(8) The reason for the coincidental chemical shift of C-29 ^1H NMR peaks in the two fucosteryl acetate epoxides and the two isofucosteryl acetate epoxides is not clear.

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S.-M. L. Chen, K. Nakanishi*
Department of Chemistry, Columbia University
New York, New York 10027

N. Awata, M. Morisaki, N. Ikekawa
Laboratory of Chemistry for Natural Products
Tokyo Institute of Technology
Meguro-ku, Tokyo, Japan

Y. Shimizu
Department of Pharmacognosy, University of Rhode Island
Kingston, Rhode Island 02881

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Metal Clusters in Catalysis. II. An Electron Spin Resonance Study of Dinuclear Metal Complex Fragments and Their Interaction with Organic Substrates

Sir:

Metal clusters are attractive catalytic species especially for template syntheses as illustrated[1] for $Ni_4[CNC(CH_3)_3]_7$. In addition, the weakest bonds in clusters may often prove to be the framework cluster bonds;[2] hence there is the further potential in cluster complexes of reversibly generating reactive fragments. In this context, the simplest, most readily available class comprises dinuclear metal complexes. Herein we describe for a group of readily dissociable iron complexes, $[(allyl)Fe(CO)_2L]_2$, catalytic chemistry and an ESR study that provides, (1) an accurate measure of Fe–Fe bond energies, (2) a kinetic, thermodynamic, and electronic view of the interaction of $(allyl)Fe(CO)_3$ with unsaturated organic substrates, and (3) a demonstration that two mononuclear isomers are usually present in each system and that these are highly fluxional.

The binuclear $[C_3H_5Fe(CO)_3]_2$ complex, A, dissociates in solution to give a paramagnetic species. Equilibria, presumed to be complex,[3a] are now shown to be singular. Analysis of ESR signal integral intensities over a temperature range of +40 to −90° establish that the solution state of A is fully[4] represented by dissociation 1.

$$\underset{\mathbf{A}}{[C_3H_5Fe(CO)_3]_2} \rightleftharpoons \underset{\mathbf{B}}{2C_3H_5Fe(CO)_3} \qquad (1)$$

No gas phase equilibria data are available but mass spectral studies show dimer to be present. Solvent effects upon equilibrium 1 were small and most significant with toluene (see Table I). The most informative solvent interaction, vis a vis catalytic reactions, is with hexenes. When A was dissolved in cold 1-hexene, the equilibrium was similar to that of A in toluene. However, a reaction of the complex, probably B, with 1-hexene occurred with *no* CO loss and an activation energy of ~10 kcal/mol[5,6] to give η^1-$C_3H_5Fe(CO)_3$(1-hexene) which in dimeric form exhibits a substantially reduced Fe–Fe bond energy. This type of olefin complex must be an important intermediate[7a] in the catalytic chemistry of A. We found that A rapidly[7b] isomerized 1-hexene to *trans*-2-hexene at 25°, initiated vinyl polymerization, e.g., ethyl vinyl ether and styrene, and rapidly polymerized allene at 22° to a solid $\text{-(-C(=CH}_2\text{)CH}_2\text{-)}_x\text{-}$ polymer. In the isomerization itinerary that follows olefin adduct formation, conventional isomerization pathways of hydride insertion-elimination[7c] or olefin adduct → η^3-allylmetal hydride → internal olefin adduct formation cannot be followed precisely. A possible intermediate is (η^1-allyl)(η^1-alkylallyl)-$FeH(CO)_3$.[7d] Interestingly, there was no extensive hydride insertion into the C_3H_5 group because the original complex A was recovered unchanged from isomerization reactions.[3b] For the analogous reaction system of A with 2-hexene, rate of adduct formation was lower than with 1-hexene.[7e] Entropy data (Table I) and the relatively large activation energy for solvation suggest that hexene loss does not occur in the dimerization of the olefin adducts, σ-$C_3H_5Fe(CO)_3$(hexene).[8]

In $C_3H_5Fe(CO)_2L$ derivatives, the iron–iron bond energy for the dimeric form is close to that of A while the entropy loss on dimerization is invariably larger than for the sterically less encumbered parent. Steric factors are evident also in the bond energy data for the phosphine series (Table I, enthalpies may be read as iron–iron bond energies). Nonetheless, barring extreme ligand bulkiness, there was a small perturbation of the iron–iron bond energy as ligands were varied in the phosphine and phosphite series; electronic ligand effects seem to be well buffered by the remaining allyl and carbonyl ligands which have donor–acceptor bonding

Table I. Thermodynamic Data for Dimer–Monomer Equilibria (1) in $C_3H_5Fe(CO)_2L{\cdot}S$ and ESR Parameters for Monomer

L[a]	Medium[a]	ΔH[b]	ΔS[c]	$(g_0 - 2)$[d]	$(g_\parallel - 2)$[e]	$(g_\perp - 2)$[e]	a_H[f] (a_P)[f]
CO	crys			0.0446	0.0068	0.0667 (0.0232)	
CO	nuj			0.0455	0.0055	0.0668	
CO	pe	13.5	37	0.0467			
CO	thf	13	41	0.0455			5.7
CO	mthf	12.5	39	0.0458	0.0051 (0.0756)	0.0646 (0.0257)	6.0
CO	tol	11	30	0.0459	0.0055	0.0668 (0.0239)	6.0
CO	1-hex	12	32	0.0449			~5.6
(CO)(1-hex)	1-hex	9	41	0.0448	0.0159 (0.0229)	0.0568 (0.0635)	5.4
(CO)(2-hex)	2-hex	13	61.5	0.0447	0.0056	0.0624	5.4
CO·(2-but)	2-but	11.5	31	0.0449	−0.0158	0.0755 (0.0242)	
$P(CH_3)_3$	tol	12	39	0.0449			6.0 (11.2)
$P(CH_3)_2C_6H_5$	tol	13	42	0.0478			6.0
$P(CH_3)_2C_6H_5$	pe	13.5	46	0.0473			6.0
$PCH_3(C_6H_5)_2$	tol	10	40	0.0482			7.4 (7.2)
$P(C_6H_5)_3$	tol	No dimerization		0.0504	−0.0046	0.0775 (0.0251)	5.7,[g] (16.7)[g]
$P(C_2H_5)_3$	tol	10.5	44	0.0463			5.7 (11.4)
$P(OCH_3)_3$	pe	14	46.5	0.0462			7.6 (7.7)

[a] Key: crys, monomer defects in dimeric crystals; pe, pentane; nuj, nujol; thf, tetrahydrofuran; mthf, 2-methyltetrahydrofuran; tol, toluene; 2-but, 2-butyne; 1-hex, 1-hexene; 2-hex, 2-hexene. [b] In kcal/mol, precision ~7%. [c] In eu, precision ~10%. [d] At 25°C, ±0.0005. [e] At −160°C, ±0.0010, less intense (isomer) signal in brackets. [f] Absolute value of isotropic hyperfine coupling constant × 10^4 cm.$^{-1}$, ±<0.2. [g] $A_{H(\parallel)} = 5.3$, $A_{P(\parallel)} = 43$, $A_{P(\perp)} = 51$ for more abundant isomer, $A_{H(\parallel)} = 6.2$ for the other isomer.

duality. A more extensive series should provide an incisive picture of how to sterically and perhaps electronically promote fragmentation in this prototype cluster class.

For all monomers to be 17-electron[9] complexes, an η^1-allyliron interaction should be present only in $C_3H_5Fe(CO)_3$(hexene) and probably the butyne analog[6] although there is a possible continuum of idealized forms that range from symmetrical η^3-allyl to η^1-allyl. ESR spectra for most complexes (solution state) exhibited the same triplet hyperfine structure, arising from two magnetically equivalent hydrogen atoms, presumably the anti[10] set in η^3-allyl and the aliphatic set in η^1-allyl forms,[11] in addition to a phosphorus doublet in phosphine and phosphite derivatives. The spin-orbit contribution to the isotropic g values (Table I), which to a first approximation reflects the ligand field strength around iron, varies only slightly (~10% maximum) with ligand variation which invariance mirrors the *relative* constancy of the iron-iron bond energies.

Relatively large variations in g_0 with temperature were observed, e.g., g_0 for B varied from 2.0459 to 2.0423 in the +25 to −94° range. This effect could be due to an equilibrium between isomers (vide infra) or specific outer sphere solvation[12] but the crucial point here is that the effects have no significant influence on the monomer-dimer equilibrium since there were no deviations from linearity in the ln K vs. $1/T$ plot over 90-130° ranges.

Definitive evidence for the presence of isomers in mononuclear complexes in frozen solutions (glasses) was obtained. In many cases, the ESR spectra of glasses comprised the superposition of signals from two different species with different sets of $g_{\parallel}$ and $g_{\perp}$ (see Table I). Whenever an accurate interpretation of these spectra was possible,[13] the more intense signal had $g_{\parallel} < g_{\perp}$. For complexes with the hexenes, the less intense signal was also characterized by $g_{\parallel} < g_{\perp}$, but for the remaining compounds the order was $g_{\parallel} > g_{\perp}$. In frozen solutions of A in 2-butyne, the two species interconverted rapidly on the ESR time scale at −90° *in the solid state* as seen from the collapse of the overlapping anisotropic spectra to a single isotropic line which was the same as in liquid solutions. A similar phenomenon was observed for B at defects in the crystals of A, where the collapse of the anistropic spectrum to the isotropic line occurred above −30°. Such interconversion processes in the solid state show that the two species observed at low temperature are two isomers of the same composition. For $C_3H_5Fe(CO)_2P(C_6H_5)_3$ in toluene glass, both isomers exhibited triplet hyperfine structure from two equivalent protons but with different values of A_H.

We defer discussion of the nature of the isomers and their unusual fluxional characteristics until X-ray crystal structure determinations for dimeric and monomeric forms and theoretical calculations[14] have been completed. Substituted allyl analogs are being synthesized so that ESR characterization of η^3- and η^1-allyl interactions may be definitive and the catalytic chemistry of the monomeric paramagnetic species is under investigation with respect to scope and mechanism.

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(3) (a) H. D. Murdock and E. A. C. Lucken, *Helv. Chim. Acta*, **47**, 1517 (1964). (b) $[C_3H_5Fe(CO)_3]_2$ appears quite stable in crystalline form at 25° but it does slowly decompose at 25° in pentane solvent.

(4) Concentration range was from 0.0003 to 0.1 *M* for total iron; concentration of monomer varied with temperature about three orders of magnitude for a specific total iron concentration.

(5) ESR spectra recorded during this reaction at −10° exhibited an isosbestic point. Accurate kinetic parameters for a variety of olefins are now being determined.

(6) 2-Butyne interaction is very fast compared to hexene adduct formation.

(7) (a) In the formation of this species in our catalytic system, a critical feature is presumed to be the $\eta^3 \rightleftharpoons \eta^1$ allyl interconversion. (b) Conversion to 2-hexene was about 60% after 1 hr. After 48 hr no 1-hexene could be detected by NMR techniques. No solvent was used in these reactions. (c) 1-Hexene isomerization also occurs in the H_2–A system where $C_3H_5FeH(CO)_3$ is probably present but the rate is lower than in the absence of hydrogen. (d) A possible mode of isomerization is $\eta^1\text{-}C_3H_5Fe(CO)_3(1\text{-hexene}) \rightleftharpoons \eta^1\text{-}C_3H_5FeH'(\eta^1\text{-}CH_2CH{=}CHCH_2CH_2CH_3)(CO)_3 \rightleftharpoons \eta^1\text{-}C_3H_5Fe(CH_2H'CH{=}CHCH_2CH_2CH_3)(CO)_3 \rightleftharpoons \eta^3\text{-}C_3H_5Fe(CO)_3$ + 2-hexene. Labeled experiments are in progress to test such hypotheses. (e) With *trans*-3-hexene and A, no isomerization was detected after 2 days.

(8) Monomer–dimer interconversion is fast relative to adduct formation.

(9) In a formal accounting.

(10) Most structure determinations show these protons to be much closer to the metal than the others.

(11) (a) Rotation about the M–C bond is presumed to be fast in η^1-allyl iron. (b) The isotropic hyperfine coupling constants (Table I) are similar for both structures. The variation in a_H of ~30% as ligands were varied corresponds to an electron spin density change from 1.1 to 1.6%.

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(14) R. Hoffmann. We acknowledge helpful discussions with R. H.

E. L. Muetterties,* B. A. Sosinsky
Spencer T. Olin Chemistry Laboratory, Cornell University
Ithaca, New York 14853

K. I. Zamaraev*
The Institute of the Chemical Physics
of the Academy of Sciences of the U.S.S.R.
2B Vorobjovskoe Shausse
Moscow, B-334, 117334, U.S.S.R.

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Species with Strong Heteronuclear Metal–Metal Bonds. Dimers with Tungsten–Molybdenum Bonds of Order 3.5 and 4.0

Sir:

Heteronuclear metal-metal bonded species containing only two metal atoms are of great importance since they constitute the simplest systems in which the effects of substituting one metal atom for another can be studied in detail. Heteronuclear species with metal-metal bond order greater than unity should be especially interesting, but seldom have they been realized. A few years ago in this laboratory the heteronuclear carboxylate dimers $MoW(O_2CR)_4$ were prepared as constituents of mixtures containing the homonuclear molybdenum dimers $Mo_2(O_2CR)_4$.[1] Until recently the separation of such mixtures was unsuccessful.

In more recent work[2] it has been shown that selective iodination of a benzene solution of $Mo_2(O_2CC(CH_3)_3)_4$–$MoW(O_2CC(CH_3)_3)_4$ mixtures effected the desired separation by precipitation of $[MoW(O_2CC(CH_3)_3)_4]I$, essentially free of any corresponding dimolybdenum product. Infrared spectra and magnetic susceptibility data led to the conclusion that the precipitated iodide contained the one-electron oxidized cation $[MoW(O_2CC(CH_3)_3)_4]^+$. It was presumed that the structure and metal-metal bonding in this cation were entirely analogous with that in the compounds $[Mo_2(O_2CC(CH_3)_3)_4]^+I_3^-$ [2] and $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$.[3] We now report the preparation[4] and molecular structure of $[MoW(O_2CC(CH_3)_3)_4]I \cdot CH_3CN$, and its reduction to $MoW(O_2CC(CH_3)_3)_4$, the first pure heteronuclear species containing a quadruple metal-metal bond.[5]

Surprisingly, solutions of $[MoW(O_2CC(CH_3)_3)_4]I$ in ac-