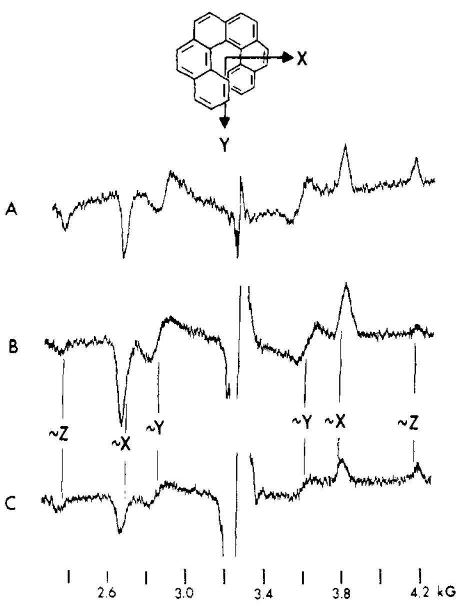


Figure 1. EPR spectra ($d\chi/dB$ vs. B) of triplet hexahelicene in isotropic rigid medium (A) and stretched film with stretch direction parallel to static field (B) and perpendicular to the field (C). All spectra were recorded at 77 K.

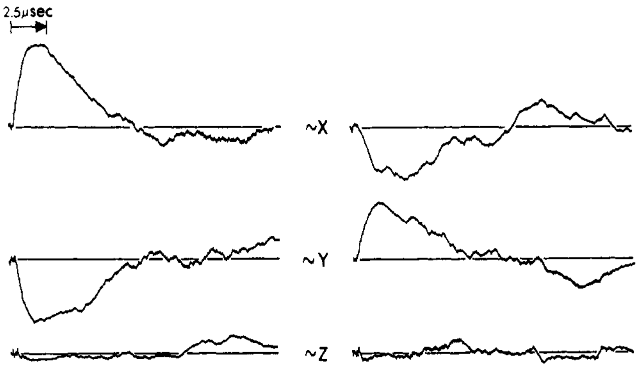


Figure 2. Transient magnetization of hexahelicene triplet in toluene glass at 77 K following excitation by pulsed nitrogen laser (337 nm, 6-ns duration). Signals above the base line are absorptive, below emissive. Each trace is the average of 200 transients, 100 on resonance minus 100 off resonance.

sorptive (Figure 2), In the stretched film with the stretch direction parallel to the field, X peaks are enhanced over Y peaks; i.e., molecules are aligned with X axes parallel to the stretch direction. To determine which directions in hexahelicene correspond to our labels we rely on the assignments of Weigang[2] in which the fluorescence is polarized with electric vector perpendicular to the helix axis and to the twofold rotation axis. The fluorescence from the stretched film is polarized with electric vector parallel to the stretch direction. Our X and Y labels are then attached to the molecular axes as in Figure 1, the Y axis being the twofold rotation axis. The zero-field Hamiltonian for triplet hexahelicene $H = DS_Z{}^2 + E(S_X{}^2 - S_Y{}^2)$ has

$$D/hC = 0.088 \pm 0.001 \text{ cm}^{-1}$$

$$E/hC = -0.006 \pm 0.001 \text{ cm}^{-1}$$

The zero-field state $|T_Y\rangle$, i.e., the eigenstate of S_Y with eigenvalue zero is predominantly excited following photoexcitation at 337 nm. Our data do not exclude excitation into $|T_Z\rangle$ with $P_Z/P_Y = (0.4 \pm 0.2)$ where P_Z and P_Y are relative probabilities of excitation of $|T_Z\rangle$ and $|T_Y\rangle$. In heptahelicene, surprisingly, the $|T_X\rangle$ and $|T_Y\rangle$ states are almost energetically degenerate. $D/hC = \pm 0.084 \pm 0.002$ cm^{-1}, $E/hC = \pm 0.002 \pm 0.001$ cm^{-1}, but that the degeneracy is accidental, different from the degeneracy imposed by symmetry as in coronene, is demonstrated by the transient experiment. No observable transients at the X–Y positions are observed, owing to the superposition of the emissive and absorptive signals. Unfortunately, we were unable to incorporate heptahelicene into films which would have permitted selective orientation.

In summary, observation of the transient magnetization in triplet hexahelicene demonstrates that the predominant path of intersystem crossing leads to population of the $|T_Y\rangle$ state, and that a small rate of population of $|T_Z\rangle$ is not excluded.

Acknowledgments. This work has been supported by the National Science Foundation. We are grateful to Professor Melvin Newman for our supply of hexahelicene and to Professor R. H. Martin for heptahelicene. We are especially indebted to Professor John Scandrett for indispensable help in making the signal averaging work.

References and Notes

(1) M. Sapir and E. Van der Donckt, *Chem. Phys. Lett.*, **36**, 108 (1975).
(2) O. E. Wergang, J. A. Turner, and P. A. Trouard, *J. Chem. Phys.*, **45**, 1126 (1966).
(3) M. A. El Sayed, W. R. Moomauw, and J. B. Chodak, *Chem. Phys. Lett.*, **20**, 11 (1973).
(4) K. Ohno, N. Nishi, M. Kihoshita, and H. Inokuchi, *Chem. Phys. Lett*, **33**, 293 (1975).
(5) S. S. Kim and S. I. Weissman, *J. Mag. Reson.*, **24**, 167 (1976).
(6) We have prepared solid solutions of hexahelicene in triptycene, but they undergo such efficient photodecomposition of the hexahelicene that they are useless for our purposes. The only product which we have identified is an abundant supply of hydrogen atoms.
(7) J. J. Dekkers, G. P. Hoornweg, C. Maclean, and N. H. Velthorst, *Chem. Phys. Lett.*, **19**, 517 (1973).

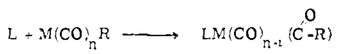
S. S. Kim, S. I. Weissman*
Department of Chemistry, Washington University
St. Louis, Missouri 63130

Received May 10, 1979

Kinetic and Thermodynamic Control of the Methyl Migration (CO Insertion) Reaction by Strong Lewis Acids

Sir:

The activation of metal-coordinated carbon monoxide and in particular the alkyl migration reaction is a subject of considerable fundamental and technological importance.[1-3] As shown in eq 1, this reaction involves the migration of the alkyl



$$\text{L} + \text{M(CO)}_n\text{R} \longrightarrow \text{LM(CO)}_{n-1}(\overset{\text{O}}{\text{C}}\text{-R}) \qquad (1)$$

group onto one of the coordinated carbonyls accompanied by the addition of a ligand to an alkyl metal carbonyl forming a metal-acyl complex. For the special case of an anionic metal carbonyl, alkyl migration is accelerated by small alkali metal ions, which ion pair with the metal carbonyl.[4] As with reaction 1, an incoming ligand is still required for this cation assisted reaction. In the course of studying the potentially more general molecular Lewis acid assistance of alkyl migration (a reaction which would not be confined to anionic alkyl metal carbonyls), we were surprised to find a very fast methyl migration reaction in the absence of added CO. The mechanism of formation, structure, and reactivity of these novel methyl migration products are discussed below.

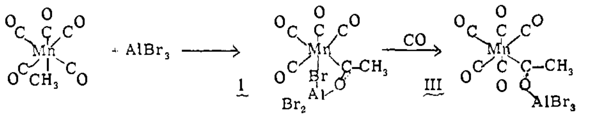
The addition of $AlBr_3$ to $Mn(CO)_5(CH_3)$ or $(\eta^5\text{-}C_5H_5)\text{-}Mo(CO)_3(CH_3)$ in toluene solution leads to a rapid color change in each case and the appearance of new low-frequency acyl infrared bands, small shifts in terminal CO stretching frequencies, and a downfield shift in the methyl ^{1}H NMR resonance. These features are known from recent work in our laboratory to be characteristic of Lewis acid coordinated metal

Table I. IR and ^{1}H NMR Data for Metal Alkyl and Acyl Compounds

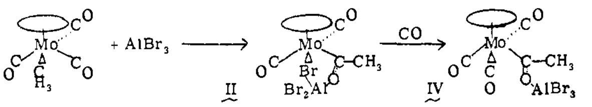
comp	ν(CO), cm^{-1}	ν(COCH$_3$), cm^{-1}	δ(CH$_3$)^a	δ(C$_5$H$_5$)^a
$CH_3Mn(CO)_5$^{b}	2111, (vw), 2009 (s), 1989 (w)		−0.21	
I^b	2106 (w), 2024 (s), 1976 (m)	1450 (w), 1381 (w)	2.33	
III^c	2141 (w), 2085 (w), 2047 (s)	1483 (m)	3.35	
$(CO)_5Mn(COCH_3)$^{b}	2118 (w), 2052 (w), 2014 (s)	1648 (m)	2.64	
$CpMo(CO)_3CH_3$^{b}	2019 (s), 1930 (vs)		0.34	4.53
II^b	2004 (s), 1915 (s)	1363 (m)	2.27	4.56
IV^b	2052 (s), 1986 (sh), 1963 (vs)	1457 (m)	2.81	4.70
$CpMo(CO)_3(COCH)_3$^{b}	2017 (s), 1940 (sh), 1923 (vs)	1661 (m)	2.44	4.68

^{a} Chemical shifts are given in parts per million downfield from Me_4Si. ^{b} Toluene and toluene-d_8 solutions. ^{c} CH_2Cl_2 and CD_2Cl_2 solutions.

acetyls.[5] Table I presents the IR and NMR data, and the reactions are summarized in eq 2 and 3.



(2)

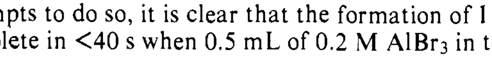


(3)

Compound I was isolated from toluene solution under an inert atmosphere as stable orange crystals. A single-crystal X-ray study of I at room temperature shows it to crystallize in a monoclinic cell $P2_1/c$; $a = 6.835$ (2), $b = 16.374$ (6), $c = 12.278$ (4) Å; $\beta = 94.18$ (2)°. Diffractometer data, corrected for Lorentz, polarization, and absorption effects, were used for solution of the structure. Refinement by full-matrix least-squares methods has progressed to conventional $R = 7\%$ using anisotropic thermal parameters.

The X-ray data demonstrate the existence of a five-membered ring, $\overline{\text{Mn–C–O–Al–Br}}$ (see Figure 1). The ring shows a 0.21-Å standard deviation from planarity. Coordination about manganese is only slightly distorted from octahedral symmetry (L–M–L angles range from 87.5 (6) to 92.4 (6)°). The Mn–Br distance is 2.579 (9) Å which is similar to the Mn–Br distance, 2.526 (5) Å, in $[BrMn(CO)_4]_2$.[6] The C–O distance in the ring, 1.304 (22) Å, indicates a bond order between 1 and 2 (cf. C–O distances of 1.24 (3) Å for $CH_3C(=O)CH_3$[7] and 1.43 Å for $CH_3CH_2OCH_2CH_3$[7]). As with $[BrMn(CO)_4]_2$ the Mn–C bond trans to Mn–Br is shorter, 1.79 (2) Å, than Mn–C bonds trans to other species, 1.86 (2) to 1.87 (2) Å. Other ring distances follow: Mn–C, 1.95 (3); O–Al, 1.81 (1); Al–Br, 2.31 (2) Å. A structure similar to that shown in Figure 1 has been proposed for $(OC)_4\overline{MnC(CH_3)OBBr}Br_2$, which was prepared by the action of BBr_3 on $MnBr(CO)_4C(CH_3)OH$.[8]

As summarized by Calderazzo, the mechanism for alkyl migration in $Mn(CO)_5(CH_3)$ involves the initial formation of a transient coordinatively unsaturated intermediate (eq 4),



(4)

which rapidly adds ligand.[3] The steady-state concentration of this intermediate is very low, and the evidence for its existence rests on kinetic analysis. The question arises as to whether the role of the Lewis acid in reactions 2 and 3 is simply one of stabilizing an otherwise unstable acetyl intermediate, or whether the acid also increases the rate of the primary alkyl migration step. The Lewis acid induced reaction is so fast that we have been unable as yet to measure its rate; however, from attempts to do so, it is clear that the formation of I is >90% complete in <40 s when 0.5 mL of 0.2 M $AlBr_3$ in toluene is mixed with 0.5 mL of 0.2 M $Mn(CO)_5(CH_3)$ in toluene at room temperature. From Calderazzo's value of k_1 in eq 4, we estimate that, if the Lewis acid were merely capturing the intermediate as it is formed, a time of ~2 × 10^3 s would be required for 90% conversion. It is clear from this comparison that the Lewis acid enters into the alkyl migration reaction at an early stage and increases the rate of the primary methyl migration step. In a theoretical discussion of methyl migration in $CH_3Mn(CO)_5$, Berke and Hoffmann[9] considered the influence of attached H^+ or Li^+ to model the observed counterion effect which was mentioned above.[4] Even though the calculated effects were small, they did find a stabilization of one orbital which they believe is crucial to the migration step. We suppose that in reactions 2 and 3 initial complex formation with a terminal carbonyl occurs (M–CO–$AlBr_3$), which greatly accelerates the methyl migration along the lines described by Berke and Hoffmann. This presumed interaction with the terminal CO has not been detected spectroscopically, but precedent for such interaction exists in more basic metal carbonyls.[10]

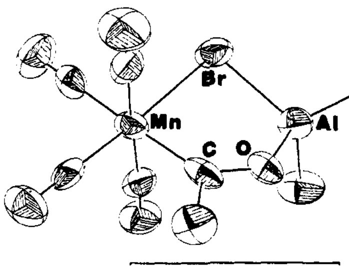


Figure 1. The structure of $\overline{Mn(CO)_4(C(CH_3)OAlBr}Br_2)$.

The above compounds, I and II, react smoothly with CO (eq 2 and 3). The products III and IV were identified spectroscopically (see Table I) and by hydrolysis to remove $AlBr_3$ and produce the corresponding simple metal acyl complexes. Adduct III also was characterized by elemental analysis and was independently prepared from $AlBr_3$ plus $Mn(CO)_5[C(CH_3)O]$.

Adduct IV, which was isolated as a thermally stable yellow powder, is particularly interesting because the parent acetyl $(\eta^5\text{-}C_5H_5)Mo(CO)_3[C(CH_3)O]$ is unstable with respect to CO loss.[11] Furthermore, recent work indicates that this acetyl is difficult or impossible to produce by high pressure CO insertion on $(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)$.[12] By contrast, the reaction of CO at 1 atm with equimolar $(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)$ and $AlBr_3$ in a chilled toluene solution produces IV in high yield and in a form which can be stored for an extended period in the absence of moisture. This example demonstrates that Lewis acids may stabilize otherwise unstable metal acyls.

The kinetics of CO uptake for the second step in reaction 2 were followed for a toluene solution at 20 °C. The resulting rate law (eq 5) can be accommodated by an associative S_N2-type mechanism or a prior Mn–Br dissociation step to produce a coordinatively unsaturated intermediate followed by CO addition.

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = k_2[\mathrm{I}]P_{\mathrm{CO}} \quad k_2 = 2.7 \times 10^{-8}\ \mathrm{s}^{-1}\ \mathrm{mm}^{-1} \quad (5)$$

The present results demonstrate that the Lewis acid $AlBr_3$ may be employed in the alkyl migration reaction to stabilize unusual products and to greatly accelerate the migration step. Similar results are obtained with a variety of Lewis acids and with protic acids; details will be presented later. The structural and mechanistic information obtained here may apply to more complex reactions such as the generation of methane[13] or cyclic ketones[14] in the presence of metal complexes, Lewis acids, and CO.

Acknowledgment. This research was supported by the National Science Foundation through Grant CHE 77018747.

References and Notes

(1) J. Tsuji, "Organic Synthesis by Means of Transition Metal Complexes", Springer-Verlag, Berlin, 1975.
(2) A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87 (1973), and references therein.
(3) F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, **16**, 299 (1977).
(4) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 4766 (1978).
(5) R. E. Stimson and D. F. Shriver, *Inorg. Chem.*, in press.
(6) L. F. Dahl and C. H. Wei, *Acta Crystallogr.*, **16**, 611 (1963).
(7) L. E. Sutton et al., "Tables of Interatomic Distances and Configuration in Molecules and Ions", Special Publ. No. 11, The Chemical Society, London, Burlington House, London, 1958.
(8) E. O. Fischer, *Adv. Organomet. Chem.* **14**, 1–32 (1976).
(9) H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 7224 (1978).
(10) D. F. Shriver, *J. Organomet. Chem.*, **94**, 259 (1975).
(11) K. W. Barnett and D. W. Slocum, *J. Organomet. Chem.*, **44**, 1 (1972); K. W. Barnett, Ph.D. Thesis, University of Wisconsin, 1967.
(12) R. B. King, A. D. King, Jr., M. Z. Iqbal, and C. C. Frazier, *J. Am. Chem. Soc.*, **100**, 1687 (1978).
(13) E. L. Muetterties, and G. C. Demitras, *J. Am. Chem. Soc.*, **99**, 2796 (1977).
(14) B. F. G. Johnson, J. Lewis, D. J. Thompson, and B. Heil, *J. Chem. Soc., Dalton Trans.* 567 (1975).
(15) (a) Northwestern University; (b) The University of Georgia; (c) University of Worwick.

Susan Beda Butts,[15a] Elizabeth M. Holt*[15b]
Steven H. Strauss,[15a] Nathaniel W. Alcock[15c]
Rebecca E. Stimson,[15a] Duward F. Shriver*[15a]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201, Department of Biochemistry
The University of Georgia, Athens, Georgia 30602, and the
Department of Molecular Sciences, University of Worwick
Coventry CV4 7AL, England
Received February 20, 1979

---

*Book Reviews**

CRC Handbook of Chemistry and Physics. 59th Edition. Edited by R. C. Weast. CRC Press, Inc., Cleveland, Ohio. 1978. 2512 pp. $44.95.

The last review in this Journal of this well-known work was of the 52nd edition, and appeared in Vol. 93, p 7122 (1971). In the intervening seven years, the number of pages has increased by nearly 200. This book is composed of separately paginated sections, to enable certain sections to be revised without disturbing others, which may continue unchanged through a number of editions. Revisions in this edition are found in the section on the chemical elements, the table of bond strengths, the table of radiation emissivity, etc. Additions include an extensive table of line spectra of the elements, a table of lattice energies, and a supplementary table of key values for thermodynamics. Some mathematical tables have been dropped, because simple calculators have supplemented them.

The most obvious shortcoming in this volume is the table of conversion factors, which has remained unrevised for so long that it does not include the SI units, such as pascal, hertz, becquerel, etc. This discrepancy should have been attended to long ago.

The CRC Handbook continues to be one of the greatest bargains in science for sheer quantity of useful information.

The Tropospheric Transport of Pollutants and Other Substances to the Oceans. Edited by NRC Workshop Staff Steering Committee (J. M. Prospero, Chairman). National Research Council, Washington, D.C. 1978. xi + 243 pp. $11.75.

This softbound volume was prepared by an international group of scientists who met in December 1975. The subject matter is divided into transport and removal processes, and data on specific pollutants and trace substances, such as metals, hydrocarbons, radionuclides, etc. There is thus much of concern to chemists in this book. There is included a chapter on Summary and Principal Conclusions and Recommendations, in which it is stated that available data are insufficient to assess possible impacts of the phenomenon, and a major research effort is required.

Natural Zeolites: Occurrence, Properties, Use. Edited by L. B. Sand and F. A. Mumpton. Pergamon Press, New York. 1978. xi + 546 pp. $75.00.

An international conference on the title subject was held in Arizona in 1976. The motivation for such a conference is suggested by a statement in the Introduction: "In less than 20 years' time, the status of the zeolite group of minerals changed from that of a museum curiosity to an important industrial commodity." This volume consists of 45 papers given at the conference; some are reviews, and others appear to be reports of original research. Eight of the papers fall into the category "physical and chemical properties", and a number of other papers on applied aspects are chemical in nature. The book is unusually well illustrated and has a subject index.

Dictionary of Scientific and Technical Terms. Second Edition. Edited by D. N. Lapedes. McGraw-Hill Book Co., New York. 1978. xv + 1771 + 58 pp. $39.50.

The first edition of this dictionary appeared in 1974 to supplement the general dictionaries in existence, in which technical terms are inadequately represented. Many new terms have had to be added.

Because of the broad scope, terms peculiar to chemistry are in the minority, but those that do appear are defined with professional competence. The criteria for listing a term are not readily apparent, however, for one finds "carbene" but not "nitrene", "nitronium" but not "nitrylium", etc., and many important chemical terms, such as "nitrosamine", "molecular sieve", "ambident", etc., are omitted, whereas "car" and "automobile" are given places. "Vigreux column" is misspelled with a superfluous "a", and is misleadingly defined as a term belonging to analytical chemistry, and defined as "An obsolete apparatus . . .". The publishers should include an organic chemist on the editorial team for any future edition.

The book is very well produced, and has many illustrations in the margins. It appears to be a generally reliable reference, and is excellent value for the price in today's market of expensive books.

Thin-Layer Chromatography. 2nd Edition. By J. G. Kirchner. Edited by E. S. Perry. Wiley/Interscience, New York. 1978. xix + 1137 pp. $60.00.

This is Volume XIV in the series "Techniques of Chemistry" under the general editorship of Arnold Weissberger. Some chapters have been completely revised, and all have been brought up to date with references through 1975, and in some cases up to 1977. Detection reagents are given expanded treatment, in recognition of their increased importance. The general outline of the first edition is main-

---

* Unsigned book reviews are by the Book Review Editor.