meters must have been largely similar to the reconstructed iceberg drift tracks. The data suggest that this surface current was driven by an inflow of waters from the south into the Arctic Ocean at deeper levels, probably below 1000 m. This implies that some form of deep-water production similar to the present North Atlantic deep water (NADW) formation must have been operative during glacial periods. It is possible that the formation of NADW never completely stopped during glacial intervals, and that it was modified and occurred in a different part of the northern North Atlantic than today. Evidence for southward-flowing surface currents along the entire width of the Norwegian and Greenland seas during glacial intervals exists from the dispersal of coal fragments of eastern Arctic origin and clastic sedimentary rocks from the Barents Shelf in IRD assemblages of the Norwegian Sea (*19*, *23*). Melting of icebergs from the Laurentide and Innuitian ice sheets in the Greenland-Iceland-Norwegian (GIN) seas could have reduced the surface water salinity and thus affected the NADW formation. This process could have initiated cold glacial conditions and contributed to their maintenance and stabilization.

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Synthesis and Characterization of a Stable Dibismuthene: Evidence for a Bi–Bi Double Bond

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Treatment of an overcrowded triselenatribismane, 2,4,6-tris(bis(trimethylsilyl)methyl)-phenyl-1,3,5-triselena-2,4,6-tribismane, with hexamethylphosphorous triamide in toluene at 100°C resulted in the quantitative formation of a stable dibismuthene [TbtBi=BiTbt, where Tbt is 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl], a compound containing a double bond formed between two bismuth atoms. The compound formed as deep purple crystals upon cooling. Ultraviolet-visible and Raman spectra, x-ray crystallographic structural analysis, and theoretical calculations provided evidence for the double bond character of the Bi–Bi bond.

The synthesis of compounds containing double bonds between heavy main group elements has stimulated wide interest (*1*) because of their unusual structure and properties compared with compounds containing second-row elements, such as olefins ($R_2C=CR_2$), azo compounds (RN=NR), and ketones ($R_2C=O$). Several stable compounds with a double bond between heavier group 14 to group 16 elements, such as $R_2E=ER_2$ [E = Si (*2*), Ge (*3*), Sn (*4*, *5*)], RE=ER [E = P (*6*), As (*7*)], and $R_2E=X$ (E = Si, Ge; X = S, Se) (*8*–*10*), have been synthesized by taking advantage of kinetic stabilization afforded by sterically demanding substituents. Distannenes $R_2Sn=SnR_2$ have also been synthesized, but they are known to dissociate into the corresponding stannylene R_2Sn: in solution (*4*, *5*, *11*). To our knowledge, no stable examples containing sixth-row elements have been reported. Here we report the synthesis of a stable dibismuthene, TbtBi=BiTbt (**1**), prepared by using an efficient steric protection group 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl (denoted as Tbt hereafter) developed by us (*12*).

Compound **1** was prepared by deselenation of triselenatribismane **2** with a phosphine reagent. The precursor **2** was readily synthesized (Fig. 1) by nucleophilic substitution of bismuth trichloride with TbtLi, giving the corresponding bismuth dichloride $TbtBiCl_2$ (**3**), followed by treatment of **3** with Li_2Se in tetrahydrofuran. Triselenatribismane **2** was isolated as a stable crystalline compound by gel permeation liquid chromatography and was then treated with an excess amount of hexamethylphosphorous triamide in tolu-

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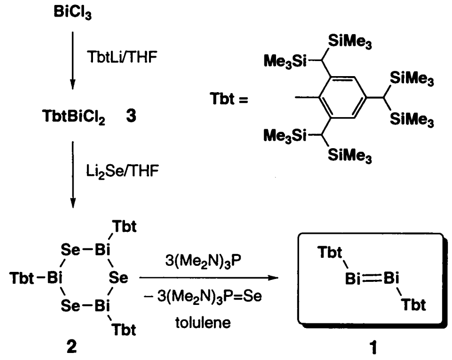

Fig. 1. Scheme for the synthesis of stable dibismuthene **1**.

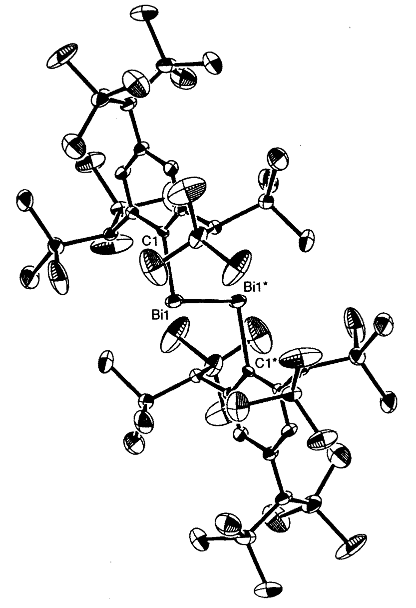

Fig. 2. X-ray crystallographic structure (an ORTEP drawing with 30% thermal ellipsoid plot) and selected crystallographic parameters of dibismuthene **1**. Selected bond lengths and angles: Bi1–Bi1* 2.8206(8) Å; Bi1–C1 2.290(7) Å; and Bi1*–Bi1–C1 100.5(2)°.

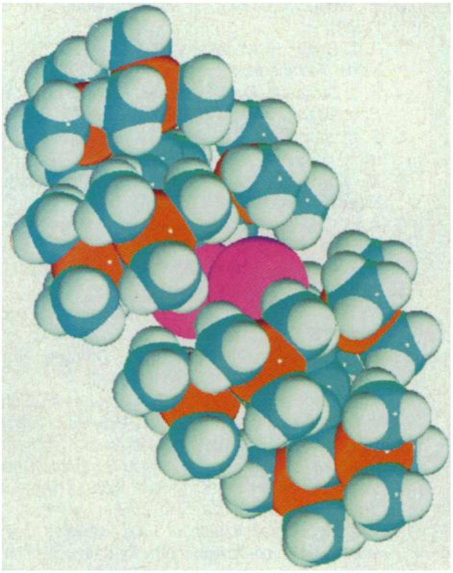

Fig. 3. Space-filling model of dibismuthene **1**.

ene at 100°C in a sealed tube. After the solution was heated for 12 hours, it turned purple, and the dibismuthene **1**, which precipitated from the mixture on cooling, could be isolated as deep purple single crystals by filtration in a glovebox filled with argon (Fig. 1). The dibismuthene **1** has a very low solubility, probably because of the high symmetry of the molecular structure, thus making its isolation quite simple.

The crystals of **1** precipitated from the reaction mixture were suitable for x-ray diffraction analysis in size and quality, and the molecular structure of **1** was determined by x-ray crystallography (Fig. 2) (*13*). Dibismuthene **1** is in the trans form and has a center of symmetry; the two bismuth atoms and the two ipso carbons of the Tbt groups attached to the bismuth atoms all lie in the same plane. The benzene rings of the Tbt groups are placed almost perpendicular to this plane, with a dihedral angle of 90.70°. As can be seen in the space-filling representation of the crystal structure of **1** (Fig. 3), the sterically demanding Tbt groups effectively surround the reactive Bi–Bi double bond moiety of **1** and thereby suppress its oligomerization.

Two important parameters in the structure of **1** are the Bi–Bi bond length [2.8206(8) Å (the number in parentheses is the error in the last digit)] and the Bi–Bi–C angle [100.5(2)°]. This Bi–Bi bond is 6% (0.169 Å) shorter than the Bi–Bi single bond length of 2.990(2) Å in $Ph_2Bi–BiPh_2$ (*14*). This agrees reasonably well with the calculated bond shortening of 7% (0.214 Å) from $H_2Bi–BiH_2$ (3.009 Å) to HBi=BiH (2.795 Å) (*15*). The bond shortenings are also comparable with those reported for diphosphenes; the experimental value is 8% (0.183 Å) from $(PhP)_5$ [2.217(6) Å] (*16*) to ArP=PAr [2.034(2) Å; Ar = 2,4,6-tri-*t*-butylphenyl] (*6*), whereas the calculated value is 9% (0.200 Å) from $H_2P–PH_2$ (2.247 Å) to HP=PH (2.047 Å) (*15*). Moreover, the bond shortening observed for **1** is in sharp contrast to the considerably elongated Sn–Sn bond in the isolated distannenes $R_2Sn=SnR_2$ [2.768(1) Å for R = $CH(SiMe_3)_2$ (*4*) and 2.910(1) Å for R = 2-*t*-butyl-4,5,6-trimethylphenyl (*11*)], the bond lengths of which are almost equal to or longer than the typical Sn–Sn single bond length [for example, 2.780(4) Å for $Ph_3Sn–SnPh_3$ (*17*)].

The observed Bi–Bi–C angle of 100.5° deviates greatly from the ideal sp^2 hybridized bond angle (120°), because the heavy Bi atom (the heaviest stable element in the periodic table) has the lowest tendency of the group 15 elements to form a hybrid orbital; the size difference of the valence *s* and *p* orbitals increases from N to Bi (the significant 6*s* orbital contraction originates mostly from the relativistic effect), and Bi prefers to maintain the $(6s)^2(6p)^3$ valence electron configuration. The use of these three orthogonal 6*p* orbitals without significant hybridization leads to a bond angle of ~90° at Bi (*18*). The Bi–Bi–C bond angle in **1**, being close to 90°, provides evidence for the core-like nature of the 6*s* electrons, that is, the so-called "inert *s*-pair effect" or "nonhybridization effect" (*19*).

Dibismuthene **1** is purple in hexane and shows two absorption maxima at 660 nm [shoulder, molar absorption coefficient (ε) 100] and 525 nm (ε 4000), which correspond to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the Bi=Bi chromophore, respectively. Relative to the values reported for diphosphenes (*6*, *20*, *21*) and diarsenes (*7*, *22*), these red shifts agree with the changes in the n, π, and π* orbital levels calculated for HE=EH (E = P, As, Sb, Bi) (*18*). These electronic spectral data suggest that **1** features double bonding between the Bi atoms even in solution, as in the cases of the lighter congeners such as diphosphenes and diarsenes. In the Fourier transform (FT)–Raman spectrum, a strong band attributable to the Bi–Bi stretching mode was observed at 134 cm^{-1} for the dibismuthene **1** (solid; excitation, He-Ne laser 632.8 nm). This is 31 cm^{-1} higher than the Bi–Bi stretching frequency of 103 cm^{-1} for $Ph_2Bi–BiPh_2$ (*23*), agreeing with the frequency shift of 34 cm^{-1} calculated for HBi=BiH (153 cm^{-1}) and $H_2Bi–BiH_2$ (119 cm^{-1}) (*15*).

Dibismuthene **1** is considerably stable in the solid state, retaining its purple color for several hours on exposure to the open air, but it undergoes slow reaction with oxygen to give quantitatively the corresponding colorless 1,3,2,4-dioxadibismuthene derivative, $(TbtBiO)_2$ **4**, the structure of which was determined by x-ray crystallographic analysis. In solution, **1** reacts with oxygen quite rapidly to give **4**.

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The Stereodynamics of a Gas-Surface Reaction

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Measurements of the influence of reactant alignment on the rates of chemical reactions provide direct information concerning the atomic motions necessary for chemical transformation. Data presented here show that at low collision energy, the dissociative adsorption of deuterium (D_2) on the (111) surface of copper has a much higher probability for broadside than for end-on collisions. Furthermore, this steric preference is sensitive to the kinetic energy of the incident molecule, almost disappearing as the energy increases to 0.8 electron volt. This study shows that the dynamic conditions of a surface chemical reaction can profoundly influence the associated steric requirements.

Reactant orientation and alignment can affect or even dictate the outcome of a chemical encounter. Such steric effects are of ubiquitous importance in chemistry. For example, the reaction K + $CH_3I \rightarrow$ KI + CH_3 proceeds only when the potassium approaches the iodine end of the CH_3I molecule (*1*). More generally, the rates of bimolecular nucleophilic substitution (S_N2) reactions are thought to be almost entirely determined by steric factors (*2*). Similarly, the activity and specificity of enzymes depend strongly on their steric interactions with the substrate (*3*), which may facilitate or preclude enzyme-substrate binding. In these reactions, a specific alignment geometry is expected to be required in order to follow the path of lowest energy between reactants and products; the preferred approach geometry will therefore reflect the structure of the reaction's transition state. Detailed knowledge of steric preferences can thus provide precise information on how the atoms are moving as the chemical reaction occurs; to gain a complete understanding, we must probe the steric requirements as a function of the collision conditions, that is, the vibration, rotation, and translation of the reactant. Unfortunately, despite the large body of empirical data substantiating the importance of steric effects, little is known about how the steric requirements depend on these aspects of the reactive encounter.

Chemical reactions occurring on surfaces offer an excellent opportunity to study chemical reactions at this level of detail. The surface naturally provides an oriented reactant that can be easily manipulated in the laboratory frame (*4*). Several theoretical calculations (*5*) have predicted strong steric effects in one of the simplest and best studied gas-surface reactions, dissociative adsorption of hydrogen at a Cu surface (*6*). The results indicate that the reaction occurs preferentially when the molecule approaches with its bond parallel to the surface. These predictions have recently been qualitatively confirmed experimentally (*7–9*), but no measurements on the kinetic-energy dependence of the steric effects were reported.

Here we report measurements of the alignment of D_2 formed in the reaction of D atoms on a Cu(111) surface as a function of the kinetic energy of the desorbing D_2. At low energy, the desorbing D_2 is strongly aligned with its bond axis parallel to the surface, but the probability of this alignment decreases rapidly with increasing energy. These results imply that the dissociative adsorption of D_2 at a Cu surface shows a strong steric preference for broadside collisions when the molecules strike the surface at low translational energy. This steric preference all but disappears as the collision energy is raised above the average activation barrier for the reaction. These measurements provide insight into the geometry of the transition state and the dynamics of the reaction in the critical energy regime near the barrier.

Our experimental approach is based on the polarization dependence of an appropriately chosen resonance-enhanced multiphoton ionization (REMPI) scheme for D_2. Linearly polarized light was used to selectively ionize D_2 in specific vibration-rotation (**v**, **J**) states (*10*) whose molecular bond axis is parallel to the electric field vector (*11*). The ionization was performed in a field-free region, such that the flight time of the ions to the detector gave a measure of the velocity of the desorbing D_2. By rotating the polarization of the

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