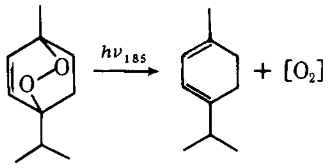
versions (<15%), the mass balance as shown by the following equalities was satisfactory to ±5%:

α-terpinene + triene **5** ≡
cyclohexyl hydroperoxide[5] + cyclohexanol + cyclohexanone

Δ ascaridole ≡ isoascaridole + α-terpinene + triene **5**

Evidently, at 185 nm, the photolysis of ascaridole leads not only to isoascaridole as at longer wavelengths[2] but also to a retro-Diels–Alder reaction as shown in eq 2.



(2)

1 **3**

The triene **5** is believed to be predominantly a secondary isomerization product derived from α-terpinene by the well-known photochemical transformation of 1,3-cyclohexadienes. This was confirmed in a separate experiment in which a solution of α-terpinene alone was irradiated at 254 nm when **5** was observed to be formed. The ratio of process 2 to process 1 at 185 nm was 1:2.

The intriguing aspect of reaction 2 is that (according to gas chromography) not a trace of the oxygen that should be released was observed to accumulate in the solution. Further, the oxidation products of the solvents that are reported above closely resemble those from the direct irradiation at 185 nm of oxygen dissolved in the same solvents.[6] In view of the 40-fold weaker absorption of oxygen at 185 nm compared with the absorption of ascaridole at the same wavelength, the possibility that the oxygen released in reaction 2 undergoes secondary photolysis can be discounted. The conclusion that is inevitable is that the retro-Diels–Alder reaction (2) gives oxygen in an electronically excited state which invariably reacts with the solvent. The parallel between the product compositions in this and the O_2–hydrocarbon system suggests that this state may be $O_2(^3\Sigma_u^-)$ but a closer examination indicates another possibility as well.

Recently, Turro, Chow, and Rigaudy[7] found that the pyrolysis of certain 1,4-anthracene endoperoxides gave in nearly quantitative yield the aromatic hydrocarbon and oxygen ($^1\Delta$). The process

$$\text{anthracene endoperoxide} \xrightarrow{\Delta} \text{anthracene} + O_2(^1\Delta) \quad (3)$$

would evidently conserve spin, whereas the process

$$\text{anthracene endoperoxide} \xrightarrow{\Delta} \text{anthracene} + O_2(^3\Sigma_g^-) \quad (4)$$

would not. The conservation of spin may or may not be a strong consideration since reaction 4 competed successfully against 3 in 9,10-anthracene endoperoxides but not in 1,4-anthracene endoperoxides.

In applying these considerations to ascaridole, it can be seen that

$$\text{ascaridole} \xrightarrow{h\nu_{185}} \alpha\text{-terpinene (ground singlet)} + O_2(^3\Sigma_u^-) \quad (5)$$

is energetically possible[8] but does not conserve spin while

$$\text{ascaridole} \xrightarrow{h\nu_{185}} \alpha\text{-terpinene (triplet)} + O_2(^3\Sigma_u^+) \quad (6)$$

would conserve spin and energy. The $^3\Sigma_u^+$ state of oxygen is 35 713 cm^{-1} (102.1 kcal/mol) above the ground state so that ~53 kcal/mol will be available to excite the α-terpinene to its triplet state. It is at present not possible to choose between these alternatives because (i) the similarity in the composition of the oxidation products from the solvent in the ascaridole–cyclohexane system to the O_2–cyclohexane system may mean that either reaction 5 is the preferred made of photodecomposition of ascaridole or, in the O_2–cyclohexane system, the active species is not $O_2(^3\Sigma_u^-)$ but $O_2(^3\Sigma_u^+)$; (ii) the fate of the α-terpinene (other than deactivation) should give information on whether it is formed in its ground state or its triplet state. Unfortunately, the host of products that are formed in the photolysis of ascaridole makes this task difficult.

We are currently undertaking the flash photolysis of ascaridole in the vapor phase and expect to determine unequivocally the character of the oxygen as it is formed in reaction 2.

Photolysis of ascaridole offers a second route to the production of an upper excited state of oxygen in the condensed phase.

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Received July 25, 1979

Crystal Structure and Dynamic Behavior of $Ir_4(CO)_{10}$(diars). A New Pathway for Carbonyl Scrambling in $M_4(CO)_{12}$ Derivatives

Sir:

The solid-state structures established for $Rh_4(CO)_{12}$ (C_{3v})[1] and $Ir_4(CO)_{12}$ (T_d)[2] formed a natural basis for the mechanism ($C_{3v} \leftrightarrow T_d$) proposed by Cotton et al. for the carbonyl scrambling in $Rh_4(CO)_{12}$.[3] Specific evidence for interconversion of T_d- and C_{3v}-like forms recently has been reported for the derivatives $Ir_4(CO)_{11}(PPh_2Me)$ (C_{3v})[4] and $Ir_4(CO)_{11}[CN(t\text{-Bu})]$ (T_d).[5] Nevertheless, ^{13}C NMR data reported for C_{3v}-like $RhCo_3(CO)_{12}$ provide evidence for a lowest energy scrambling process that is incompatible with $C_{3v} \leftrightarrow T_d$ interconversions.[6] Rationales for this apparent anomaly have been advanced in two recent discussions of carbonyl scrambling in $M_4(CO)_{12}$ derivatives.[7,8] We report herein a second anomalous case in the compound $Ir_4(CO)_{10}$(diars) (diars = 1,2-bis(dimethylarsino)benzene), which displays dynamic behavior that in part requires a new mechanistic proposal.

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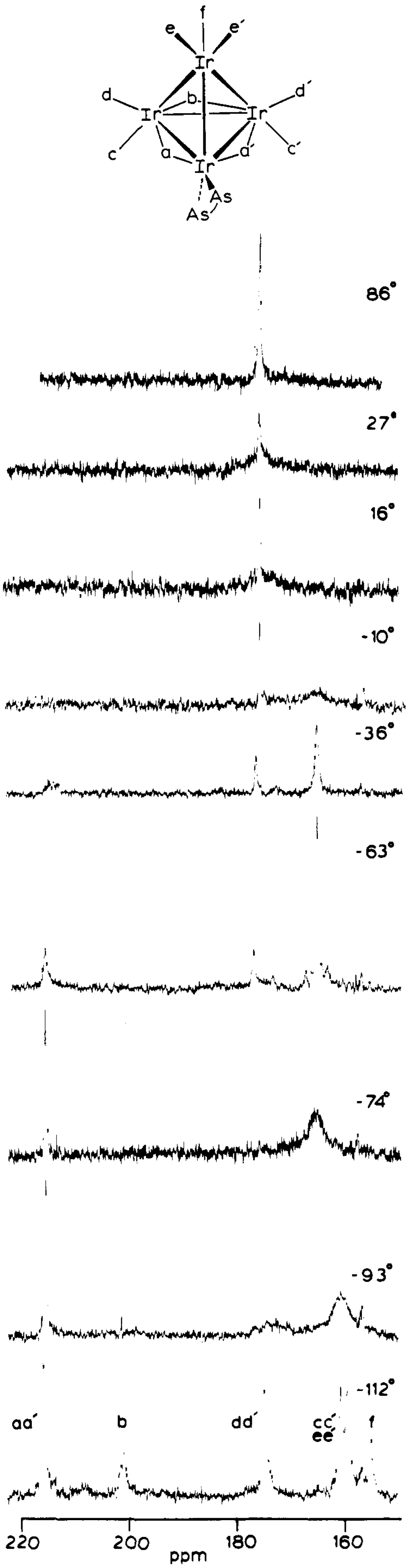

Figure 1. 25-MHz ^{13}C NMR spectra at various temperatures for ^{13}CO-enriched $\mathrm{Ir_4(CO)_{10}}$(diars), together with assignments.

Treatment of a solution of $\mathrm{Ir_4(CO)_{12}}$ in refluxing THF with 1 equiv each of diars and $\mathrm{Me_3NO{\cdot}2H_2O}$, followed by separation of the product mixture by TLC, provided $\mathrm{Ir_4(CO)_{10}}$(diars) in 34% yield as a crystalline yellow solid, moderately stable under ambient conditions.[9] The limiting ^{13}C NMR spectrum of this compound (214.8 (2 C), 200.3 (1 C), 174.6 (2 C), 161.0 (2 C), 159.4 (2 C), 155.3 (1 C) ppm in $\mathrm{CD_2Cl_2}$-$\mathrm{CFCl_3}$; see Figure 1) is very similar to that of $\mathrm{Ir_4(CO)_{10}}$·(1,5-cyclooctadiene),[10] in each case suggesting a C_{3v}-like structure with substitution at a basal iridium atom (vide infra). However, in contrast to the diene derivative, $\mathrm{Ir_4(CO)_{10}}$(diars) shows only weak, broad bridging carbonyl IR bands (2071 (m), 2038 (s), 2026 (w), 2001 (m), 1996 (w), 1847 (vw, br), 1805 (w, br) cm^{-1} in $\mathrm{C_6H_{12}}$) and it is fluxional at very low temperatures. Therefore, as a basis for discussion of the dynamic behavior of $\mathrm{Ir_4(CO)_{10}}$(diars), its crystal structure has been determined.

The complex crystallizes in the centrosymmetric orthorhombic space group *Pnma* with a = 19.038 (7) Å, b = 10.584 (3) Å, c = 14.186 (6) Å, V = 2858 (2) Å^3, Z = 4, and ρ(calcd) = 3.10 g cm^{-3} for mol wt 1335. Diffraction data were collected with a Syntex P2$_1$ automated four-circle diffractometer using Mo Kα radiation and a θ-2θ scan routine.[11] Data were corrected for absorption (μ = 211 cm^{-1}) and for Lorentz and polarization factors and the structure was solved via Patterson, difference-Fourier, and full-matrix least-squares refinement techniques. All nonhydrogen atoms were located directly and hydrogen atoms were included in their idealized positions. The final discrepancy indices are R_F = 7.3% and R_{wF} = 5.5% for those 1746 reflections with $|F| > \sigma(F)$ and $4° < 2\theta < 45°$.

The molecular geometry is illustrated in Figure 2. The four iridium atoms define a tetrahedral cluster and the molecule possesses crystallographically imposed $C_s(m)$ symmetry. The mirror plane contains the $\mathrm{C_6H_4As_2}$ fragment of the diars ligand, atoms Ir(2) and Ir(3), and carbonyl groups C(11B)-O(11B) and C(21)-O(21). The diars ligand chelates to Ir(3) with Ir(3)-As(1) = 2.369 (4) and Ir(3)-As(2) = 2.393 (4) Å. The molecule contains one symmetrically bridging carbonyl group (Ir(1)-C(11B) = Ir(1′)-C(11B) = 2.077 (27), C(11B)-O(11B) = 1.17 (4) Å; ∠Ir(1)-C(11B)-O(11B) = ∠Ir(1′)-C(11B)-O(11B) = 139.6 (23), ∠Ir(1)-C(11B)-Ir(1′) = 80.9 (10)°) and two crystallographically related asymmetrically bridging (or "semibridging") carbonyl groups, C(31B)-O(31B) and C(31B′)-O(31B′). Dimensions within these symmetry related (m) systems are as follows: Ir(3)-C(31B) = 2.012 (25), Ir(1)··C(31B) = 2.257 (22), C(31B)-O(31B) = 1.14 (3) Å; ∠Ir(3)-C(31B)-O(31B) = 145.5 (20), ∠Ir(1)··C(31B)-O(31B) = 134.9 (19), ∠Ir(1)··C(31B)-Ir(3) = 79.4 (8)°.

There are slight differences in iridium-iridium distances within the cluster. The symmetrically bridged Ir(1)-Ir(1′) distance is 2.694 (2) Å; the "semibridged" Ir(1)-Ir(3) and Ir(1′)-Ir(3) distances are each 2.733 (1) Å; the nonbridged distances are Ir(1)-Ir(2) = Ir(1′)-Ir(2) = 2.723 (2) and Ir(2)-Ir(3) = 2.731 (2) Å. While the differences are slight, we believe that these results are the first to provide a differentiation between symmetrically carbonyl-bridged and nonbridged Ir-Ir distances in neutral derivatives of $\mathrm{Ir_4(CO)_{12}}$.[12] (Note that asymmetrically bridged distances are expected to be almost indistinguishable from nonbridged distances.)

All other distances are in the expected ranges (terminal Ir-CO = 1.830 (34)-1.904 (27), terminal C-O = 1.12 (3)-1.16 (4) Å).

Assignments for the limiting low-temperature ^{13}C NMR spectrum (−112 °C) shown in Figure 1 are entirely consistent with the solid-state molecular structure and with those made previously for derivatives of $\mathrm{Ir_4(CO)_{12}}$.[4,10] As the sample temperature is raised from −112 to −93 °C, the resonance due to bridging carbonyls a/a′ remains sharp, whereas all of the

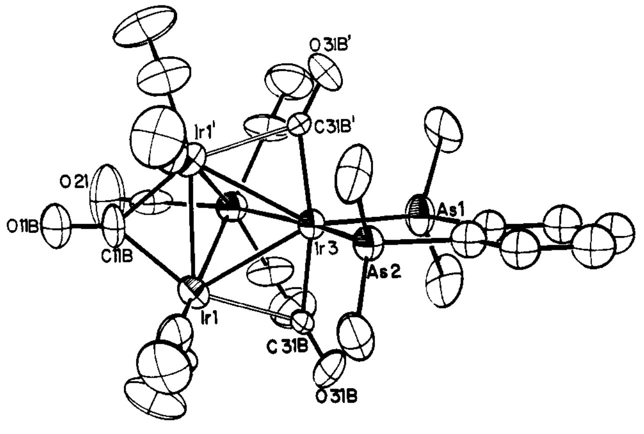

Figure 2. Molecular geometry of $Ir_4(CO)_{10}$(diars). The crystallographic mirror plane lies about 10° from the horizontal in this view. Note the asymmetric bridging carbonyl groups which (in this solid-state structure) act so as to donate electron density from the formally electron-rich Ir(3) to the formally electron-poor atoms Ir(1) and Ir(1').

other resonances broaden. At −63 °C the latter resonances have sharpened into two new signals at 177.0 (2 C) and 165.6 (6 C) ppm. The signal of 177.0 ppm is in the appropriate position to result from averaging of carbonyls b and f (calcd 177.8 ppm), whereas the signal at 165.6 ppm appears to arise from carbonyls c/c', d/d', and e/e' (calcd 165.0 ppm). The signal due to a/a' is sharp at −63 °C, but begins to broaden by −36 °C, together with the six-carbon signal at 165.6 ppm. By 16 °C these resonances have coalesced into a broad hump superimposed on the sharp signal at 177.0 ppm. However, the latter is noticeably broader at 27 °C and by 86 °C only one sharp signal remains.

Three separate temperature ranges for carbonyl site equilibration are apparent. One is a uniquely low temperature range from −112 to about −63 °C, whereas the higher ranges, which begin about −63 and 27 °C, are close to those observed previously for $Ir_4(CO)_{11}(PPh_2Me)$[4] and $Ir_4(CO)_{11}[CN(t\text{-}Bu)]$.[5] The equilibration evidenced in the middle range can be rationalized by interconversion of triply edge-bridged, C_{3v}-like structures with unbridged T_d-like structures, as in the previous cases. Characteristically, the $C_{3v} \leftrightarrow T_d$ mechanism does not average the two carbonyls pseudotrans to the sites of substitution, namely b and f, with the remaining carbonyls. On the other hand a mechanism cannot be deduced for the complete equilibration that takes place above 27 °C, although it may involve localized exchange at an apical iridium atom.

The exchange pattern observed in the lowest temperature range requires a novel interpretation, which we propose in terms of the mechanism shown in Figure 3. Migration of carbonyl a (or a') in I to an unsymmetrical face bridging position together with migration of carbonyl f to an edge-bridging position generates an intermediate configuration II of C_s symmetry. Continuing the movement of carbonyl a to a new edge together with movement of carbonyl b to a terminal position regenerates the static structure, configuration I'. In this way carbonyls b and f equilibrate separately from carbonyls c/c', d/d', and e/e' and at the same time carbonyls a/a' remain distinct. Equilibration of the two arsenic atoms also is implied, which is consistent with our observation of only one As-Me ^1H NMR signal.[13] The new mechanism has elements similar to those of a carbonyl scrambling process proposed for C_s $(\eta^5\text{-}C_5H_5)_3Rh_3(CO)_3$.[14] In both cases movement of an edge-bridging carbonyl across a triangular face to a new edge is coupled with edge-terminal and terminal-edge shifts of two other carbonyls.

The origin of the new low energy carbonyl scrambling process in $Ir_4(Co)_{10}$(diars) is not obviously related to distortions in the solid-state structure. A closely related structure, also with semibridging carbonyls for charge balance, is adopted by $[Ir_4(CO)_{11}Br^-]$;[12d] yet carbonyl scrambling in the complex parallels that of $Ir_4(CO)_{11}(PPh_2Me)$.[15] The small bite of the diars ligand compresses the angle between terminal positions at Ir(3) (∠As-Ir(3)-As = 85.9 (1) vs. ∠OC-Ir(1)-CO = 98 (1)°), but the bite angle of 1,5-cyclooctadiene should be similar[16] and $Ir_4(CO)_{10}$(1,5-cyclooctadiene) is not fluxional at room temperature.[10] Furthermore, the derivatives $Ir_4(CO)_8(diars)(PMe_3)_2$ and $Ir_4(CO)_9(diars)(PPh_2Me)$, having further substitution in the radial positions (d/d'; see Figure 1), also are nonfluxional under ambient conditions.[13] To uncover additional examples of the behavior shown by $Ir_4(CO)_{10}$(diars), the preparation of related $M_4(CO)_{12}$ derivatives is being pursued.

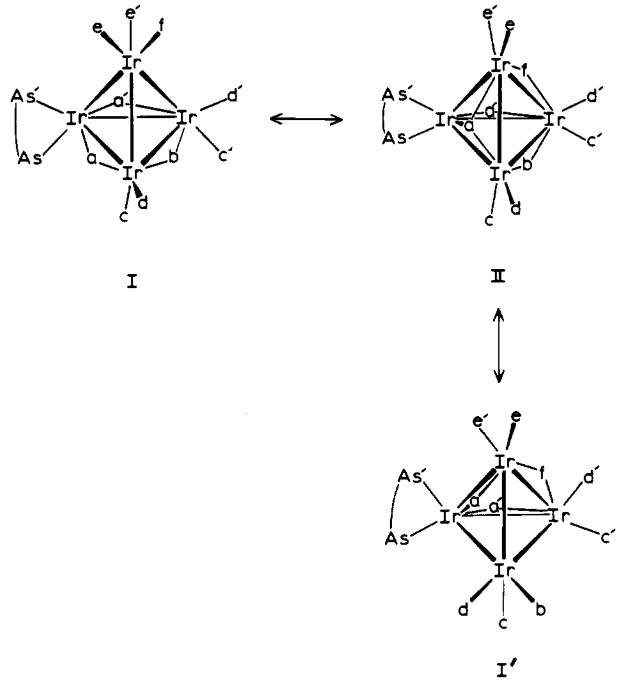

Figure 3. Proposed lowest energy carbonyl scrambling pathway for $Ir_4(CO)_{10}$(diars).

Acknowledgments. This work was generously supported by the National Science Foundation through Grants CHE77-04981 (to M.R.C.) and CHE75-14460 (to J.R.S.).

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(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.
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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

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

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

$$K = k_1/k_{-1} = K_a/K_s \tag{2}$$

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