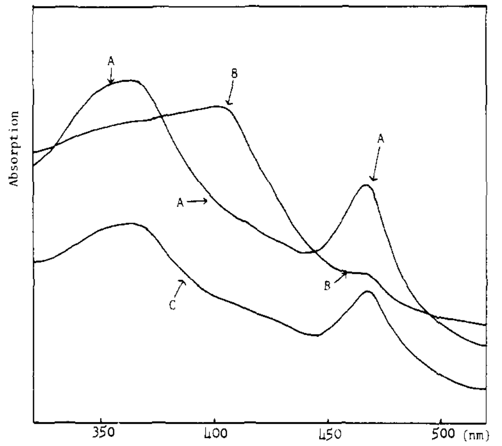

Figure 3. Electronic spectrum of a lecithin membrane: A, Hm·Mn(III) membrane; B, treatment of A with NaOCl for 1 min; C, treatment of B with aqueous ascorbic acid for 1 min.

concentration) containing KCl(1.0 M) to adjust its ionic strength. After 1 min, most of the Mn(III) in the membrane was effectively converted into Mn(IV) (more than 80%) as ascertained by electronic spectral changes as shown in Figure 3. Spectra were obtained after washing the membranes rapidly three times with aqueous alkaline solution (pH 12) to remove traces of NaOCl absorbed on the surface.

The Hm·Mn(IV) in the membrane was stable enough for spectroscopic measurements. The Mn(IV) membranes were then treated with aqueous ascorbic acid (0.01 M), containing KCl (1.0 M), for 1 min. After rapid washing with the aqueous solution of pH 12, Hm·Mn(IV) was estimated by electronic spectral changes, which showed that most of the Hm·Mn(IV) was converted to Hm·Mn(III) (70–80%) (Figure 3).

Spontaneous transport of ascorbic acid through the lecithin-Hm·Mn(III)-*n*-decane membrane from B (0.01 M ascorbic acid and 1.0 M KCl) to A (1.0 M KCl) was measured by the spectroscopic determination of ascorbic acid (265 nm) in A. It was $(3.8 \pm 0.3) \times 10^{-12}$ mol min^{-1}, ca. 3000 times slower than the reduction of the Mn(IV) membrane by ascorbic acid. The continuous electron transfer through the lecithin-Hm·Mn membrane from the ascorbic acid solution (5.0×10^{-5} M) to the sodium hypochlorite solution (1.3×10^{-1} M) was also studied by use of a salt bridge. The amount of the ascorbic acid oxidized was 7.4×10^{-10} mol min^{-1} (ca. 2.3 turnover per Mn in 25 min), 195 times faster than the rate of spontaneous transport. This strongly indicates that the oxidation-reduction did not result from material transport but from one-way electron transport as shown in Figure 1. Treatment of Mn(IV) membranes with an aqueous solution of pH 4 containing 1.0 M KCl instead of aqueous ascorbic acid again reduced Mn(IV) to Mn(III) as in the homogeneous system,[1] but the rate was considerably slower than that of the ascorbic acid reduction.

These electron translocating membranes are versatile, allowing the preparation of one-way oxidation-reduction electron transport systems or the effective separation of electrons from positive holes.

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(5) J. M. Tobias, D. P. Agin, and R. Powlowski, *J. Gen. Physiol.*, **45**, 989 (1962).
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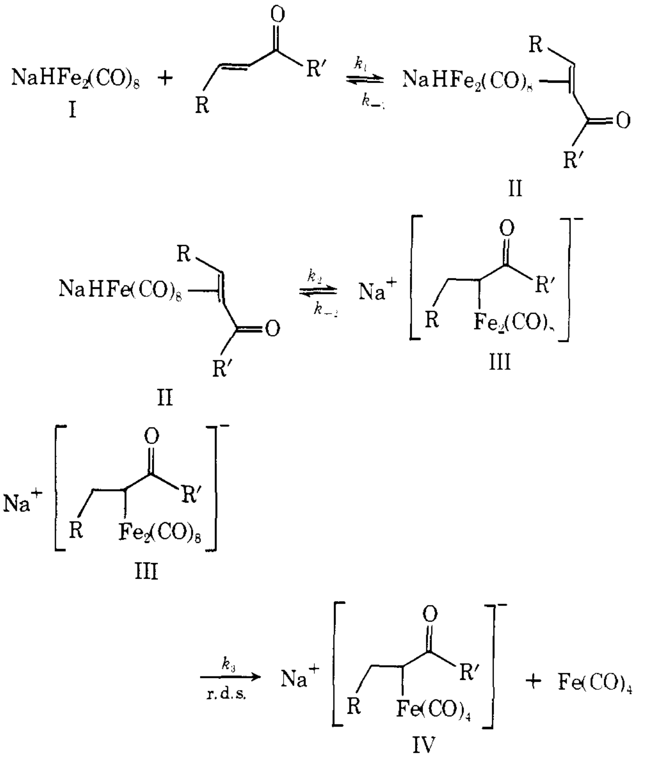
Binuclear Clusters in Organic Synthesis. Synthetic and Mechanistic Studies of the Reduction of α,β-Unsaturated Carbonyl Compounds by $NaHFe_2(CO)_8$

Sir:

Transition metal clusters offer the possibility of reaction paths involving adjacent metal centers acting on a common substrate. Although many studies exist probing the structure,[1] bonding,[1] and fluxional[2] behavior of carbonyl cluster compounds and their hydrides,[3] little is known about their chemical reactivity[4] and correspondingly even less about their detailed reaction mechanisms.[5,6] Only one cluster has been shown to be a useful synthetic reagent.[7]

Scheme I. Proposed Mechanism for the Reduction of α,β-Unsaturated Carbonyl Compounds by $NaHFe_2(CO)_8$



Reactions Occurring after the Rate-Determining Step

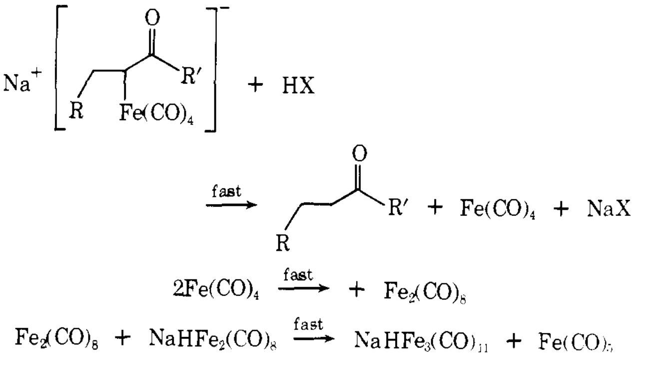
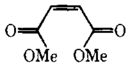
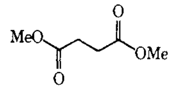
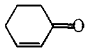
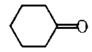
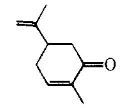
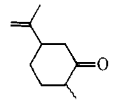
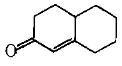
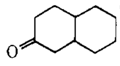
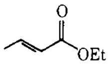
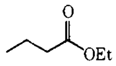
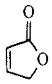
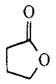
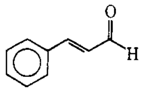
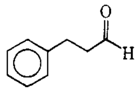
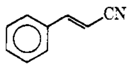
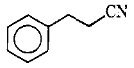
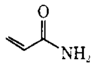
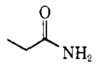


Table I. Reductions in THF

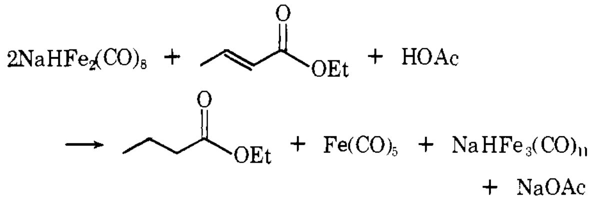
Entry	Substrate	Product	Yield[a]	Moles of substrate-NaHFe$_2$(CO)$_8$:HOAc	Time (hr)
1			100	1:1:1	0.01
2			100	1:2.1:2.1	0.1
3			76	1:5:5	20
4		[b]	45	1:2:2	2
5			92	1:2.1:2.1	3
6			90 (76)	1:2.1:2.1	0.5
7			90	1:2:2	0.5
8			96	1:2:2	3
9			(50)	1:2:2	8

[a] Determined by VPC using internal standards. Numbers in parentheses correspond to isolated yields. [b] Cis to trans ratio 4:1 determined by GLC.

Herein, we report synthetic and preliminary mechanistic studies of the reduction of only the olefinic bond in α,β-unsaturated carbonyl compounds by the binuclear hydride, $NaHFe_2(CO)_8$.

When $Na_2Fe(CO)_4 \cdot 1.5dioxane$[8] is treated with 1 equiv of $Fe(CO)_5$ in THF, CO is evolved and red $Na_2Fe_2(CO)_8 \cdot X(THF)$ precipitates.[9] Addition of 1 equiv of acetic acid to a suspension of $Na_2Fe_2(CO)_8$ in THF yields[10,11a] a reddish brown solution of $NaHFe_2(CO)_8$. This solution shows ν_{CO} at 1987 (s), 1940 (s), 1880 (s), 1802 (s), 1770 (m), and 1730 cm^{-1} (w), and a ^1H NMR singlet at δ −8.47 (32°). A crystal structure of $(PPN)^+(HFe_2(CO)_8)^-$ shows,[12] two bridging CO's and implies a bridging hydride. Reductions of α,β-unsaturated ketones esters, lactones, aldehydes, amides, and nitriles with $NaHFe_2(CO)_8$ proceed in high yield, Table I.

Using ethyl crotonate as a model substrate, kinetic data[11b] demonstrate the reaction[13] is first order each in $NaHFe_2(CO)_8$



$$2NaHFe_2(CO)_8 + CH_3CH{=}CHCO_2Et + HOAc \longrightarrow CH_3CH_2CH_2CO_2Et + Fe(CO)_5 + NaHFe_3(CO)_{11} + NaOAc \quad (1)$$

and α,β-unsaturated carbonyl compound, but zero order in acetic acid (k_2 (GLC)) = $(1.0 \pm 0.1) \times 10^{-3}\ M^{-1}\ s^{-1}$), with stoichiometry as shown. The reaction is also essentially uninhibited by CO and unaffected by added $Fe(CO)_5$. These facts and the following observations are consistent with the mechanism proposed in Scheme I. ^1H and ^{13}C NMR studies in the absence of HOAc show the primary product[14] to be $Na^+[RCH_2CH(Fe(CO)_4)COR']$ (IV, Scheme I), which is converted to RCH_2CH_2COR' in <1 min upon addition of HOAc. The observation of an inverse isotope effect[15] $k_D/k_H = 3.5$, suggests reversible migratory insertion (II ⇄ III) followed by the rate determining step (III → IV) Scheme I. This prior equilibrium is quantitatively consistent with the observed isotope effect.[16] Reversibility was established by isotopic labeling. Reaction of $NaDFe_2(CO)_8$ with $CH_3CH{=}CHCO_2Et$ and excess DOAc gives $NaHFe_2(CO)_8$ and organic products having one or two deuteriums at the β-position and zero or one deuterium at the α-position; however, no product could be found containing two α deuteriums. The presence of significant amounts of $CH_3CD_2CH(D)CO_2Et$ and $NaHFe_2(CO)_8$ requires reversible migratory insertion. The failure to observe any α,α-d_2 demonstrates regiospecific addition[17] yielding III, Scheme I.

Further evidence suggests that II and III (Scheme I) are binuclear iron complexes. Added $Fe(CO)_5$ does not inhibit these reductions, ruling out reversible rupture of the iron-iron bond which would form the unsaturated hydride $NaHFe(CO)_3$. Under identical conditions the binuclear $NaHFe_2(CO)_8$ is >26 times more reactive than $NaHFe(CO)_4$, ruling out this mononuclear hydride[18a] as the kinetically active species.[18b] Our data rule out a CO dissociative process of the type often found for metal clusters containing bridging carbonyls,[5] and suggest an associative first step.[19] However, the detailed bonding in $NaHFe_2(CO)_8$ $(RCH{=}CHCO_2R')$ remains unclear.[20] Concerted $NaHFe_2(CO)_8$ addition yielding III is also consistent with our data. A further important and unexpected conclusion is that cleavage of the iron-iron bond in $Na^+[RCH_2CH(Fe_2(CO)_8)COR']^-$ is faster than proton addition, reductive-elimination to yield[21] RCH_2CH_2COR'. Evidence for the three reactions after the rate-determining step has also been obtained.[22]

The unusual mechanism revealed by this study[23] argues well for the prospect of developing new and novel chemistry in binuclear and higher cluster compounds. Further observations on the synthetic utility and ion-pairing effects in these reactions as well as ligand substitution and decomposition mechanisms for $NaHFe_2(CO)_8$ will be reported subsequently.

Note Added in Proof. We have found that at higher HOAc concentrations, protonolysis of **III** becomes kinetically important.

Acknowledgment. This work was supported by NSF Grant MPS75-17018.

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(4) D. Seyferth, G. H. Williams, A. T. Wehman, and M. O. Nestle, *J. Am. Chem. Soc.*, **97,** 2107 (1975); G. D. Mercer, J. S. Shu, T. B. Rauchfuss, and D. M. Roundhill, *Ibid.*, **97,** 1967 (1975). Muetterties has recently studied a nickel cluster which, among other reactions, catalyzes acetylene trimerization. V. W. Day, R. O. Day, J. S. Kristoff, F. J. Hirsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97,** 2571 (1975); E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84,** 959 (1975).

(5) For mechanistic studies of the substitution reactions involving carbonyl clusters see K. J. Karel, and J. R. Norton, *J. Am. Chem. Soc.*, **96,** 6812 (1974); D. DeWitt, J. P. Fawcett, A. J. Poë, and M. V. Twigg, *Coord. Chem. Rev.*, **8,** 81 (1972), and references contained therein; A. Poë and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 1860 (1974), and references contained therein; J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Chem. Soc., Chem. Commun.*, 267 (1973).

(6) Two recent studies have shown that odd d^n binuclear carbonyl clusters may act, via homolysis, as sources of reactive paramagnetic monomers. J. P. Fawcett, R. A. Jackson, and A. Poë, *J. Chem. Soc., Chem. Commun.*, 733 (1975); E. L. Muetterties, B. A. Sosinsky, and K. I. Zamaraev, *J. Am. Chem. Soc.*, **97,** 5299 (1975).

(7) In this case the nature of the active species has not been defined. T. Kitamura, N. Sakamoto, and T. Joh, *Chem. Lett.*, 379 (1973).

(8) Commercially available from Ventron Corporation, Alfa Products.

(9) GLC and ^1H NMR analysis shows X to be between 3 and 4. Removal of THF under vacuum affords $Na_2Fe_2(CO)_8$ as a yellow powder.

(10) The sodium acetate by-product is easily removed by centrifugation, although its presence does not hinder synthetic reductions.

(11) (a) $NaHFe_2(CO)_8$ was prepared by adding dry HOAc to isolated $Na_2Fe_2(CO)_8$, centrifuging, and using the homogeneous supernatant. Strict anerobic conditions were maintained at all times. THF was distilled under nitrogen from sodium and benzophenone. (b) The reaction was monitored by quenching aliquots with excess HOAc and dimethyl maleate and analyzing for both reactants (e.g., ethyl crotonate) and products (e.g., ethyl butyrate) by flame ionization GC using the internal standard technique. Following the appearance of reduced product directly by ^1H NMR in THF, d_8 gave the same rate constant within experimental error as the GLC kinetics.

(12) H. B. Chin, Ph.D. Thesis, University of Southern California, Los Angeles, Calif., 1975.

(13) Organic products and $Fe(CO)_5$ were measured by GLC. Iron hydride concentrations were determined by ^1H NMR.

(14) $Na^+(CH_3CH_2CH(Fe(CO)_4)C(=O)OEt)^-$ prepared independently from $NaHFe(CO)_4$ and *trans*-ethyl crotonate had ^{13}C and 100-MHz ^1H NMR spectra identical with that of our observed product.

(15) H. Simon and O. Berngruber, *Tetrahedron*, **26,** 1401 (1970); C. D. Ritchie, "Physical Organic Chemistry, the Fundamental Concepts", Marcel Dekker, New York, N.Y., 1975, pp 217, 237.

(16) The inverse isotope effect requires that $k_{-2} > k_3$ and that the concentration of III be small. The isotope effect arises from zero point energy differences between C–H and Fe–H vs. C–D and Fe–D vibrations. Using $Ru_4H_4(CO)_{12}$ as a model (S. A. R. Knox, J. W. Koepke, M. A. Andrews, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97,** 3942 (1975)), two bands are observed at 1585 and 1290 cm^{-1} which shift to 1153 and 909 cm^{-1} in the deuteride. For the alkyl intermediate, chloroform was used as a model. The chloroform C–H bond shows a stretching vibration at 3019 cm^{-1} and a twofold degenerate bending vibration at 1259 cm^{-1}. These values are shifted to 2256 and 908 cm^{-1}, respectively, in $CDCl_3$ (see R. W. Alder, R. Baker, and J. M. Brown, "Mechanisms in Organic Chemistry", Wiley-Interscience, London, 1971, p 15). These values give $K_D/K_H = 3.3$. While these calculations are not intended to be definitive, they do show that a preequilibrium of the type II $\rightleftharpoons$ III will account for the observed isotope effect.

(17) It has been shown in our laboratory that $NaHFe(CO)_4$ regiospecifically and irreversibly adds iron to the α-position. J. P. Collman, *Acc. Chem. Res.*, **8,** 342 (1975).

(18) (a) We have shown Noyori's preparation ($Fe(CO)_5 + NaOH + CH_3OH$) affords a light pink solution of slightly impure $NaHFe(CO)_4$. R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.*, **37,** 1542 (1972). (b) T. Mitsudo, Y. Watanabe, M. Yamashite, and Y. Takegami, *Chem. Lett.*, 11, 1385 (1974). We and Takegami have shown that addition to α,β-unsaturated carbonyl compounds are greatly inhibited by CO. The slow step in these reactions is presumably CO dissociation, $NaHFe(CO)_4 \rightleftharpoons CO + NaHFe(CO)_3$. We have demonstrated rapid ^{13}CO exchange with $NaHFe(CO)_4$.

(19) For a CO dissociative pathway with most of the iron present as $NaHFe_2(CO)_8$, one expects a rate law $\propto [NaHFe_2(CO)_8]^{1/2}$ [olefin] or $[NaHFe_2(CO)_8]$ $[\text{olefin}]^0$ while a second-order rate law was observed under all conditions. The lack of ^{13}CO exchange with $NaHFe_2(CO)_8$ on the time scale of reduction of faster substrates (e.g., dimethyl maleate) and the CO independence of the reductions are also inconsistent with a CO dissociative pathway.

(20) The empty, low-energy, antibonding, intermetallic orbital in binuclear cluster compounds may be important in this association. R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97,** 6042 (1975), and references contained therein.

(21) If protonation occurred prior to k_3, the rate would depend on the [HOAc], but the overall rate is independent of [HOAc].

(22) We have studied kinetically using NMR the rapid reaction of $[(Ph_3P)_2N]^+[CH_3CH(Fe(CO)_4)CO_2Et]^-$ and HOAc in THF Dimerization of $Fe(CO)_4$ (derived from photolysis of $Fe(CO)_5$ in a nitrogen matrix) has been reported. (M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 2276 (1974).) If $NaHFe_2(CO)_8$ is treated with strong acid, H_2, $NaHFe_3(CO)_{11}$, and $Fe(CO)_5$ are observed, suggesting the following reactions have occurred:

$$NaHFe_2(CO)_8 + HX \rightarrow Fe_2(CO)_8 + H_2 + NaX$$

$$Fe_2(CO)_8 + NaHFe_2(CO)_8 \rightarrow NaHFe_3(CO)_{11} + Fe(CO)_5$$

(23) During the submission of this communication, Shapley,[24] in a study of the reactions of $H_2Os_3(CO)_{10}$, has independently obtained evidence which supports some steps of this mechanism. Specifically, he found the addition of $H_2Os_3(CO)_{10}$ to ethyl acrylate is regiospecific, yielding the hydrido alkyl intermediate $HOs_3(CO)_{10}(CH(CH_3)CO_2Et)$. His data also indicate reversibility in the migratory insertion step, and suggest the reverse of the insertion step competes favorably with intramolecular reductive-elimination from the hydridoalkyl intermediate yielding alkane (e.g., $CH_3CH_2CO_2Et$) and the highly unsaturated $Os_3(CO)_{10}$.

(24) J. B. Keister and J. R. Shapely, *J. Am. Chem. Soc.*, **98,** 1056 (1976).

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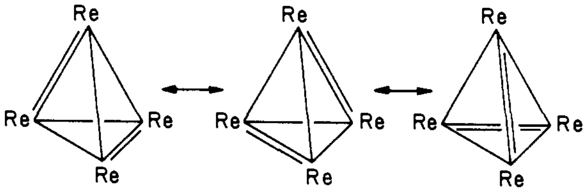
The Molecular Structure of $H_4Re_4(CO)_{12}$. Evidence for Face-Bridging Hydrogen Atoms

Sir:

$H_4Re_4(CO)_{12}$[1] is unusual among metal cluster compounds in that it is one of the few non-EAN, or "unsaturated",[2] carbonyl clusters known to exist. To account for the unsaturation and for the high symmetry[3] of the compound, resonating multiple-bonded structures (I) were proposed.[1] The high symmetry of the molecule also suggested triply bridging (face-bridging) positions for the hydrogen atoms.



(I)

In earlier papers we and others have shown how bridging hydrogen positions can be inferred from distortions in metal-metal distances.[4-6] In this communication we show that in certain instances the orientation of carbonyl groups can constitute a powerful indication of hydrogen positions in a metal cluster. We also introduce in this work a Fourier-averaging method that can be used to derive average hydrogen positions in molecules of high symmetry.

$H_4Re_4(CO)_{12}$ was prepared by pyrolyzing $H_3Re_3(CO)_{12}$ in refluxing *n*-octane for 2 h.[1] Recrystallization from CH_2Cl_2 afforded small dark red crystals having the following unit cell parameters: space group $P2_1/c$ (monoclinic); $a = 14.449$ (3), $b = 10.103$ (2), $c = 13.860$ (3) Å; $\beta = 110.66$ (1)°; $V = 1893.1$ Å^3; $Z = 4$. One quadrant of data was collected on an automated Nonius CAD-3 diffractometer with Mo Kα radiation up to a 2θ maximum of 45°.[7] The structure was solved by heavy atom methods. All non-hydrogen atoms were located and re-