What factors are responsible for the difference in the reactivities of silanethione and silanone? As Figure 4 shows, the frontier orbital π (−10.3 eV) and π^* (0.5 eV) energy levels of silanethione are 2.0 eV higher and 1.0 eV lower, respectively, than the π (−12.3 eV) and π^* (1.5 eV) levels of silanone. If the reactions would be "frontier-controlled", one should see a more facile attack of water on silanethione than on silanone. As seen in Figure 8, this is not the case. Apparently, the lower reactivity of silanethione is due to the fact that the silicon–sulfur double bond is less polarized than the silicon–oxygen double bond.

Despite the less polarized double bond, silanethione is still too reactive to be isolated under normal conditions. In the interest in preparing an isolable silanethione, one should note that the transition state for the $H_2Si{=}S$ + H_2O reaction lies only 5.7 kcal/mol below the reactants, in marked contrast with the energy difference of 16.3 kcal/mol between the reactants and transition state in the $H_2Si{=}O$ + H_2O reaction. This means that the reactivity of silicon–sulfur double bonds can be more easily controlled not only by the steric effect of very bulky substituents but also by the electronic effect of relatively small substituents.[34] Obviously, the electronic effect of small substituents should reduce further the dipolar character in the silicon–sulfur double bond of $H_2Si{=}S$ (and increase the HOMO–LUMO energy gap).

Concluding Remarks

Comparisons with silanone as well as formaldehyde reveal several intriguing aspects of the structural and energetic properties of silanethione in the ground, excited, and protonated states. An important finding is that silicon is much less reluctant to form double bonds with sulfur than with oxygen. Thus, silanethione is more stable and less reactive than silanone. The major obstacle to the successful isolation of silanethione is the relatively high reactivity. In order to design an isolable silanethione, the hydrogen atoms in $H_2Si{=}S$ should be replaced by substituents that deduce the polarity of the silicon–sulfur double bond. A theoretical study along this line is in progress.

Acknowledgment. All calculations were carried out at the Computer Center of the Institute for Molecular Science and at the Computer Center of Tokyo University with the IMSPAK (WF10-8) and GAUSSIAN 80 (WF10-24) programs in IMS Computer Center library program package. We are grateful to Dr. D. A. Dixon for sending a preprint of ref 24 prior to publication.

Registry No. Si, 7440-21-3; S, 7704-34-9; $H_2Si{=}S$, 69639-29-8; H_2O, 7732-18-5; $H_2C{=}O$, 50-00-0; $H_2Si{=}O$, 22755-01-7; HSiSH, 99278-16-7; H_2SiSH^+, 80401-43-0; $HSiSH_2^+$, 101630-69-7; H_2SiOH^+, 66639-72-3; $HSiOH_2^+$, 101630-70-0.

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[34] For a theoretical attempt to reduce the reactivity of silicon–carbon double bonds by the electronic effect, see: Nagase, S.; Kudo, T.; Ito, K. In *The Proceedings of the Applied Quantum Chemistry Symposium*; Smith, V. H., et al., Eds.; D. Reidel Publishing: Dordrecht, Netherland, in press.

[35] **Note Added in Proof.** As described in the text, the 1,2-H shifts in $H_2Si{=}S$ and $H_2Si{=}O$ are found, also at the MP2 and MP3 levels of calculation, to proceed via a nonplanar transition state, except that at the MP2 level a planar transition state becomes slightly more favorable for the 1,2-H shift in $H_2Si{=}O$.

Titanium-Catalyzed Cycloaddition–Cycloreversion Cascade in the Reaction of Norbornadiene with Bis(trimethylsilyl)acetylene

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Received September 11, 1985

The $TiCl_4$–Et_2AlCl catalyst induces endo-[2 + 2] cycloaddition of bis(trimethylsilyl)acetylene to norbornadiene. At 20 °C the adduct undergoes a catalyzed Cope rearrangement followed by disrotary ring opening which yields 2,3-bis(trimethylsilyl)-*cis*-bicyclo[4.3.0]nona-2,4,8-triene as a single low molecular weight product. At elevated temperatures the Cope rearrangement is followed by a 1,3-sigmatropic shift and ring opening, yielding isomeric 3,4-bis(trimethylsilyl)-*cis*-bicyclo[4.3.0]nona-2,4,8-triene. The $TiCl_4$–Et_2AlCl system also catalyzes the Diels–Alder addition of bis(trimethylsilyl)acetylene to either 1:1 adduct, affording a single tricyclic triene, 8,9,10,11-tetrakis(trimethylsilyl)tricyclo[5.2.2.0^{2,6}]undeca-3,8,10-triene. The latter can be used for a facile preparation of 1,2,4,5-tetrakis(trimethylsilyl)benzene. The reaction mechanism and the products of the catalyst deactivation are discussed.

Introduction

The homogeneous Ziegler–Natta catalysts, derived either from (arene)titanium(II) complexes or from $TiCl_4$ combined with an excess of Et_2AlCl, have recently been shown to induce [6 + 2] cycloadditions of 1,3,5-cycloheptatriene to various trienophiles,[1,2] as well as [4 + 2] cycloadditions of conjugated dienes to bis(trimethylsilyl)acetylene (BTMSA).[3] The $TiCl_4$–Et_2AlCl catalyst proved to be especially active in inducing cross-additions of unsaturated substrates, and we were encouraged by its catalytic properties to explore the reaction of BTMSA with the highly reactive bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD). Of special interest was the mode of the NBD addition, since in the reaction with 1,3,5-cycloheptatriene we obtained products of both the [2 + 2 + 2] and the [6 + 2] addition.[2] In the transition-metal-catalyzed cycloaddition

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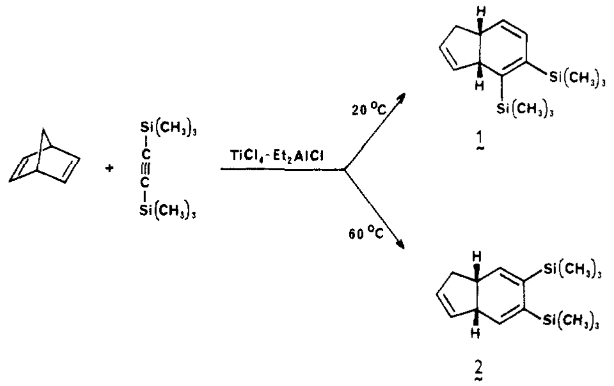
[1] Mach, K.; Antropiusová, H.; Tureček, F.; Hanuš, V.; Sedmera, P. *Tetrahedron Lett.* **1980**, *21*, 4879. Tureček, F.; Hanuš, V.; Sedmera, P.; Antropiusová, H.; Mach, K. *Collect. Czech. Chem. Commun.* **1981**, *46*, 1474.

[2] Mach, K.; Antropiusová, , H.; Hanuš, V.; Sedmera, P.; Tureček, F. *J. Chem. Soc., Chem. Commun.* **1983**, 805. Mach, K.; Antropiusová, H.; Petrusová, L.; Hanuš, V.; Tureček, F.; Sedmera, P. *Tetrahedron* **1984**, *40*, 3295.

[3] Mach, K.; Antropiusová, H.; Petrusová, L.; Tureček, F.; Hanuš, V.; Sedmera, P.; Schraml, J. *J. Organomet. Chem.* **1985**, *289*, 331.

0276-7333/86/2305-1215$01.50/0

Scheme I



reactions NBD behaves more often as a [2 + 2] dienic component, while [2 + 2] additions involving only one of the NBD double bonds have been observed in a few cases only, e.g., in the reaction with methylenecyclopropane on Ni,[4] allene on Pd,[5] butadiene on Fe,[6] and diphenylacetylene on Ni.[7]

In preliminary experiments we observed that the $TiCl_4$–Et_2AlCl catalyst showed very low activity to bring about NBD to BTMSA addition under conditions employed for the [4 + 2] cycloadditions,[3] i.e., when the complex of titanium with BTMSA was formed first. Only accidentally we discovered that a much more active catalytic species was formed transiently when the catalyst components were mixed in the presence of *both* unsaturated reactants. The catalyzed reaction afforded quite unexpected products resulting from a complex cycloaddition–cycloreversion sequence. The objective of this paper is to suggest a mechanism accounting for this unusual transformation and to discuss the properties of the catalyst and its deactivation products.

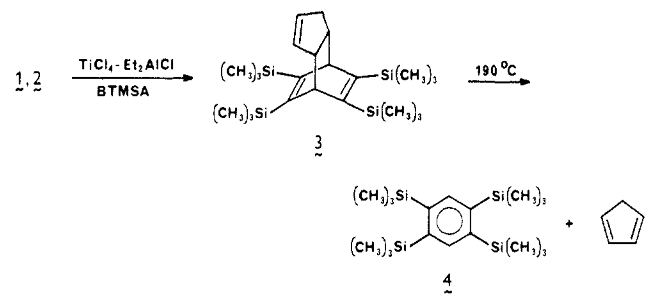
Results and Discussion

Products. The reaction between NBD and BTMSA, catalyzed by an in situ prepared $TiCl_4$–Et_2AlCl system (Ti:Al = 1:20), yielded 2,3-bis(trimethylsilyl)-*cis*-bicyclo[4.3.0]nona-2,4,8-triene (**1**) and its 3,4-isomer (**2**) dependent upon the reaction conditions (Scheme I).

Pure (>95%) isomer **1** was obtained in 30% yield when the catalyst components and the reagents were mixed at a low temperature (<−50 °C), and the reaction mixture then was warmed *quickly* to room temperature. Warming the cold reaction mixture *quickly* to 60 °C yielded mainly **2** (85%) accompanied by **1** (10%) and another 1:1 adduct (5%) in a 45% overall yield. The main byproducts were an insoluble NBD polymer, soluble oligomers consisting of NBD and BTMSA units, and a yellow BTMSA polymer. The competing polymerization of NBD that takes place already at low temperatures requires that this component be used in a twofold molar excess over BTMSA in order to achieve complete consumption of the latter.

The structure of **1** was largely established from the ^{13}C NMR spectrum which showed two distinct sp^2 quaternary carbon atoms (δ 146.88 (s) and 142.45 (s)), four sp^2 methines, two sp^3 methines, one sp^3 methylene, and the silicon-bound methyls. Careful homonuclear (^1H–^1H) and selective heteronuclear (^1H–^{13}C) decoupling made it possible for us to assign most of the ^1H and ^{13}C signals in the corresponding NMR spectra (for the assignment see Experimental Section). The structure of **1** is further corroborated by the mass spectrum which displays molecular ions ($C_{15}H_{26}Si_2$, m/z 262) and $(M–CH_3 - CH_4)^+$ fragments, the latter being characteristic of the presence of a 1,2-bis(trimethylsilyl)ethene subunit.[3]

Scheme II



The structure of **2** was also inferred from the spectral data. Due to the nearly symmetrical nature of the diene system in **2**, the ^{13}C chemical shifts of the quaternary sp^2 carbons are very closely spaced (δ 135.00 (s) and 134.56 (s)). The vicinal position of the trimethylsilyl groups followed from the small interaction constant of H-2 and H-5 in the ^1H NMR spectrum (see Experimental Section) and also from the presence in the mass spectrum of $(M - CH_3 - CH_4)^+$ fragments (vide supra).

The active catalyst for the reaction between NBD and BTMSA is formed during the short period of warming of the reaction mixture from −50 to ca. 20 °C. The catalytic reaction is exothermic which, however, may be due in part to the NBD polymerization. The proportion of adducts **1** and **2** changes continuously with the temperature to which the reaction mixture is quickly warmed. While fast warming to 20 °C gives pure **1**, at 40 °C **2** already prevails, reaching 85% of the total of 1:1 adducts at 60 °C. It should be noted that even under the optimized conditions for the preparation of **2** the composition of the products, as well as the overall yield, sometimes deviated from the given figures, mainly due to not quite reproducible mixing and warming procedures. Isomer **2** can also be obtained by the isomerization of **1** catalyzed by the $TiCl_4$–Et_2AlCl system. In contrast, the reverse isomerization **2** → **1** does not take place, as confirmed by a control experiment.

Both **1** and **2** undergo further a catalyzed addition of BTMSA, yielding a single common adduct, **3** (Scheme II). The 2:1 adduct **3** is also formed when BTMSA and NBD react in 1:1 molar ratio as in this case BTMSA is in an effective excess over NBD due to losses of the latter by polymerization. The structure of **3** was inferred from ^1H, ^{13}C, and ^{29}Si NMR spectra. Heating **3** to 190 °C in vacuo afforded 1,2,4,5-tetrakis(trimethylsilyl)benzene (**4**). This chemical conversion provided further support for the structural assignment to **3**.

Reaction Sequence and Mechanism. The formation of **1** and **2**, as well as their further conversion to the common cycloadduct **3**, raised the question of the reaction mechanism. We assume that the reaction commences with an endo-[2 + 2] cycloaddition of η^4-NBD and η^2-BTMSA coordinated in a low-valent titanium complex (Scheme III).[8] The cycloaddition must be accompanied by reorganization in the ligand sphere of the complex due to the different coordination properties of the reactants and the product. The tricyclic intermediate **5** undergoes a very facile Cope rearrangement which proceeds already at 20

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[4] Noyori, R.; Ishigami, T.; Hayashi, N.; Takaya, H. *J. Am. Chem. Soc.* **1973**, *95*, 1674.

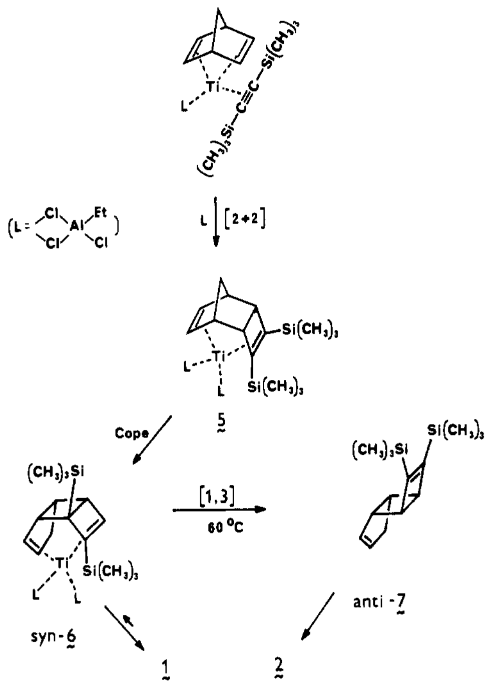
[5] Coulson, D. R. *J. Org. Chem.* **1972**, *37*, 1253.

[6] Greco, A.; Carbonaro, A.; Dall'Asta, G. *J. Org. Chem.* **1970**, *35*, 271.

[7] Schrauzer, G. N. *Adv. Catal.* **1968**, *18*, 373.

[8] L is probably $EtAlCl_2$ (or Et_2AlCl) coordinated through two chlorine atoms, as found by X-ray analysis in (arene)titanium(II) complexes: Thewalt, U.; Stollmaier, F. *J. Organomet. Chem.* **1982**, *228*, 149. The number of ligands (L) in the complexes is tentative only.

Scheme III



°C and is also catalyzed by the titanium complex.[9,10] The further fate of intermediate 6 (Scheme III) depends on the reaction temperature. At 20 °C it undergoes catalyzed opening of the bicyclo[2.2.0]hex-2-ene ring to yield 1. At an elevated temperature a 1,3-sigmatropic shift which flips over the cyclobutene ring to produce the anti isomer 7 competes with the ring opening, and the sequence is terminated by a catalyzed ring opening in 7 which affords the isomeric triene 2.[11]

The isomerization of 1 to 2 probably is made possible by the reversible conversion of 1 to 6. Of two possible modes of closing the bicyclohexene ring in 1 (syn or anti), the latter is disfavored because of steric congestion of the bridgehead trimethylsilyl group which would be inward-oriented in an anti isomer of 6. On the other hand, an analogous ring closure in 2 would preferentially produce the anti isomer 7, because here a syn route would give rise to a less stable isomer. Should we further suppose that the 1,3-sigmatropic rearrangement is possible only in the syn isomers due to coordination of both double bonds to titanium, the one-way isomerization 1 → 6 → 7 → 2 appears logical and self-consistent. Another possible explanation is that, provided 2 is much more stable than 1, the isomerization is reversible and is thermodynamically driven, but in the absence of pertinent thermochemical data this cannot be firmly established.

The formation of 3 from 1 and BTMSA can also be rationalized by the isomerization mechanism involving first the conversion of 1 to 2 which then undergoes a catalyzed Diels–Alder reaction. It is worth noting that a direct Diels–Alder addition of BTMSA to 1 would have required a highly strained transition state with four trimethylsilyl groups arranged in vicinal positions.

The Catalyst and Its Deactivation. The reaction of $TiCl_4$ with Et_2AlCl (1:20) in the presence of coordinating substrates leads to the formation of homogeneous catalytic systems. Such systems catalyze the cyclotrimerization of butadiene[10a,12] and cycloadditions of 1,3,5-cycloheptatriene[1,2] or BTMSA[3] to reactive unsaturated hydrocarbons. The catalytically active complexes are (usually) stable only in solution, and their structures can only be deduced tentatively from limited physicochemical investigations. It is believed that the catalytic complex contains Ti(II) coordinated both to the unsaturated substrates and to ethylaluminum chloride compounds.[2,3,10a,12c,d]

In the [4 + 2] cycloaddition of BTMSA to conjugated dienes the leading role was played by BTMSA which formed a green, thermally stable and diamagnetic titanium complex.[3] It was suggested that the [4 + 2] addition proceeded in the complex when one of the two coordinated molecules of BTMSA was replaced by the diene. In the present case, however, the primary formation of the BTMSA complex led only to a less than 10% yield of 1, while the rest of NBD completely polymerized. Even under optimum conditions for the preparation of 1 or 2, the yields were only moderate and the catalytic system was rapidly deactivated. The formation of adduct 1 or 2 during rapid warmup of the reaction mixture was accompanied by the formation of an insoluble NBD polymer, and the heterogeneous reaction mixture was not amenable to investigation by most spectroscopic methods. Nevertheless, ESR and UV–vis investigation of the reaction systems under various conditions made it possible to explain the extensive catalyst deactivation and gave some clue to the nature of the active catalyst itself.

The heterogeneous, dirty brown-green reaction mixture, prepared by rapid warming to 60 °C, contained paramagnetic species that gave two singlet ESR lines at g = 1.973 (ΔH = 1.3 mT, $a_{\mathrm{Ti}(5/2,7/2)}$ = 1.5 mT) and g = 1.953 (ΔH = 4.0 mT), with the former prevailing. An average estimate of concentrations of both paramagnetic species amounted to as much as 50% of the overall titanium concentration. The species giving the singlet at g = 1.973 remained in solution, while the other paramagnetic species was contained in the insoluble polymer. The solution displayed a rather weak absorption band at 620 nm and a continuous absorption which decreased toward long wavelengths in the visible region of the spectrum.

Both paramagnetic species arose from the interaction of the Et_2AlCl–$TiCl_4$ mixture with NBD: in the absence of BTMSA they were obtained in an amount corresponding to 80–100% of the overall titanium concentration. The soluble paramagnetic compound prepared from NBD and Et_2AlCl–$TiCl_4$ was separated as a blue-green solution in hexane, but attempts to obtain crystalline material were unsuccessful due to the presence of an excess of ethylaluminum compounds and low molecular weight NBD oligomers. The ESR spectrum and the electronic absorption spectrum of the hexane solution (λ_{max} = 353 (ϵ ~10^3) and 712 nm (ϵ ~80) were virtually identical with those of the complex $CpTi^{III}(AlCl_2Et_2)(AlCl_3Et)$ (Cp = η^5-C_5H_5)[13] (8). Since we have found that cyclopentadiene

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[9] In contrast, 3,4-diphenyltricyclo[4.2.1.$0^{2,5}$]nona-2,7-diene, the product of the [2 + 2] addition of NBD to diphenylacetylene was stable in the presence of nickel catalysts up to 120 °C: Schrauzer, G.; Glockner, P. *Chem. Ber.* **1964**, *97*, 2451.

[10] (a) Of the mechanisms suggested for the transition-metal-catalyzed Cope rearrangement,[10b] that involving bis(η^3-allyl)metal complex appears to be probable on the grounds of a finding that analogous titanium complexes are involved in the catalytic cyclotrimerization of butadiene induced by similar systems: Poláček, J.; Antropiusová, H.; Hanuš, V.; Petrusová, L.; Mach, K. *J. Mol. Catal.* **1985**, *29*, 165. (b) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205.

[11] Another conceivable route to 2 would involve an exo attack of BTMSA on the η^4-NBD complex, followed by 1,3-isomerization to an endo isomer with transposed trimethylsilyl groups, Cope rearrangement, and disrotary ring opening. Although this mechanism cannot be excluded in the direct formation of 2 from NBD and BTMSA, it would not account for the isomerization of 1 to 2, because the two routes would have no common intermediates.

[12] (a) Wilke, G. *Angew. Chem.* **1957**, *69*, 397. (b) Takahashi, H.; Yamaguchi, M. *J. Org. Chem.* **1963**, *28*, 1409. (c) Zakharkin, L. I.; Akhmedov, V. M. *Zh. Org. Khim.* **1966**, 2, 998, 1557. (d) Wilke, G. *J. Organomet. Chem.* **1980**, *200*, 349.

reacts with (arene)titanium(II) complexes of the type $(C_6H_6)Ti(AlX_4)_2$ (X = Cl or partly Et) and with the $TiCl_4$–$Et_{3-x}AlCl_x$ (x = 1, 2) systems to give smoothly $CpTi(AlEt_mCl_n)_2$ ($m + n = 4$, $m = 0$–2) complexes,[13] we suggest that the catalytic systems, besides initiating the NBD polymerization, brings about the retro-Diels–Alder reaction of NBD oligomers to split off cyclopentadiene. An ESR signal indistinguishable from that of **8** also was obtained when **3** was treated with the catalyst solution at 100 °C, indicating that the catalyzed retro-Diels–Alder reaction occurred at this temperature. The other ESR signal at $g = 1.953$ is assigned to a Ti(III) complex containing an organic ligand which is a part of the NBD polymer.

The absorption band at 620 nm which occurred in the electronic absorption spectrum of the reaction solution obtained in the presence of both NBD and BTMSA belonged to a BTMSA–titanium complex, while the bands of **8** were hidden under the continuous absorption. The former complex was formed quantitatively in an independent experiment by reacting BTMSA with the Et_2AlCl–$TiCl_4$ catalyst and was characterized by a distinct absorption band at 620 nm ($\epsilon \sim 850$).[3] In contrast to the NBD–BTMSA systems which produced optimum yields of **1** or **2** upon rapid warmup to 20 or 60 °C, those obtained by slow warming to either temperature afforded, after the polymer had settled out, a green solution which contained (according to the intensity of the band at 620 nm) mainly the BTMSA–titanium complex and which showed ESR signals of low intensity. The solution of the BTMSA–titanium complex to which NBD was added showed only negligible activity for producing **1** but instead induced NBD polymerization without being deactivated. These results show that BTMSA and NBD compete for the low-valent titanium atom to give the species inducing the polymerization of NBD.

On the other hand, the [2 + 2] addition of NBD to BTMSA is catalyzed by a short-lived species that probably contains endo-coordinated η^4-NBD[14] and at most one BTMSA ligand, as required by the mechanistic considerations (Scheme III). Since the large excess of diethylaluminum chloride is necessary for obtaining the soluble catalytic system, it is reasonable to assume that ethylaluminum chloride ligands are found in the inner and outer coordination spheres and participate in the catalytic cycles.

Conclusion

The transient organometallic species formed from $TiCl_4$ and Et_2AlCl in the presence of NBD and BTMSA has unique catalytic properties in that it induces several different reactions in the series. The formation of adduct **1** is the result of a cycloaddition–rearrangement–cycloreversion sequence with two symmetry-forbidden reactions being involved. The isomeric triene **2** arises by a four-step cascade of which three steps are symmetry-forbidden. Due to the presence of the versatile vinyltrimethylsilane moiety, both **1** and **2** may serve as convenient and readily accessible starting points for the preparation of functionalized bicyclo[4.3.0]nonane derivatives. Studies in this direction are under way.

Experimental Section

Methods and Materials. A high-vacuum technique based on all-sealed glass devices and breakable seals was used for all sample transfers and sample manipulations. BTMSA (Fluka) was degassed and distilled in vacuo. NBD (Fluka) was degassed and distilled in vacuo onto solid dimeric titanocene[15] and allowed to stay for 2 days. For the removal of trace impurities that could have quenched the catalyst, NBD was distilled onto the crystalline (arene)titanium(II) complex $(C_6H_6)Ti(AlCl_4)_2$, and after this mixture was shaken for 5 min, it was distilled into a storage ampule. During the latter purification step about one tenth of the NBD polymerized while in contact with the Ti(II) complex. Toluene (Fluka) was shaken with sulfuric acid, dried over $LiAlH_4$, and purified by the same procedure as that for NBD. $TiCl_4$ (Intern. Enzymes) was distilled in vacuo and diluted with toluene to give a 0.1 M solution. Et_2AlCl (Fluka) was purified from traces of the sesquichloride by heating with anhydrous sodium chloride to 180 °C; it was then distilled in vacuo and diluted with toluene to give 1.0 M solution. BTMSA and NBD and the solutions of the catalyst components were distributed in vacuo into ampules equipped with breakable seals and sealed in.

Instrumentation. ESR spectra were taken on an ERS-220 spectrometer (Academy of Sciences, ZWG, Berlin, GDR) in X-band. Sample tubes were sealed to the ampules in which the reactions were carried out as described in preparations of **1**–**3**. The quantitative evaluation of concentrations of paramagnetic species was achieved by comparing the areas under the integrated records with that of a standard sample of $Cp_2TiAlCl_3Et$. Electronic absorption spectra were recorded on a Varian Cary 17 D spectrometer in sealed quartz cells (Hellma). Mass spectra were measured on a JEOL D-100 spectrometer either using a direct inlet or coupled to a gas chromatograph (3% SE-30 on Chromosorb W, 2 m). Infrared spectra were taken on a Nicolet MX-1E FT instrument. NMR spectra were measured on a Varian XL-200 spectrometer (FT mode, 200.057 MHz for ^1H, 50.309 MHz for ^{13}C, and 39.743 MHz for ^{29}Si) in $CDCl_3$ using the residual signal of $CHCl_3$ (7.25 ppm) or tetramethylsilane (for ^{29}Si) as a reference. The protonation of carbon atoms in the ^{13}C NMR spectra was determined by the attached-proton-test and gated-decoupling pulse sequences. The ^{29}Si NMR spectra were obtained by using an INEPT pulse sequence.[16]

Preparation and Reactions. 1. Preparation of 2,3-Bis(trimethylsilyl)-*cis*-bicyclo[4.3.0]nona-2,4,8-triene (1). Et_2AlCl (6 mL of 1.0 M solution in toluene) and $TiCl_4$ (3 mL of 0.1 M solution) were mixed at −78 °C to give an orange solution. BTMSA (2 mL) and NBD (2 mL) were added under cooling with liquid nitrogen, and the reaction ampule with the frozen mixture was sealed off. The mixture was warmed rapidly to 20 °C by shaking in a water bath and then thermostated at 20 °C for 1 h. Then it was opened to air; the contents were diluted with benzene (10 mL), poured into water, and thoroughly washed. The organic layer was dried with sodium sulfate and distilled in vacuo. After the solvents were removed at 30–40 °C, a fraction distilling at 80–100 °C (≥0.5 mmHg) was collected to afford 0.7 g (30% based on BTMSA) of pure **1**. Anal. Calcd for $C_{15}H_{26}Si_2$ (**1**): C, 68.62; H, 9.98. Found: C, 68.98; H, 10.02. **1**: IR (neat) 3058 (m), 3022 (m), 2950 (s), 2924 (sh), 2900 (s), 2845 (m), 1509 (w), 1447 (w), 1408 (m), 1342 (w), 1260 (sh), 1250 (s), 1090 (w), 1034 (m), 1004 (m), 974 (m), 856 (sh), 835 (vs), 755 (s), 732 (sh), 695 (s), 650 (sh), 642 (m), 620 (m), 580 (w), 560 (w), 487 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.01 (dd, $J_{4,5} = 9.8$, $J_{4,6} = 2.4$ Hz, H-4), 5.86 (dddd, $J_{9,8} = 5.8$, $J_{9,1} = 3.1$, $J_{9,7} = 3.0$ Hz, H-9), 5.41 (m, H-8), 5.34 (dd, $J_{5,4} = 9.8$, $J_{5,6} = 2.9$ Hz, H-5), 3.50 (dm, $J_{1,6} = 9.6$ Hz, H-1), 3.03 (m, H-6), 2.73 (m, H-7′), 2.25 (m, $J_{7,7'} = 15.5$, $J_{7,9} = 3.0$, $J_{7,8} = 3.0$ Hz, H-7), 0.18 (s, 9 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 146.88 (s), 142.45 (s), 132.00 (ddd, $^1J = 161$ Hz, $^3J = 6$ Hz), 129.86 (dq, $^1J = 158$ Hz, $^3J = 6.0, 5.0$ Hz), 128.80 (ddd, $^1J = 161$ Hz, $^3J = 5.0$ Hz), 126.64 (dd, $^1J = 157$ Hz, $^2J = 4.5$ Hz, C-4), 48.22 (dm, $^1J = 129$ Hz, C-1), 40.79 (tm, $^1J = 129.5$ Hz), 35.75 (dm, $^1J = 132$ Hz), 1.81 (q), 1.41 (q); ^{29}Si NMR ($CDCl_3$) δ −5.99, −6.46; MS m/z (relative intensity): 262 (M^+, 0.5), 231 (0.3), 188 (7.7), 173 (31), 159 (19), 145 (6.4), 131 (5), 73 (100), 59 (24).

Preparation of 3,4-Bis(trimethylsilyl)-*cis*-bicyclo[4.3.0]nona-2,4,8-triene (2). The same reactants as in the experiment above were mixed. The frozen mixture was warmed rapidly to 60 °C by shaking in a water bath and maintained at 60 °C for

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1 h. The usual workup afforded 1.1 g (45% based on BTMSA) of a mixture consisting of **2** (85%), **1** (10%), and an unidentified 1:1 adduct of NBD and BTMSA (5%) (by GC analysis). The spectral data of **2** (IR, NMR) were obtained with the mixture and corrected for the contribution of **1**. **2**: IR (neat) 3057 (m), 3017 (m), 2950 (s), 2927 (sh), 2900 (s), 2845 (m), 1535 (m), 1440 (w), 1405 (w), 1248 (s), 1048 (m), 854 (sh), 835 (vs), 752 (s), 708 (m), 690 (m), 682 (m), 643 (m), 630 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.14 (dm, $J_{1,2} = 5.0$, $J_{2,5} = 1.2$ Hz, H-2), 5.89 (dd, $J_{5,6} = 3.6$ Hz, H-5), 5.86 (m, H-7), 5.68 (m, H-8), 3.27 (dm, $J_{1,6} = 11$ Hz, H-6), 2.83 (dddd, $J_{1,6} = 11$ Hz, $J_{1,9'} = 6.8$, $J_{1,9} = 8.5$, $J_{1,2} = 5$ Hz, H-1), 2.61 (dm, $J_{9,9'} = 15.6$, $J_{9,1} = 8.5$ Hz, H-9), 2.14 (ddq, $J_{9',8} = 2.3$, $J_{9',7} = 2.3$ Hz, H-9′), 0.12 (s, 9 H), 0.02 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 140.84 (d), 135.71 (d), 135.00 (s), 134.56 (s), 131.82 (d), 131.58 (d), 43.23 (d), 40.42 (t), 36.26 (d), 1.08 (q); ^{29}Si NMR ($CDCl_3$) δ −4.57, −4.66; MS m/z (relative intensity) 262 ($M^{+}\cdot$, 1), 247 (5.5), 231 (1.6), 174 (10.1), 173 (13), 159 (14.3), 145 (3.5), 131 (3), 73 (100), 59 (14.5), 45 (12.3).

Preparation of 8,9,10,11-Tetrakis(trimethylsilyl)tricyclo[5.2.2.0^{2,6}]undeca-3,8,10-triene (3). A. Crude compound **2** (1.2 g, 4.5 mmol), BTMSA (0.76 g, 4.4 mmol), Et_2AlCl (2 mL of the 1.0 M solution), and $TiCl_4$ (1 mL of the 0.1 M solution) were mixed under cooling to −78 °C and then rapidly warmed to 60 °C under vigorous stirring. After 1 h at 60 °C the mixture was diluted with benzene (10 mL), washed with water, and dried with sodium sulfate. The solvents were evaporated in vacuo at 40 °C, a fraction distilling at 80–100 °C (0.2 g) was separated, and the residue was sublimed onto a cold finger at 100 °C to yield 1.2 g of a crystalline material which was further purified by double recrystallization from ethanol; mp 72–73 °C. The liquid distillation product contained mainly **1** and **2** and traces of another 1:1 BTMSA–NBD adduct (m/z 262 ($M^{+}\cdot$), trimethylsilylindene (m/z 188 ($M^{+}\cdot$)), bis(trimethylsilyl)indene (m/z 260 ($M^{+}\cdot$)), and bis- and tetrakis(trimethylsilyl)benzenes (m/z 222 ($M^{+}\cdot$), 366 ($M^{+}\cdot$)), according to GC–MS. Anal. Calcd for (**3**): C, $C_{23}H_{44}Si_4$ (**3**): C, 63.80; H, 10.24. Found: C, 63.75; H, 10.12. **3** IR (KBr pellet) 3048 (w), 3041 (w), 2978 (m), 2952 (s), 2927 (m), 2900 (m), 2843 (w), 1523 (w), 1438 (w), 1407 (w), 1248 (s), 1083 (m), 1004 (w), 988 (w), 973 (m), 933 (m), 834 (vs), 752 (s), 716 (m), 690 (m), 681 (m), 635 (m), 544 (w), 513 (w), 457 (w), 423 (w), cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.41 (dm, $J_d = 5.6$ Hz, 1 H), 5.35 (dm, $J_d = 5.6$ Hz, 1 H), 4.27 (d, $J = 3.0$ Hz, 1 H), 4.25 (d, $J = 2.9$ Hz, 1 H), 2.51 (m, 1 H), 2.02–2.27 (m, 2 H), 1.68 (dm, $J_d = 15.2$ Hz, 1 H), 0.17 (s, 9 H), 0.16 (s, 9 H), 0.14 (s, 9 H), 0.12 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 157.65 (s), 157.47 (s), 156.83 (s), 153.79 (s), 133.02 (d), 131.53 (d), 53.98 (d), 53.09 (d), 52.41 (d), 40.28 (d), 36.77 (t), 1.45 (q), 1.32 (q, 2C), 1.23 (q); ^{29}Si NMR ($CDCl_3$) δ −8.23, −8.29, −8.89, −9.29; MS m/z (relative intensity) 432 ($M^{+}\cdot$, 0.05), 353 (16), 352 (31), 351 (84), 335 (33), 293 (20), 263 (30), 247 (6), 155 (5), 152 (4), 145 (3), 73 (100), 59 (6), 45 (14).

B. A mixture of **1** (0.8 g, 1.8 mmol) and BTMSA (0.38 g, 2.2 mmol) was treated with the same amount of the catalyst as under **A**. This procedure afforded the liquid fraction (0.2 g) and a solid (0.6 g) which gave 0.45 g of **3** after recrystallization from ethanol.

C. Treating NBD (1 mL) and BTMSA (2 mL) with the in situ prepared catalyst under the conditions described for the preparation of either **1** or **2** yielded a mixture from which **3** was isolated by vacuum sublimation. The yield of **3** was 0.5 g when the reaction was run at 20 °C and 0.8 g at 60 °C.

Preparation of 1,2,4,5-Tetrakis(trimethylsilyl)benzene (4). Compound **3** (0.3 g) was heated in vacuo in a 20-mL ampule at 190 °C for 2 h. Cyclopentadiene and dicyclopentadiene were evaporated in vacuo at 40 °C, and the crystalline residue was twice crystallized from ethanol to give 0.23 g (90%) of **4**: mp 169–171 °C (lit.[17] 173 °C); IR (KBr pellet) 3076 (w), 2947 (s), 2897 (m), 1405 (w), 1268 (sh), 1247 (s), 1178 (m), 1087 (m), 835 (vs), 756 (s), 693 (m), 678 (m), 644 (m), 632 (m), 500 (m), 441 (m), 433 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.39 (s, 36 H), 8.00 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 144.75 (s), 141.50 (d), 1.83 (s); ^{29}Si NMR ($CDCl_3$) δ −2.90; MS m/z (relative intensity) 366 ($M^{+}\cdot$, 44), 351 (90), 335 (47), 263 (44), 247 (8), 205 (5), 152 (13), 73 (100), 45 (18).

Isomerization of 1 to 2. Compound **1** (0.5 g) was mixed with Et_2AlCl (2 mL of the 1.0 M solution) and $TiCl_4$ (1 mL of the 0.1 M solution) at −78 °C, and the mixture was rapidly warmed to 60 °C. After workup a mixture of $C_{15}H_{26}Si_2$ isomers was obtained which was identical by GC–MS with that described for the preparation of **2**. Isomerization of **2** (1.1 g) under conditions used for the preparation of **1** (1 h at 20 °C) yielded only the unchanged starting compound in 80% yield.

Registry No. **1**, 101652-96-4; **2**, 101652-97-5; **3**, 101652-98-6; **4**, 17156-61-5; BTMSA, 14630-40-1; NBD, 121-46-0; Et_2AlCl, 96-10-6; $TiCl_4$, 7550-45-0.

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Gas-Phase Chemistry of Transition-Metal-Containing Anions with Nitroalkanes and *n*-Butyl Nitrite

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Received September 10, 1985

The gas-phase ion/molecule reactions of iron-, cobalt-, and chromium-containing anions with a series of nitroalkanes and *n*-butyl nitrite are reported here. A mechanism is proposed in which the anion reacts by a charge-transfer mechanism which results in the cleavage of $C-NO_2$ and N–O bonds, leading to intermediates of the type $RM(CO)_xNO_2^-$ and $RNOM(CO)_xO^-$. These intermediates may then fragment or rearrange further. If charge transfer is the first mechanistic step leading to the observed products, the exothermicity of the charge transfer may determine the number of reaction pathways which are thermodynamically accessible. Thus, on the basis of the observed chemistry of alkyl halides, alcohols, bromochloroalkanes, chloro alcohols, and nitroalkanes, an ordering of the electron affinities of the organometallic reactant species studied here is reported.

Introduction

Recently, the gas-phase ion/molecule chemistry of $Fe(CO)_{3,4}^-$, $Cr(CO)_{3-5}^-$, $Co(CO)_{2,3}^-$, and $CoNO(CO)_{1,2}^-$ with a series of *n*-chloroalkanes, *n*-alcohols, 1,*n*-bromochloroalkanes, and 1,*n*-chloroalcohols was reported.[1] In the chloroalkane reactions, all products could be explained via the formation of a metal insertion/charge transfer intermediate 1. Ligand displacement, chlorine abstraction, and

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