Table I. Enthalpies (25°, kcal/mol)

Adduct	ΔH_{exptl}	ΔH_{soln}	ΔH_{v}	$\Delta H_{\text{r}}°$	$\Delta H_{\text{r}}°_{(\text{g})}$	$\Delta H_{\text{r}}°_{(\text{soln})}$[a]
$(CF_3)_2C(OH)_2$	−24.4 ± 0.2	−3.99 ± 0.04	17.0 ± 0.2	−20.4 ± 0.2	−13.9 ± 0.4	−22.4 ± 1.2
$(CF_3)_2C(OH)OCH_3$	−24.7 ± 0.3	−3.44 ± 0.02	17.4 ± 0.2	−21.3 ± 0.3	−12.8 ± 0.5	−22.7 ± 1.3

[a] Derived from the relation $\Delta H_{\text{r}}° - \Delta H_{\text{r}}°_{(\text{soln})} = \Delta H_{\text{soln}}(\text{HFA}) - \Delta H_{\text{soln}}(\text{adduct})$, assuming $\Delta H_{\text{soln}}(\text{HFA}) = -2 \pm 1$ kcal/mol.

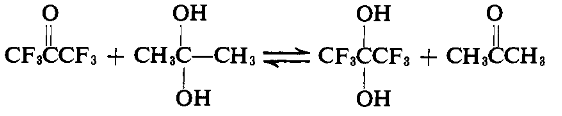
with other carbonyl compounds. In both cases the "standard-state" reaction differs only slightly from the heat of reaction in solution. According to the enthalpy cycle, this latter difference is limited to the difference in the heat of solution of the carbonyl compound and its adduct. The heat of solvation for both reactions, $\Delta H_{\text{r}}°_{(\text{soln})} - \Delta H_{\text{r}}°_{(\text{g})}$, is about −9 kcal/mol. Since it is unlikely that the heat of solvation of the reactants will exceed those of the product, the heat for the solution reaction should represent the maximum or limiting value for this type of reaction. The scarcity of reliable data makes comparison with other gas-phase reactions undesirable; however, comparison can be made with the hydration of similar carbonyl compounds in solution.

Table II. Heats of Hydration of Carbonyl Compounds (kcal/mol)

Compd	$\Delta H_{\text{r}}°_{(\text{soln})}$
$CH_3C(=O)CH_2Cl$	−2.0[a]
$CH_3C(=O)CHCl_2$	−5.5[a]
CH_3CHO	−5.1[a]
CCl_3CHO	−14.0[a]
$CF_3C(=O)CF_3$	−22.4

[a] Reference 1a.

Table II shows that the heat of hydration of HFA is much larger than analogous compounds and also the heat of reaction increases with halogen substitution (*ca.* 3–3.5 kcal/halogen atom). Levy, Cargioli, and Racela have reported that multiple halogen substitution also produces an approximately linear decrease in ketone basicity (*ca.* 2 H_0 units per halogen).[5] The heat of hydration of acetone is too low to have been measured reliably but assigning $\Delta H_{\text{r(soln)}} = -1 \pm 1$ kcal/mol allows the formulation of the following equilibrium



$$CF_3\overset{\overset{\displaystyle O}{\|}}{C}CF_3 + CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{-}CH_3 \rightleftharpoons CF_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}CF_3 + CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

$\Delta H = -21$ kcal/mol

The rather large enthalpy associated with the disproportionation reaction can be analyzed in terms of carbonyl group stabilization. In substituted alkenes it is customary to regard differences in heats of hydrogenation as a measure of the stabilizing effect of the substituent. Similarly the heats of hydrogenation of formaldehyde (−22 kcal/mol) and acetone (−13 kcal/mol)[6] show a 9-kcal stabilizing effect for two methyl groups at a carbon–oxygen double bond. To account for the enthalpy in the equilibrium reaction above, one may then infer that two CF_3 groups destabilize a carbonyl bond by *ca.* 12 kcal. This conclusion is in agreement with the remarkable reactivity of HFA[7] in carbonyl addition reactions.

Another method of assessing strain in a molecule is the comparison of experimental heats of formation with calculated heats of formation by a method of group increments.[8] The heats of formation derived from our experimental data were compared to values calculated from the group increment scheme of Cox and Pilcher.[8b] These values are given in Table III.

Table III. Heats of Formation (25°, kcal/mol)

Compd	State	$\Delta H_{\text{f}}°$ Obsd	$\Delta H_{\text{f}}°$ Calcd	Strain (Obsd − calcd)
$(CF_3)_2C(OH)_2$	(g)	−370.7	−409.13	38.4
	(c)	−387.7		
$(CF_3)_2C(OH)OCH_3$	(g)	−359.9	−405.20	45.3
	(l)	−377.3		
$CF_3C(=O)CF_3$	(g)	−299[a]	−352.8	53.8

[a] Reference 7.

Table III predicts a large amount of strain in HFA which is relieved in the hemiacetal or hydrate by 9 and 15 kcal, respectively. This strain is not apparent in the structure of HFA; the bond angles, carbon–oxygen, and carbon–carbon bond distances of HFA[9] and acetone[10] are the same within the combined experimental errors.

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(5) G. C. Levy, J. D. Cargioli, and W. Racela, *J. Amer. Chem. Soc.*, **92**, 6238 (1970).

(6) Derived from heat of formation data reported in J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

(7) C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, **1**, 145 (1967).

(8) (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) ref 6, p 588.

(9) G. Boulet, *Diss. Abstr.*, **25**, 3283 (1964).

(10) C. Kato, S. Konaka, T. Ijima, and M. Kimura, *Bull. Chem. Soc. Jap.*, **42**, 2148 (1969).

F. E. Rogers,* R. J. Rapiejko
Department of Chemistry, University of Dayton
Dayton, Ohio 45409

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Transition Metal Promoted Isomerizations of Highly Strained Polycyclic Systems. A Mechanistic Insight[1]

Sir:

The rearrangement of highly strained ring systems by transition metal catalysts has recently attracted considerable attention. Although many examples of such rearrangements are now known, relatively little is available in the line of definitive evidence concerning the mechanism of these isomerizations. A typical case is that of tricyclo[4.1.0.0^{2,7}]heptane (I), which,

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(1) Paper XXIV on the Chemistry of Bent Bonds. For the previous paper in this series, see P. G. Gassman, G. R. Meyer, and F. J. Williams, *Chem. Commun.*, in press.

depending on conditions, can give 3-methylenecyclohexene,[2] bicyclo[4.1.0]hept-2-ene,[3] 1,3-cycloheptadiene,[4,5] or bicyclo[3.2.0]hept-6-ene.[6] We now wish to report the details of an extensive investigation of the transition metal promoted rearrangement of **1** and of 1-methyltricyclo[4.1.0.0^{2,7}]heptane (**2**).[7] On the basis of the data obtained in our studies, we wish to suggest that stepwise bond cleavage occurs with the various transition metal catalysts acting as *extremely specific* Lewis acids.

Recently, we have proposed that the transition metal promoted rearrangement of bicyclo[1.1.0]butane derivatives occurs *via* the intermediacy of the metal-complexed carbene metal-bonded carbonium ion hybrid, **3**.[2,7,8] This view is to be contrasted with that of other workers who have discussed these rearrangements in terms of a [$_\sigma 2_a + {}_\sigma 2_a$] bond reorganization, which is a thermally disallowed concerted reaction.[4,9,9a] In order to discern which of these two concepts most closely resembled the actual mechanism, we sought to establish that the cleavage of highly strained bicyclo[1.1.0]butane derivatives was a stepwise process which led eventually to an intermediate which could be represented in a *formal* fashion by **3**.

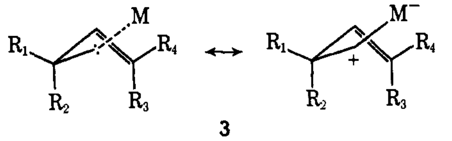

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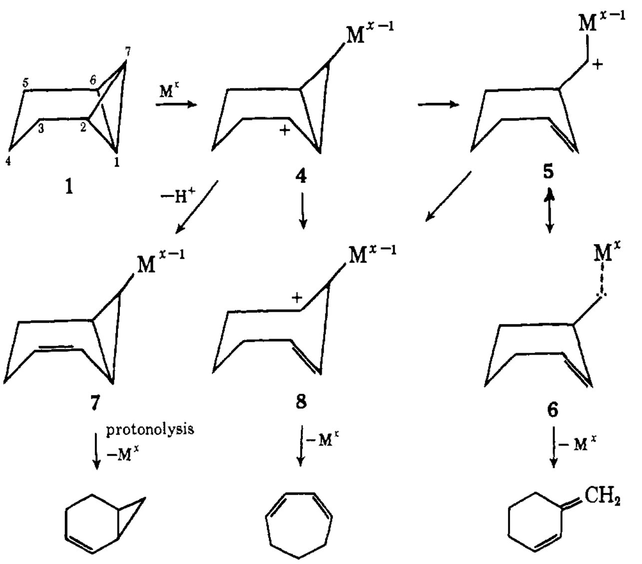
Table I summarizes our results for the metal-promoted rearrangement of **1**. The data presented in this table show that there is a gradual crossover of products for the 11 metals used. We feel that the whole range of products observed can be explained in terms of the stepwise mechanism shown below.[10] Initial attack of the transition metal catalyst, acting as a Lewis acid, could produce **4** *via* cleavage of the C_2–C_7 bond. All of the observed products can be adequately explained on the basis of the intermediacy of **4**. Subsequent cleavage of the C_1–C_7 bond would produce an intermediate represented by the resonance contributors **5** and **6**. A hydrogen shift at this point would produce 3-methylenecyclohexene. Loss of a proton from **4** would yield **7** which on protonolysis[11] with ejection of the catalyst would give bicyclo[4.1.0]hept-2-ene. 1,3-Cycloheptadiene could arise either from **4** *via* cleavage of the C_1–C_6 bond to give **8** as a precursor, or from the 5–6 hybrid *via* a vinyl migration to yield **8**.



In order to add substance to our hypothesis, we attempted to trap **4** by running the reaction in a more nucleophilic solvent. Treatment of **1** with rhodium dicarbonyl chloride dimer in methanol[12] resulted in the formation of a 75% yield of a 4:1 mixture of **9** and **10**.

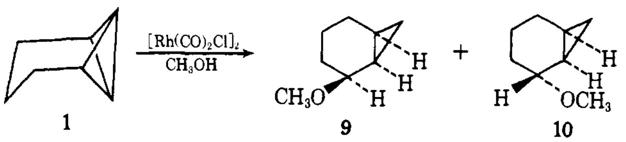
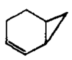
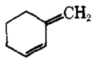


Table I. Metal-Promoted Isomerizations of Tricyclo[4.1.0.0^{2,7}]heptane (**1**)

Catalyst	Conditions temp, time, solvent	—% yield of products^a— 		
$AgBF_4$	~40°, minutes, $CDCl_3$^{c,d}			100
ZnI_2	25°, 16 hr, Et_2O		11	88
$HgBr_2$	50°, 48 hr, Et_2O		8	85
$[Rh(CO)_2Cl]_2$	25°, 15 min, CH_3CN		98	
$[Ir(CO)_3Cl]_2$	25°, 14 hr, $CHCl_3$		91	
$[(\pi\text{-allyl})PdCl]_2$	25°, 30 min, $CHCl_3$		94	
$(C_6H_5CN)_2PdCl_2$	25°, 20 hr, CH_3CN		69	
$[C_6F_5Cu]_4$	25°, 2 hr, $CHCl_3$		74	
$[(C_6H_5)_3P]_2Rh(CO)Cl$	65°, 48 hr, CH_3CN	5	92	
$[Ru(CO)_3Cl_2]_2$	25°, 40 hr, CH_3CN	12	44	
PtO_2	65°, 48 hr, CH_3CN	24	62	
$SnCl_2 \cdot 2H_2O$	60°, 24 hr, $CHCl_3$	40		
$AlCl_3$	Ether^e	b		

[a] All yields reported from this laboratory represent the average of at least two runs. [b] Yield not reported. [c] Reference 4. [d] Reference 5. [e] Reference 3.

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(2) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, 93, 1042 (1971).

(3) W. R. Moore, H R. Ward, and R. F. Merritt, *ibid.*, 83, 2019 (1961).

(4) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *ibid.*, 92, 7002 (1970).

(5) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, 93, 1043 (1971).

(6) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).

(7) P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, 93, 1812 (1971).

(8) P. G. Gasssman and F. J. Williams, *ibid.*, 92, 7631 (1970).

(9) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, 93, 1288 (1971).

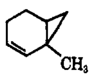
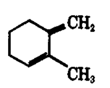
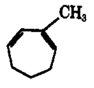
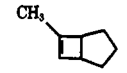
(9a) NOTE ADDED IN PROOF. Subsequent to the submission of this communication and to the appearance of our initial postulate of a metal-complexed carbene–metal-bonded carbonium ion intermediate,[7,8] a publication appeared which abandons this "concerted" mechanism and replaces it by an "argento carbonium ion" concept. See L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, 93, 2335 (1971). It should be noted that this "argento carbonium ion" is little more than a resonance contributor of our previously postulated intermediate.

(10) Subsequent to the completion of our work a related study involving the metal-catalyzed rearrangement of tri-*tert*-butylprismane was published [K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *ibid.*, 93, 1270 (1971)]. In some respects there is a similarity between the stepwise mechanism which we are proposing for the rearrangement of **1** and that which Maitlis and coworkers have suggested. Both mechanisms use the transition metal catalyst as an electron acceptor. For an additional discussion see J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, *Chem. Commun.*, 40 (1971).

(11) For a recent discussion of the mechanism of such protonolysis see: T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, 93, 1049 (1971).

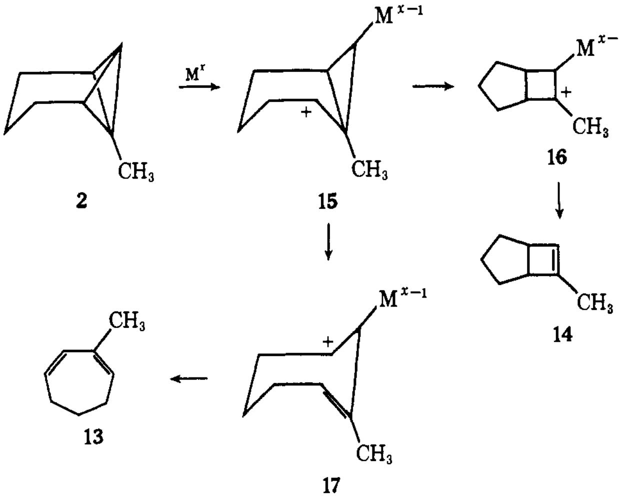
(12) A control experiment demonstrated that rhodium dicarbonyl chloride dimer could be recovered unchanged from methanol. Hence, it would appear that the observed reaction was not due to the formation of some new catalyst from methanol and rhodium dicarbonyl chloride dimer.

Table II. Metal-Promoted Isomerizations of 1-Methyltricyclo[4..1.0.$0^{2,7}$]heptane

Catalyst	Conditions temp, time, solvent	% yield of products			
		 11	 12	 13	 14
$[Rh(CO)_2Cl]_2$	25°, 15 min, $CHCl_3$		96		
$[Ir(CO)_3Cl]_2$	25°, 14 hr, $CHCl_3$		93		
$[(\pi\text{-allyl})PdCl]_2$	25°, 30 min, $CHCl_3$		93		
$[C_6F_5Cu]_4$	25°, 6 hr, $CHCl_3$		56		
ZnI_2	25°, 16 hr, Et_2O			48	12
$HgBr_2$	60°, 24 hr, Et_2O			24	42
$SnCl_2 \cdot 2H_2O$	60°, 24 hr, Et_2O	53			

This is the same ratio of ethers as was found in the methanolysis of **1** catalyzed by sulfuric acid.[13] This indicates to us that transition metal carbonyls can behave as Lewis acid catalysts. Furthermore, the trapping of a carbonium ion type intermediate by nucleophilic solvent tends to support our hypothesis that multiple bond cleavage promoted by transition metal catalysts is a stepwise process leading in some instances to **3**.

Table II lists the products observed in the reaction of various catalysts with **2**.[14] Comparison of Table I with Table II shows that the rearrangement of **1** was very similar to the rearrangement of **2** with most catalysts. The exceptions were zinc iodide and mercuric bromide which gave 6-methylbicyclo[3.2.0]hept-6-ene (**14**) as an added product. The formation of **14** adds support to the stepwise hypothesis advanced above. Initial attack of the catalyst on **2** would be expected to yield the cyclopropylcarbinyl cation **15**. A cyclopropylcarbinyl–cyclobutyl cation rearrangement would now produce the *tertiary* cation **16**,[15] which would yield **14** on the loss of M^x. The formation of **13** could be readily explained on the basis of a **2** → **15** → **17** → **13** reaction pathway.



We feel that the data presented in this communication offer support for the reasonable hypothesis that the transition metal promoted rearrangement of highly strained polycyclic systems is a stepwise process in which the transition metal complex acts like a Lewis acid. We feel that our observations indicate the inadequacy of those mechanisms for transition metal catalyzed rearrangements of certain highly strained polycyclics in which metal ions "promote facile $[{}_{\sigma}2_a + {}_{\sigma}2_a]$ skeletal rearrangement."

The major question which remains to be answered is how the different catalysts control the eventual product-forming step of the reaction. We are continuing to investigate this aspect of these intriguing rearrangements.

Acknowledgment. We are indebted to the National Science Foundation and to the Alfred P. Sloan Foundation for support of this work.

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(13) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970).

(14) Satisfactory elemental analyses have been obtained on all new compounds. Compounds **11**, **13**, and **14** were independently synthesized. The details of these syntheses will be reported in a full paper.

(15) Alternately, **16** could be formed by the homoallylic participation of the double bond of **17**.

(16) National Science Foundation Trainee, 1968–1971.

Paul G. Gassman,* Thomas J. Atkins[16]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received April 23, 1971

Concerning the So-Called "Ladder Structure" of Equilibrated Phenylsilsesquioxane

Sir:

In a communication to this journal a decade ago,[1] the alkaline equilibration of phenylsilsesquioxane, $(PhSiO_{3/2})_x$, was reported to yield a highly ordered, thermodynamically stable, stereoregular, linear double-chain structure. Subsequent papers,[2] patents,[3] and textbook references[4] in the intervening years indicate that widespread acceptance this view has been achieved. The above notwithstanding, we report herein recent ob-

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(1) J. F. Brown, Jr., L. H. Vogt, Jr., A. Katchman, J. W. Eustance, K. M. Kiser, and K. W. Krantz, *J. Amer. Chem. Soc.*, **82**, 6194 (1960).

(2) (a) J. F. Brown, Jr., *J. Polym. Sci., Part C*, No. 1, 83 (1963); (b) K. A. Andrianov, G. A. Kurakov, F. F. Sushentsova, V. A. Myagkov, and V. A. Avilov, *Polym. Sci. USSR*, **7**, 1637 (1965); (c) V. N. Tsvetkov, K. A. Andrianov, Ye. L. Vinogradov, V. I. Pakhomov, and S. Ye. Yakushkina, *ibid.*, **9**, 1 (1967); (d) V. N. Tsvetkov, K. A. Andrianov, I. N. Shtennikova, G. I. Okhrimenko, L. N. Andreyeva, G. A. Fomin, and V. I. Pakhomov, *ibid.*, **10**, 636 (1968); (e) T. E. Helminiak, G. L. Benner, and W. E. Gibbs, *Polym. Prepr. Amer. Chem. Soc., Div. Polym. Chem.*, **8**, 284 (1967); (f) O. Quadrat, *Collect. Czech. Chem. Commun.*, **35**, 2564 (1970).

(3) (a) J. F. Brown, Jr., and L. H. Vogt, Jr., U. S. Patent 3,017,386, Jan 16, 1962; (b) A. Katchman, U. S. Patent 3,162,614, Dec 22, 1964; (c) K. W. Krantz, U. S. Patent 3,294,717, Dec 27, 1966; (d) K. W. Krantz, U. S. Patent 3,294,737, Dec 27, 1966; (e) K. W. Krantz, U. S. Patent 3,294,738, Dec 27, 1966; (g) K. W. Krantz, U. S. Patent 3,318,844, May 9, 1967; (g) K. W. Krantz, U. S. Patent 3,372,133, March 5, 1968.