Ru_4(CO)_{12}]^-$ as the only species present in the homogeneous solution. The IR spectrum was the same as that of the isolated monoanion of **7a** in methanol.

Reaction of 7a in Methanolic Veronal/Veronalate Buffer. A pH 12.7 buffer solution was prepared under nitrogen from a 0.052 M methanol solution of veronal (5,5′-diethylbarbituric acid, pK_a = 12.7 in CH_3OH[12]) to which was added the appropriate amount of dry sodium methoxide. $H_4Ru_4(CO)_{12}$ (**7a**, 11.1 mg, 0.0149 mmol) was placed in a second bulb under nitrogen. The buffer solution (6 mL) was added by syringe to give a yellow slurry. IR monitoring of the solution showed that reaction progressed slowly over 17 h to give a homogeneous orange solution containing only the soluble monoanion $[H_3Ru_4(CO)_{12}]^-$.

Infrared Experiments: Absorptivities. The absorptivities of all hydride complexes were determined as in our previous work with isolable hydrides.[1] The absorptivities of most anions were determined from solutions in which they were the only absorbing species; these solutions were prepared either from the isolated anions or by the complete deprotonation in situ of the appropriate hydrides. In the case of $HMn(\eta^6\text{-}C_6H_6)(CO)_2$, even a large excess of phenoxide did not give complete deprotonation; the difference between the total metal concentration and the concentration of metal hydride observed in the IR experiment was used to determine the anion concentration. The absorptivities of the mononuclear metal hydrides and their deprotonated forms, at the frequencies of their carbonyl stretching vibrations, are found in Table I. For polynuclear hydride complexes whose IR absorptions overlapped with those of the corresponding anions, absorptivities for both the hydride and the anion were measured at the absorption maxima of both species. These are also included in Table I.

Equilibrium Constants. The pK_a values of the hydrides were determined, as in our previous work,[1] by treating solutions of the hydrides with bases which effected partial deprotonation and established equilibria of the type in eq 1. [MH] and [M$^-$] were

$$MH + B \overset{K_{eq}}{\rightleftharpoons} M^- + BH^+ \qquad (1)$$

determined by IR, using the absorptivities in Table I. For the polynuclear hydrides, whose absorptions overlapped with those of the corresponding anions, absorbances were measured at several absorption maxima for both the hydride and its anion; the concentrations of both species were calculated by an overdetermined least-squares method. [B] and [BH$^+$] were calculated from the total base initially added, after correction for any association of B and BH$^+$. The hydride pK_a was then calculated by using the measured pK_{eq} and the known pK_a of the base in acetonitrile (eq 2). The results are shown in Table II.

$$pK_a = pK_{eq} + pK_a(BH^+) \qquad (2)$$

Results and Discussion

The seven-coordinate cyclopentadienyldicarbonylrhenium dihydride (**1**; pK_a = 23.0 in Table II) is only slightly less acidic than the six-coordinate $HRe(CO)_5$ (pK_a

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Table I. Transition-Metal Hydride Infrared Carbonyl Stretching Frequencies and Molar Absorptivities[a]

transition-metal hydride	ν_{CO}, cm^{-1}	molar absorptivities,[b] M^{-1} cm^{-1}	
		ϵ(MH)	ϵ(M$^-$)
(CO)$_2$CpReH$_2$ (**1**)	2013	1780	
	1934	3280	
	1844		2460
	1765		2600
HMn(CO)$_4$(PEtPh$_2$)	2060	1402	
	1962	4024	
	1937		3191
	1837		1786
	1803		6336
HMn(CO)$_4$(PPh$_3$)	2060	1380	
	1964	3530	
	1809		5030
	1843		1520
	1940		2660
(η^3-C$_6$H$_9$)Mn(CO)$_3$ (**2**)	2016	3553	
	1829		3037
	1809		2594
(η^6-C$_6$H$_6$)Mn(CO)$_2$H^c (**3**)	1960	2500	
	1900	1830	
(μ-H)$_2$Fe$_3$(CO)$_9$[μ_3-P(4-C$_6$H$_4$OCH$_3$)] (**4**)	2031	7540	132
	1999	3620	3270
	1987	504	2130
	1961	941	2590
	1894	83.0	2860
(μ-H)$_2$Fe$_3$(CO)$_9$(μ_3-P-*t*-Bu) (**5**)	2095	1350	10.8
	2055	4260	22.3
	2029	7580	1110
	1996	2960	6670
	1968	943	8490
	2038	3210	1070
	1954	451	5216
	1896	49.1	610
(μ-H)Fe$_3$(CO)$_9$(μ_3-S-C$_6$H$_{11}$) (**6**)	2082	1440	40.7
	2046	6440	62.5
	2021	8030	156
	2005	5090	290
	1952	809	3043
	2032	1910	2210
	1970	498	14,500
	1943	544	5820
	1916	88.0	2350
H$_4$Ru$_4$(CO)$_{11}$(P(OCH$_3$)$_3$) (**7b**)	2097	1192	
	2066	6661	
	2030	6430	
	2003	3695	
	2056		1732
	2021		6832
	1999		6445
	1982		6079
	1954		3225
H$_4$Ru$_4$(CO)$_{10}$(P(OCH$_3$)$_3$)$_2$ (**7c**)	2078	1841	
	2056	6606	
	2019	6178	
	1994	3736	4188
	2033		2009
	2001	3065	8224
	1978		4552
	1967		5166
	1944		3335

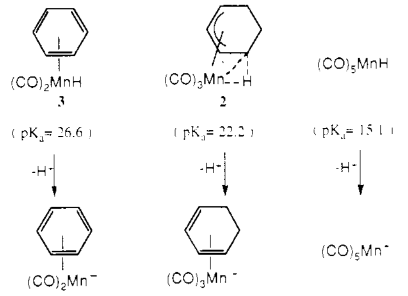
[a] All absorptivities were determined by using several different concentrations. [b] Absorptivities for a single frequency are included for both MH and M$^-$ only when overlapping peak analysis was necessary. [c] Since complete deprotonation could not be achieved even with a large excess of phenoxide, anion concentration for partial deprotonation experiments was determined by subtracting metal hydride concentration from the total metal concentration.

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

transition-metal hydride	base [pK_a(BH$^+$), K_f][a]	pK_a[b]
CpRe(CO)$_2$H$_2$	TMG (23.3, 0)	23.0 (2)
HMn(CO)$_4$(PPh$_3$)	NEt$_3$ (18.5, 0)	20.4 (1)
HMn(CO)$_4$(PEtPh$_2$)	pyrrolidine (19.6, 32)	21.6 (2)
(η^3-C$_6$H$_9$)(CO)$_3$Mn	TMG (23.3, 0)	22.2 (1)
(η^6-C$_6$H$_6$)(CO)$_2$MnH	phenoxide (26.6, 6.3 × 10^5)	26.8 (3)
(μ-H)$_2$Fe$_3$(CO)$_9$(μ_3-P-4-C$_6$H$_4$OCH$_3$)	4-bromoaniline (9.6, 0)	9.0 (1)
	2,4-dichloroaniline (8.0, 0)	
	4-cyanoaniline (7.6, 0)	
(μ-H)$_2$Fe$_3$(CO)$_9$(μ_3-P-*t*-Bu)	aniline (10.56, 0)	11.4 (2)
(μ-H)Fe$_3$(CO)$_9$(μ_3-S-C$_6$H$_{11}$)	morpholine (16.6, 10)	16.9 (2)
H$_4$Ru$_4$(CO)$_{11}$[P(OCH$_3$)$_3$]	aniline (10.56, 0)	12.4 (1)
H$_4$Ru$_4$(CO)$_{10}$[P(OCH$_3$)$_3$]$_2$	pyridine (12.3, 3.98)	15.4 (2)

[a] Data from previous papers in this series or references therein. K_f = [BHB$^+$]/[B$^-$][BH] for the self-association equation: B + BH$^+$ = BHB$^+$. [b] At 25 °C. Values in parentheses are uncertainties in the least significant figure.

Scheme I



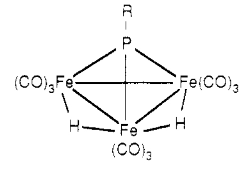
= 21.1[1c]). This comparison offers no evidence of the enhanced acidity predicted for **1** by Bursten and Gatter[3] as a result of its seven-coordinate geometry. However, it is impossible to say to what extent the effect of seven-coordination is negated by the effect of the cyclopentadienyl ligand present in **1** and not in HRe(CO)$_5$. (Comparison of the previously reported[1c] pK_a value of CpFe(CO)$_2$H with that of H$_2$Fe(CO)$_4$ and that of CpRu(CO)$_2$H with that of H$_2$Ru(CO)$_4$ suggests that the presence of cyclopentadienyl ligands decreases the acidity of carbonyl hydrides.)

The pK_a given for HMn(CO)$_4$(PPh$_3$) in Table II (20.4) shows that the substitution of PPh$_3$ for CO in HMn(CO)$_5$ (pK_a = 15.1[1c]) decreases its acidity by 5.3 pK_a units. This effect is comparable to the decrease in acidity upon replacement of CO in HCo(CO)$_4$ by P(OPh)$_3$ (3 pK_a units) or by PPh$_3$ (7 pK_a units).[1c] The effect of the further change from triphenylphosphine in HMn(CO)$_4$(PPh$_3$) (pK_a = 20.4) to diphenylethylphosphine in HMn(CO)$_4$(PEtPh$_2$) (pK_a = 21.6) is a decrease in acidity of 1.2 more pK_a units. Thus even a small change in the electron-donating ability of the other ligands present results in a measurable change in the acidity of a hydride ligand.

On the basis of the pK_a values of CpRe(CO)$_2$H$_2$ (pK_a = 23.0) and HRe(CO)$_5$ (pK_a = 21.1[1c]), one might be led to believe that all hydride complexes of the same metal have similar acidities. However, there are substantial differences between the acidity of HMn(CO)$_5$(pK_a = 15.1[1c]) and the acidities of the manganese hydrides in Table II. As discussed above, replacement of one carbonyl in HMn(CO)$_5$ by a phosphine ligand decreases the acidity of the hydride ligand by 5–6 pK_a units. Replacement of more than one carbonyl by a polyene ligand leads to further decreases in hydride acidity. For example, replacement of two carbonyls to give the agostic hydride complex (η^3-C$_6$H$_9$)(CO)$_3$Mn (**2**) results in a pK_a of 22.2. The hydride in the benzene complex (η^6-C$_6$H$_6$)(CO)$_2$MnH (**3**) has a pK_a of 26.8, the largest that we have measured. Examination of Scheme I shows clearly how the anions resulting from deprotonation of HMn(CO)$_5$, **2**, and **3** are related by the substitution of olefin ligands for carbonyls.

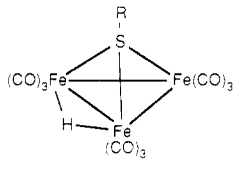
The above data indicate a decrease in acidity of approximately 4 pK_a units for each carbonyl ligand replaced in $HMn(CO)_5$, with the acidities of all these manganese hydrides spanning 11.7 pK_a units! The acidity of the agostic hydride complex **2** follows this rule; i.e., it is approximately that expected if the complex were $HMn(CO)_3(\eta^4$-cyclohexadiene), with a terminal hydride ligand. Apparently the acidity of an agostic hydride, bridging a metal and a carbon atom, does not differ appreciably from that expected for an analogous complex in which the hydride is attached only to the metal.

The pK_a values of the clusters in Table II allow us to examine the acidities of hydrides that bridge two metals. The trinuclear iron clusters $(\mu$-$H)_2Fe_3(CO)_9(\mu_3$-P-*p*-$C_6H_4OCH_3)$ (**4**), $(\mu$-$H)_2Fe_3(CO)_9(\mu_3$-P-*t*-Bu) (**5**), and $(\mu$-$H)Fe_3(CO)_9(\mu_3$-S-$C_6H_{11})$ (**6**) differ in the nature of the apical group that bridges the three iron atoms, and their acidity is extremely sensitive to changes in this apical group. Variation of the alkyl group of the phospinidine cap from the anisyl in **4** (pK_a = 9.0) to the *tert*-butyl in **5** (pK_a = 11.4) changes the pK_a of these clusters by 2.4 units. Although both **4** and **5** are moderately strong acids, the cyclohexylthio-capped cluster **6** is much weaker (pK_a = 16.9).



4: R = anisyl

5: R = *tert*-butyl



6: R = cyclohexyl

Polynuclear hydrides are not necessarily more acidic than mononuclear ones. For example, $H_2Os_2(CO)_8$ has a pK_a only 0.4 unit less than that of $H_2Os(CO)_4$ in acetonitrile;[1a] $H_2Os_3(CO)_{12}$ has a pK_a only 0.5 unit less than that of $H_2Os(CO)_4$ in methanol.[2b] The hydride ligands in all three compounds are terminal, and the negative charge of the anions arising from deprotonation of $H_2Os_2(CO)_8$ and $H_2Os_3(CO)_{12}$ is probably localized on a single osmium (as has been shown[1a] for $[HOs_2(CO)_8]^-$). However, if a polynuclear anion has its negative charge delocalized over more than one metal center, we expect it to be more stable than an analogous mononuclear anion; the protonated form of such a delocalized polynuclear anion will be a stronger acid than the protonated form of the corresponding mononuclear anion. We expect a bridging hydride to be more acidic than its terminal counterpart if, and only if, its deprotonated form is a delocalized anion.[13-15] (On the basis of their results with $H_4Os_4(CO)_{12}$ in methanol, Walker, Pearson, and Ford have suggested that for analogous complexes of the same element, bridging hydrides will be more acidic than terminal hydrides.[2b]) A similar situation is familiar in carbanion chemistry: the relatively localized anion resulting from the deprotonation of cycloheptatriene[16] is much less stable than the delocalized one arising from the deprotonation of cyclopentadiene; cycloheptatriene is therefore 20 pK_a units less acidic than cyclopentadiene.

The phosphinidine complex **5** has the same pK_a as $H_2Fe(CO)_4$ (pK_a = 11.4), while **4** (pK_a = 9.0) is much more acidic than $H_2Fe(CO)_4$. However, neither $H_2Fe(CO)_4$ nor any other iron complex with a terminal hydride ligand can usefully be compared with the RP-capped trinuclear hydrides **4** and **5** or with the RS-capped trinuclear hydride **6**.

A better idea of the comparative acidity of bridging and terminal hydrides can be obtained from the series of phosphite-substituted tetranuclear ruthenium hydride clusters $H_4Ru_4(CO)_{12-x}(P(OCH_3)_3)_x$ (x = 0, **7a**; x = 1, **7b**; x = 2, **7c**). We have not thoroughly investigated the unsubstituted cluster $H_4Ru_4(CO)_{12}$ (**7a**) since it is only sparingly soluble in acetonitrile. In contrast, the monosubstituted cluster $H_4Ru_4(CO)_{11}(P(OCH_3)_3)$ (**7b**) and the disubstituted cluster $H_4Ru_4(CO)_{10}(P(OCH_3)_3)_2$ (**7c**) have proven soluble enough to allow measurement of the pK_a values in Table II (12.4 (1) and 15.4 (2), respectively). If we make the plausible assumption that the unsubstituted **7a** is an even stronger acid than **7b** and **7c**, we can conclude that **7a** is a much stronger acid than $H_2Ru(CO)_4$: pK_a = 18.7 (2).[1c] As **7a** is a tetranuclear carbonyl hydride and $H_2Ru(CO)_4$ is a mononuclear carbonyl hydride, the comparison is fair and supports the prediction that bridging hydrides should be much stronger acids than their terminal counterparts.

The present acetonitrile data, however, seemed inconsistent with the results reported by Walker, Pearson, and Ford[2b] on **7a–c** in methanol. Our acetonitrile pK_a values were smaller than their methanol pK_a values (**7a**, 11.7; **7b**, 14.7; **7c**, >15), implying that these clusters were weaker acids in methanol than in acetonitrile—a result surprising in light of other properties of the two solvents[17] and contrary to previous experience.[18] In the case of **7b**, the only cluster for which both groups had reported exact pK_a values in their respective solvents, our acetonitrile value (Table II) was 2.3 pK_a units *less* than their[2b] methanol value.

Walker, Pearson, and Ford[2b] used UV/vis spectroscopy to characterize **7a–c** and the corresponding anions generated by addition of excess sodium methoxide base in methanol solution. They carried out kinetic and thermodynamic measurements in methanol solution using stopped-flow UV/vis spectroscopy at a cluster concentration of ca. 10^{-5} M and methoxide concentrations of 10^{-2} – 10^{-1} M. They then derived their apparent rate constants, k_f and k_r, from a plot of k_{obsd} versus $[MeO^-]$, using eq 3,

$$k_{obsd} = k_f[MeO^-] + k_r \tag{3}$$

and used their k_f/k_r ratio to calculate their equilibrium constants for the deprotonation of **7a–c** and their corre-

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[13] In other words, the structure of the anion formed upon deprotonation, rather than the structure of the hydride, will influence the pK_a. As bridging hydride ligands usually give delocalized anions upon deprotonation, those hydrides will usually be more acidic than analogous terminal hydride ligands. We predict $H_2Fe_2(CO)_8$, which has a ^1H NMR chemical shift[14] suggesting that its hydrides are terminal, to be a much stronger acid than $H_2Fe(CO)_4$ because of the symmetric structure of $[HFe_2(CO)_8]^-$.[15]

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[16] (a) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393. (b) Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* **1976**, *98*, 4222. (c) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1981, 260.

[17] The Gutmann donor number (DN) for methanol is 19.0, whereas it is 14.1 for acetonitrile (Gutmann, V. *Coordination Chemistry in Non-Aqueous Solutions*; Springer-Verlag: New York, 1968; p 15. Gutmann, V.; Schmid, R. *Coord. Chem. Rev.* **1974**, *12*, 263). Thus solvent methanol is normally a stronger base toward protons than is acetonitrile.

[18] Coetzee[21b] has remarked that "Since acetonitrile is a weaker base than water, all acids are dissociated less in the former solvent than in the latter." A similar statement can be made for acetonitrile and methanol. The acetonitrile pK_a has been greater than the methanol pK_a for all hydrides previously examined in both solvents; see Table 3.3 in: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 91.

sponding pK_a values. They checked their pK_a value for **7a** by UV/vis study of the equilibration of **7a** in a methanolic veronal/veronalate buffer system (pH 12.7).

In an effort to reconcile our results with those of Walker, Pearson, and Ford, we deprotonated **7a** (with ethanolic KOH) and **7b** (with sodium phenolate in THF) and isolated the resulting monoanions as PPN salts. The [PPN][$H_3Ru_4(CO)_{12}$] isolated from the deprotonation of **7a** showed the IR and NMR spectra reported for this monoanion in the literature.[7] When we dissolved either isolated **7a** or its isolated monoanion in methanol, we observed the same λ_{max} values (362 and 344 nm, respectively) reported by Walker, Pearson, and Ford[2b] for **7a** and its monoanion in this solvent. We therefore added **7a** to the same methanolic veronal/veronalate buffer system used by Walker, Pearson, and Ford and examined the position of the deprotonation equilibrium *by IR* in the resulting homogeneous solution. Although the reaction took 17 h at room temperature, we observed only the monoanion of **7a**. (The IR spectrum obtained in the veronal/veronalate experiment was the same as that observed when the monoanion of **7a** was dissolved in methanol and was virtually identical with that observed for the pure monoanion of **7a** in acetonitrile.) The pK_a of **7a** in methanol must therefore be much less than the 11.7 reported by Walker, Pearson, and Ford.

The IR and ^{1}H NMR data in acetonitrile for the monoanion we isolated from the deprotonation of **7b** confirmed that it was [PPN][$H_3Ru_4(CO)_{11}(P(OCH_3)_3)$]. The spectra of the isolated anion agreed with the IR and NMR spectra we observed in acetonitrile during the partial deprotonation of **7b** by aniline (used above to measure the acetonitrile pK_a of **7b**). When we dissolved **7b** in methanol, we observed the same λ_{max} (356 nm) reported by Walker, Ford, and Pearson for **7b** in methanol. However, when we dissolved our isolated [PPN][$H_3Ru_4(CO)_{11}(P(OCH_3)_3)$] in methanol, we observed a λ_{max} (343 nm) significantly different from that (353 nm) found by Walker, Pearson, and Ford when they treated **7b** with excess NaOMe in methanol.

One can imagine two different anions that might be formed by the reaction of a carbonyl cluster such as **7a–c** with methoxide ion. One would of course arise from deprotonation; the other would have a carbomethoxy ligand resulting from methoxide attack on a carbonyl ligand (i.e., [$H_4Ru_4(CO)_{10}(CO_2Me)(P(OCH_3)_3)$]$^-$ from **7b**, reaction 4).

$$H_4Ru_4(CO)_{11}(P(OCH_3)_3) + MeO^- \rightarrow [H_4Ru_4(CO)_{10}(CO_2Me)(P(OCH_3)_3)]^- \tag{4}$$

Gross and Ford have observed facile carbomethoxy ligand formation upon reaction of $Ru_3(CO)_{12}$ with $NaOCH_3$ in methanol and in THF/methanol solutions.[19] Walker, Pearson, and Ford considered carbomethoxy ligand formation and discounted it[2b] because NMR identified [$H_3Ru_4(CO)_{12}$]$^-$ as the only product of the reaction of **7a** with NaOMe in methanol.

However, failure to *observe* a carbomethoxy anion does not mean that one has not been formed. Such an anion could easily be the kinetic product under the fast conditions of a stopped-flow experiment but not be the thermodynamic product seen in an NMR experiment on the laboratory time scale. The rate constant k_1 (8.43×10^1 M^{-1} s^{-1}) reported by Walker, Pearson, and Ford for the deprotonation of **7b** by methoxide (reaction 5) is surprisingly

$$H_4Ru_4(CO)_{11}(P(OCH_3)_3) + MeO^- \xrightarrow{\text{“}k_1\text{”}} [H_3Ru_4(CO)_{11}(P(OCH_3)_3)]^- + MeOH \tag{5}$$

large for a deprotonation reaction. For comparison, our preliminary rate constant k_2 for the deprotonation of **7b** by $PhND_2$ in acetonitrile (reaction 6) is 5×10^{-4} M^{-1} s^{-1}, slower by more than 10^5.[20,21]

$$H_4Ru_4(CO)_{11}(P(OCH_3)_3) + PhND_2 \xrightarrow{k_2} [H_3Ru_4(CO)_{11}(P(OCH_3)_3)]^- + PhND_2H^+ \tag{6}$$

We therefore believe it likely that the reaction observed by Walker, Pearson, and Ford in their stopped-flow experiments is reaction 4 with **7b** and a similar carbomethoxy anion formation reaction with **7a**. The equilibrium constant they derived from their kinetic measurements may be that for methoxide addition (as in reaction 4) instead of that for deprotonation (as in reaction 5).

Conclusions. (1) The seven-coordinate hydride complex $CpRe(CO)_2H_2$ is not a stronger acid than the six-coordinate hydride complex $HRe(CO)_5$. (2) The nature of the ancillary ligands can have a substantial effect on the acidity of transition metal hydride complexes of a given transition metal. In particular, variation of R′ in the phosphine ligand of $HMn(CO)_4PR_2R'$ and in the phosphinidene complexes $(\mu\text{-}H)_2Fe_3(CO)_9(\mu_3\text{-}PR')$ results in a significant change in the acidities of these complexes. (3) The acidity of the agostic hydride in $(\eta^3\text{-}C_6H_9)Mn(CO)_3$ is similar to that expected if it were a terminal hydride. (4) The hydride ligands that bridge two metal centers in $H_4Ru_4(CO)_{12-x}(P(OCH_3)_3)_x$ ($x = 0$, **7a**; $x = 1$, **7b**; $x = 2$, **7c**) are more acidic than the terminal hydrides in $H_2Ru(CO)_4$, supporting the idea that bridging hydrides are more acidic than terminal ones if the anions arising from the deprotonation of the former are delocalized.

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Registry No. **1**, 78809-05-9; **2**, 76830-97-2; **3**, 103191-68-0; **4**, 75495-80-6; **5**, 75514-42-0; **6**, 81877-18-1; **7a**, 34438-91-0; **7b**, 34438-92-1; **7c**, 84254-45-5; $HMn(CO)_4(PEtPh_2)$, 92816-72-3; $HMn(CO)_4(PPh_3)$, 16925-29-4; $(\mu\text{-}H)Fe_3(CO)_9(\mu_3\text{-}SC_6H_{11})$, 81877-18-1; [$((C_6H_5)_3P)_2N$][$H_3Ru_4(CO)_{11}(P(OCH_3)_3)$], 115419-72-2; [$((C_6H_5)_3P)_2N$]Cl, 21050-13-5; [$H_3Ru_4(CO)_{12}$]$^-$, 70073-18-6; sodium veronalate, 144-02-5; veronal, 57-44-3.

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(20) From the methanol pK_a value cited by Walker, Pearson, and Ford[2b] and their reported pK_a for **7b**, the equilibrium constant for reaction 5 is 1.0×10^2. From the pK_a values of **7b** and aniline[21] in acetonitrile, the equilibrium constant for reaction 6 is 1.4×10^{-2}. The ratio of the equilibrium constant for reaction 5 to that for reaction 6 is thus 7.1×10^3, substantially *less* than the ratio of the rate constants for these two reactions; i.e., the rate ratio is 24 times the equilibrium constant ratio. A similar rate-equilibrium comparison between deprotonation by MeO^- in MeOH[2b] and deprotonation by aniline in acetonitrile,[1d] for removal of a proton from $Os(CO)_4H_2$, gives a rate ratio (3.8×10^3) which is only 7.5 $\times 10^{-9}$ times the equilibrium constant ratio (5.1×10^{11}).

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