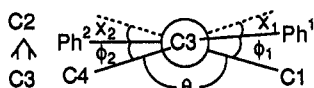


Table I. Time Constants for Thermal Trans–Cis Isomerization of *trans*-Cycloheptenes

compd	solvent	temp, °C	time const, s ⁻¹
<i>trans</i> -1	DMSO- <i>d</i> ₆	80	1.59 (±0.10) × 10 ⁻⁶
		100	8.86 (±0.35) × 10 ⁻⁶
		120	4.72 (±0.68) × 10 ⁻⁵
<i>trans</i> -cycloheptene	MeOH	1.0	1.19 × 10 ^{-3a}
<i>trans</i> -1-phenylcycloheptene	cyclohexane	ambient	2.77 × 10 ^{-3b}

^aCalculated on the basis of ref 15. ^bCalculated on the basis of ref 16.

NMR measurements at room temperature and the X-ray crystallographic analysis of *trans*-1 show a symmetrical conformation. ¹H NMR measurement of *trans*-1 at low temperature (–70 °C) is also consistent with a symmetrical form. A molecular mechanics calculation (MM2) of *trans*-1 also supports the symmetrical structure as the one having 11.4 kcal less strain compared with the unsymmetrical form. The most interesting point of the structure of *trans*-1 is the twisting around the C=C double bond. The torsion angle of C(1)–C(2)–C(3)–C(4) was found to be 180° – θ = 32.7°. This value is, however, in fair agreement with the value for the unsymmetrical calculated structure rather than that of the symmetrical form. The twist angle Φ [(φ₁ + φ₂)/2] and the pyramidal deformation X [(χ₁ + χ₂)/2] were also found



X-ray:	θ = 147.3°, φ ₁ = 19.9°, φ ₂ = 19.2°, χ ₁ = 12.8°, χ ₂ = 13.5°
MM2(symmetrical):	131.5° 42.2° 40.7° 6.3° 7.8°
MM2(unsymmetrical):	147.7° 31.0° 17.2° 1.3° 15.1°

to be 19.6° and 13.2°, respectively. The bond angles around the ring atoms of *trans*-1 are almost normal except for the expanded Si(1)–Si(2)–Si(3) bond angle. Interestingly, the bond lengths of C(1)–C(2) and C(3)–C(4) are slightly shortened while those of C(1)–Si(1), C(4)–Si(3), Si(1)–Si(2), and Si(2)–Si(3) are stretched from corresponding normal bond lengths. These deformations of the bond angle and lengths must occur to mitigate the twist of the C=C double bond. The C=C double bond [C(2)–C(3) = 1.344 Å] is slightly stretched compared with that of *trans*-stilbene in the solid state (1.228–1.330 Å).^{12,13} The expansion of the C=C double bond may result from the twisting of the double bond. Furthermore, two benzene rings incline at 47.3° and 51.1° from the planes of C(3)–C(2)–C(5) and C(2)–C(3)–C(6), respectively, though the torsion angles of *trans*-stilbene are ranged between 3.6 and 5.7° in the solid state.¹²

Photochemical reaction of *trans*-1 was examined as a general property of the olefins. Irradiation (254 nm) of *trans*-1 in benzene-*d*₆ gave photoisomerized *cis*-1. In this isomerization, it was found that a photoequilibrium existed and the photostationary *trans*/*cis* ratio was 0.49 (Figure 2). This value is higher than the photosensitized isomerization of *trans*-cycloheptene.¹⁴

Thermal stabilities of *trans*-1 were also examined. When a benzene-*d*₆ solution of *trans*-1 in an NMR tube was heated at 80 °C, *trans*-1 was stable even after 72 h. However, heating of the DMSO-*d*₆ solution at 80 °C tended to initiate the reaction and gave isomerized *cis*-1. These results may be explained by stabilization of the transition state caused by solvation with the polar solvent. At several temperatures, the measurements of the *trans*/*cis* ratio by ¹H NMR at regular time intervals in DMSO-*d*₆ gave a straight line for a plot of log [*trans*-1] as a function of time,

and the rate constants obtained are shown in Table I. The rate constants of the thermal *trans*–*cis* isomerization are very small compared with those of *trans*-cycloheptene¹⁵ and *trans*-1-phenylcycloheptene.¹⁶ It is found that the introduction of the three silicon atoms in *trans*-cycloheptene is useful to stabilize the *trans*-trisilacycloheptene. A plot of log *k* as a function of reciprocal of temperature also gave a good linear relationship, and the following thermodynamic parameters were obtained: *E*_a = 23.2 ± 1.3 kcal mol⁻¹, log *A* = 8.6 ± 0.7, Δ*G*[‡]₃₇₃ = 30.6 ± 2.6 kcal mol⁻¹, Δ*H*[‡]₃₇₃ = 22.5 ± 1.3 kcal mol⁻¹, Δ*S*[‡]₃₇₃ = –21.7 ± 11 cal K⁻¹ mol⁻¹. At 120 °C, continued heating gave other minor products, which include 2,3-diphenylbutadiene, *cis*-1,2-diphenyl-4,4-dimethyl-4-silacyclopentene, and *cis*-1,2-diphenyl-4,4,5,5-tetramethyl-4,5-disilacyclohexene which were identified by GCMS and ¹H NMR measurements of the mixture and unidentified silicon compounds. These products were found to be formed from *trans*-1 because the heating of *cis*-1 under the same conditions gave no reaction.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Molecular Design by heteroatom No. 02230101 from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Detailed information of the X-ray crystal analysis of *trans*-1 including data collection and reductions and structure solution and refinement, the Arrhenius plot for the thermal *trans*–*cis* isomerization of 1 in DMSO-*d*₆, and tables of experimental details, positional and thermal parameters, general temperature factor expressions, root-mean-square amplitudes of thermal vibration, and bond distances and angles (22 pages); listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Observation of a Weakly Bound Mn(CO)₅⁺/CH₄ Complex

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Intramolecular reductive elimination of an alkane molecule from alkyl hydride organometallic complexes (e.g., [(Cp)₂Re(H)CH₃]Cl and (Cp)₂W(H)CH₃) has received considerable attention recently.^{1–4} This is partly due to the intense interest in the reverse oxidative addition process, which, in the case of alkanes, results in hydrocarbon activation.⁵

To explain exchange of deuterium from the hydride position with hydrogen in the methyl ligand and an inverse kinetic isotope effect for the elimination of methane, organometallic/methane σ complexes were invoked as intermediates. The structure of the complexes could not be established with certainty, but involvement

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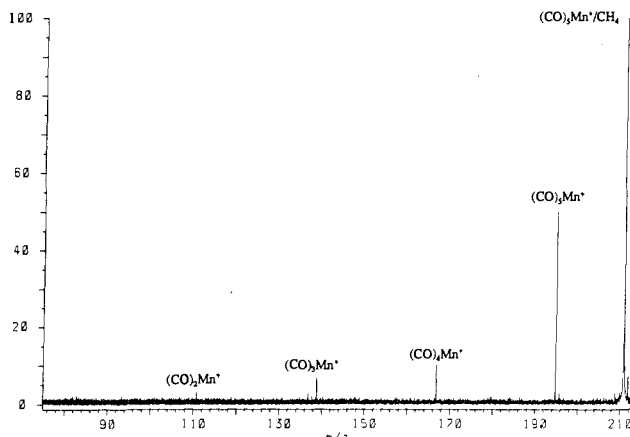
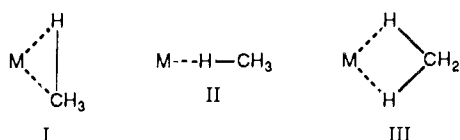


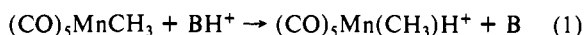
Figure 1. Collision-induced dissociation mass spectrum of isolated $[\text{Mn}, \text{C}_6, \text{O}_5, \text{H}_4]^+$ ions with Ar as target gas (5×10^{-8} mbar) and a 100-ms interaction time. The center-of-mass energy was 4.0 eV. With a shorter interaction time and/or a lower center-of-mass energy, $(\text{CO})_5\text{Mn}^+$ is the only fragment observed.

of either $\eta^2 \text{H}-\text{C}(\text{H})_3$ interaction with the metal center (resembling the $\eta^2 \text{H}-\text{H}$ organometallic complexes⁶) (I) or one⁷ (II) or two⁸



(III) methane hydrogen atoms bridging with the metal center in two-electron three-center bonds was suggested. Such transition-metal/alkane complexes have not yet been definitively identified, but low-temperature matrix isolation studies⁹ and room-temperature solution studies¹⁰ support their existence. Recently it was shown that all atomic ions of the first transition series *except* Mn^+ form stable "adducts" with methane under multicollision conditions¹¹ (0.75 Torr He). However, the exact structure of the adducts could not be established.

Pentacarbonylmethylmanganese, $(\text{CO})_5\text{MnCH}_3$, is known to undergo reductive elimination of methane in acidic media.¹² In a study to identify the reactive intermediates for this process, the gas-phase reactions of pentacarbonylmethylmanganese with a variety of proton donors were examined¹³ (reaction 1) and the



proton affinity of $(\text{CO})_5\text{MnCH}_3$ was established as 761 ± 13 $\text{kJ}\cdot\text{mol}^{-1}$.¹⁴ Collision-induced dissociation of $(\text{CO})_5\text{Mn}(\text{CH}_3)\text{H}^+$ was found to produce $(\text{CO})_5\text{Mn}(\text{CH}_3)\text{H}^+$ by loss of CO, whereas loss of CH_4 was *not* observed. The Mn–(CO) bond strength in $(\text{CO})_5\text{Mn}(\text{CH}_3)\text{H}^+$ was estimated to be 46 ± 8 $\text{kJ}\cdot\text{mol}^{-1}$.¹⁴

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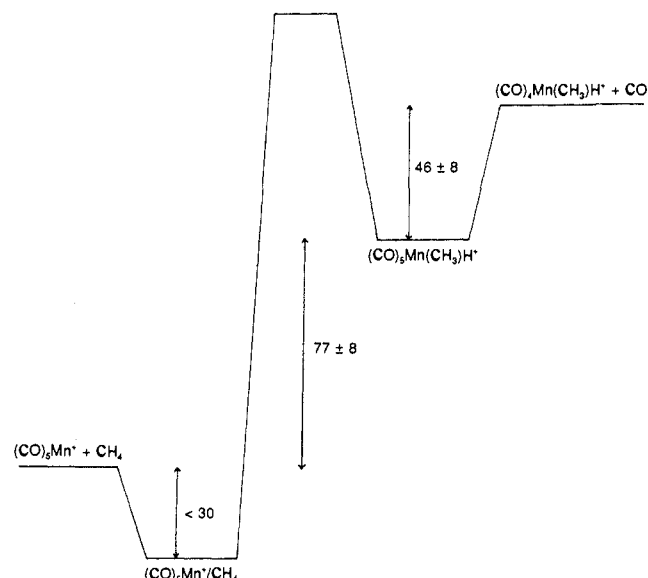


Figure 2. Schematic potential energy surface relating $(\text{CO})_5\text{Mn}(\text{CH}_3)\text{H}^+$, $(\text{CO})_5\text{Mn}^+/\text{CH}_4$, and their dissociation products. The height of the central barrier separating $(\text{CO})_5\text{Mn}(\text{CH}_3)\text{H}^+$ and $(\text{CO})_5\text{Mn}^+/\text{CH}_4$ could not be determined. All values are in $\text{kJ}\cdot\text{mol}^{-1}$. See text for details.

Unexpectedly, $(\text{CO})_5\text{Mn}^+$ was the product of the reaction between $(\text{CO})_5\text{MnCH}_3$ and proton donors with proton affinities of the conjugate acid between 838 and 761 $\text{kJ}\cdot\text{mol}^{-1}$.¹⁴ The latter observation was ascribed to protonation at a different site, producing a weakly bound complex, followed by CH_4 loss.

In our high-pressure mass spectrometry studies of organometallic species a $[\text{Mn}, \text{C}_6, \text{O}_5, \text{H}_4]^+$ ion was observed when $\text{Mn}_2(\text{CO})_{10}$ was used as precursor and CH_4 as chemical ionization agent. All experiments were performed with a Bruker Spectrospin CMS 47 Fourier transform ion cyclotron resonance (ICR) spectrometer^{16a} equipped with a high-pressure external ion source.^{16b} Chemical ionization pressures up to 3 Torr and 2 keV electrons were used for ionization. The product ions were transferred to the low-pressure ICR cell and trapped, followed by a 2-s delay to thermalize the ions by collisions with argon present in the ICR cell. By ejection of all other ions from the ICR cell, the $[\text{Mn}, \text{C}_6, \text{O}_5, \text{H}_4]^+$ ions were isolated. An rf pulse at the exact cyclotron frequency of the latter ion was then used to increase its translational energy to a known value. In the subsequent delay collision-induced dissociation (CID) took place with Ar as target gas (5.0×10^{-8} mbar). The fragmentation products were analyzed by both broad-band and narrow-band detection.

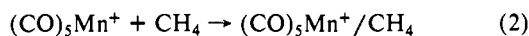
The high-pressure mass spectrum of $\text{Mn}_2(\text{CO})_{10}/\text{CH}_4$ was dominated by $\text{Mn}_2(\text{CO})_{10}\text{H}^+$, but an appreciable amount of the $[\text{Mn}, \text{C}_6, \text{O}_5, \text{H}_4]^+$ ion was also observed (ca. 20% of $\text{Mn}_2(\text{CO})_{10}\text{H}^+$, m/z 391¹⁷). Figure 1 shows that the dominant process upon collisional activation of the latter species is loss of CH_4 ; significantly, loss of CO is *not* observed. Thus, this ion cannot be $(\text{CO})_5\text{Mn}(\text{CH}_3)\text{H}^+$, which loses CO and not CH_4 .¹³ An examination of the dependence of CH_4 loss on the center-of-mass energy of $[\text{Mn}, \text{C}_6, \text{O}_5, \text{H}_4]^+$ (using the procedure described in ref 18) revealed that the CH_4 unit is only weakly bound, probably by less than 30 $\text{kJ}\cdot\text{mol}^{-1}$. Saillard et al.^{7b} calculated the bond energy with respect to CH_4 loss from the isoelectronic Cr- $(\text{CO})_5/\text{CH}_4$ complex (type II) to be 23 $\text{kJ}\cdot\text{mol}^{-1}$. We propose that the $[\text{Mn}, \text{C}_6, \text{O}_5, \text{H}_4]^+$ ions are a $(\text{CO})_5\text{Mn}^+/\text{CH}_4$ complex,

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formed in the high-pressure ion source by interaction between $(\text{CO})_5\text{Mn}^+$ and CH_4 (reaction 2). Multiple ion-molecule col-



lisions in the high-pressure ion source provided thermalization of the weakly bound complex. The present experiments do not allow us to identify the exact nature of the interaction between CH_4 and $(\text{CO})_5\text{Mn}^+$.

Combining the present results with those of ref 13 yields the potential energy surface shown in Figure 2. Exchange of the CH_4 unit in the complex with CD_4 was not successful. This can be ascribed to lack of a coordination site for the incoming CD_4 .

The high-pressure mass spectrum of $\text{Mn}_2(\text{CO})_{10}/\text{CH}_4$ also showed the presence of $[\text{Mn}, \text{C}_5, \text{O}_5, \text{H}_2]^+$ and $[\text{Mn}, \text{C}_5, \text{O}_6, \text{H}_2]^+$ (ca. 7% and 2% of m/z 391, respectively¹⁷). The CID mass spectra of these ions were dominated by $(\text{CO})_5\text{Mn}^+$, corresponding with loss of H_2 and H_2O , respectively. The energy dependence of the CID spectra suggests that these species are weakly bound $(\text{CO})_5\text{Mn}^+/\text{H}_2$ and $(\text{CO})_5\text{Mn}^+/\text{H}_2\text{O}$ complexes.

In summary, we have obtained unambiguous evidence for the existence of weakly bound organometallic/ CH_4 complexes, which may play an important role in reductive elimination and oxidative addition reactions. Further experiments are in progress to establish the reaction mechanism that generates the $(\text{CO})_5\text{Mn}^+/\text{CH}_4$ complex and to obtain a more accurate binding energy of this complex. Preliminary results indicate that other organometallic species, e.g., $\text{Re}_2(\text{CO})_{10}$, yield similar complexes.

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Kinetic Acidity of Cubane

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We have determined the kinetic acidity of cubane by the application of a ^3H NMR spectroscopic approach.¹ An earlier measurement of the acidity of cubane² has been subject to some controversy.³

Kinetic acidities are a useful measure of the acidity of weak carbon acids⁴ and are obtained by measuring rates of base-catalyzed proton-exchange reactions. It has been found that one-bond ^{13}C - ^1H NMR coupling constants ($^1J_{\text{CH}}$) correlate closely with kinetic acidities for cyclic aliphatic hydrocarbons⁵ (see Figure 1). This correlation holds even for strongly strained systems such as cyclopropane. Cubane, a strained polycycloalkane, would be anticipated to also fit this correlation. On the basis of its $^1J_{\text{CH}}$

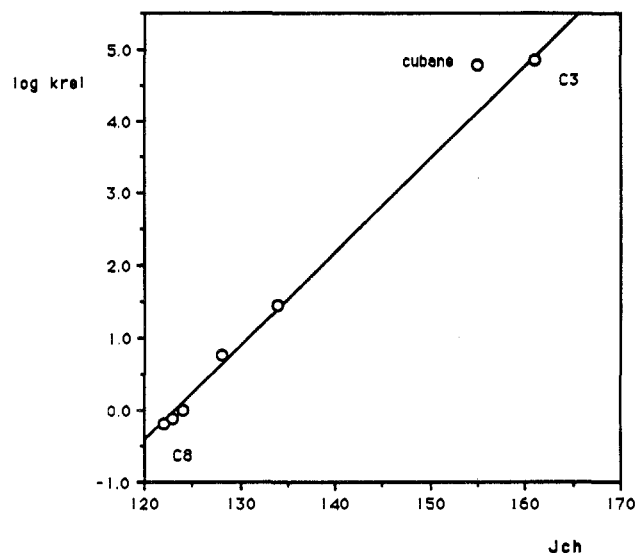


Figure 1. Logarithm of kinetic acidity (CsCHA tritiodeprotonation) relative to cyclohexane vs one-bond ^{13}C - ^1H NMR coupling constant. The point for cubane is superimposed on the previous correlation (ref 5b) based on cycloalkanes, $n = 3-8$.

Table I. Cubane Tritium Incorporation and Loss

experiment	$[\text{CsCHA}]^a$	cubane: ^b $10^6 k_1^c$	<i>p</i> -xylene ring: ^b $10^4 k_1^c$	rel rate: cubane/ <i>p</i> -xylene
tritiodeprotonation	0.123	2.9	4.4	0.0066
protiodetrutiation	0.086	0.88	1.7	0.0052

^a Calculated from the volume of 0.2 N CsCHA added. ^b Pseudo-first-order rate constant (s^{-1}). ^c Statistically corrected.

value of 155 Hz,⁶ the predicted kinetic acidity of cubane from the correlation is 1.4×10^{-4} times that of benzene.

It thus came as a surprise when it was reported by Luh and Stock² that the kinetic acidity of cubane is 1.2 times that of benzene, a value almost 4 orders of magnitude greater than predicted on the basis of $^1J_{\text{CH}}$. Ritchie and Bachrach were prompted by this result to do calculations³ on the cubane system, in an attempt to explain its behavior. They concluded that cubane is thermodynamically more acidic than cyclopropane, and they rationalized the results on the basis of greater rehybridization in the cubane system on deprotonation.⁷ On the other hand, the value of the Laplacian at the bond critical point for the C-H bond suggests a lower acidity for cubane.³

We had planned to reinvestigate the kinetic acidity of cubane for some time, but the experimental techniques available were difficult to apply. The detection methods we have used routinely for kinetic acidity studies (scintillation counting, mass spectrometry) do not always guarantee the identity of the substance being analyzed for isotopic exchange, thus leading to potential errors due to the presence of impurities. The application of tritium NMR spectroscopy as a new technique for monitoring proton exchange kinetics¹ presented us with the opportunity to study cubane.

The exchange experiments on cubane were accomplished by incorporating tritium (tritiodeprotonation) from *N*-tritiated cyclohexylamine (CHA), catalyzed by cesium cyclohexylamide (CsCHA), in an analogous manner to that described previously.¹ The rate of tritium incorporation at 297 K was determined in a competition experiment with *p*-xylene, for which the kinetic acidity is known.¹ The tritium NMR spectrum of the sample consisted of four singlets at δ 7.24 (xylene ring), δ 4.25 (cubane), δ 2.45 (xylene methyl), and δ 1.36 (amino position of CHA). For this study we also conducted a protiodetrutiation experiment, as follows: the sealed NMR tube containing the substrates from the trit-

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