with L-Selectride (Aldrich) or methyllithium, followed by HBF_4 etherate, to dihydrofuran complexes **8**.[15] This was then precipitated from solution, washed free of impurities, and finally decomplexed by brief exposure to iodide in acetone solution.

Further synthetic applications of the chemistry of these organoiron complexes is being examined.

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Registry No. 3a, 78251-22-6; **3b**, 92695-23-3; **4** (R = Et; Nu_1 = Ph), 92719-92-1; **4** (R = Et; Nu_1 = 2-cyclohexanone), 92695-24-4; **5**-*t* (R = Me; Nu_1 = Me), 92695-25-5; **5**-*t* (R = Et; Nu_1 = Me), 92761-54-1; **5**-*c* (R = Et; Nu_1 = Me), 55337-32-1; **5**-*t* (R = Et; Nu_1 = *n*-Bu), 92695-26-6; **5**-*c* (R = Et; Nu_1 = *n*-Bu), 92761-55-2; **5**-*t* (R = Et; Nu_1 = 2-cyclohexanone), 92695-27-7; **6**-*c* (Nu_1 = N_2 = Me), 56323-74-1; **6**-*t* (Nu_1 = Nu_2 = Me), 56323-76-3; **6**-*c* (Nu_1 = Nu_2 = *n*-Bu), 92719-93-2; Fp(isobutylene)BF_4, 41707-16-8; $Me_2Cu(CN)Li_2$, 80473-70-7; (*n*-Bu)$_2$Cu(CN)Li_2, 80473-69-4; Me_2CuLi, 15681-48-8; PhMgBr, 100-58-3; dicarbonyl(η^5-2,4-cyclopentadien-1-yl)[(4,5-η)-1-phenyl-1,2-dihydrofuran]iron(1+), 92695-28-8; dicarbonyl(η^5-2,4-cyclopentadien-1-yl)-[(2,3-η)-3a,4,5,6,7,7a-hexahydroindene]iron(1+), 92695-31-3; lithium cyclohexanone enolate, 56528-89-3; lithium acetophenone enolate, 55905-98-1; (Z)-2-propen-1-ylcyclohexanone, 92695-29-9; (E)-2-propen-1-ylcyclohexanone, 92695-30-2; (Z)-1-propenylbenzene, 766-90-5; (E)-1-propenylbenzene, 873-66-5; (Z)-1-hexenylbenzene, 15325-54-9; (E)-1-hexenylbenzene, 6111-82-6.

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(15) The stereochemistry shown for these complexes in Scheme II and Table I follows from the stereospecificity defined earlier for Fp driven reactions and from preferred trans addition of nucleophile to adduct **7**. The structural assignment for **8** is supported by greater shielding of H-4 and H-5 protons in the dihydrofuran complexes compared with the free dihydrofurans. These protons must consequently be in the shielding region of the Fp group (along the Cp ring–centroid iron axis)[5] and hence cis to these protons.

Preparation of *n*-Octadecaborane(22), *n*-B₁₈H₂₂, by Oxidative Fusion of Dodecahydrononaborane(1–) Clusters

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Oxidative fusion of small clusters has great potential as a synthetic route to larger cluster systems. Application to the synthesis of carborane and metallocarborane systems is well documented.[1] We now report the preparation of n-$B_{18}H_{22}$ by the oxidation of $Me_4NB_9H_{12}$ with metal halides including Hg(I), Hg(II), Sn(IV), and Fe(II) salts.

n-$B_{18}H_{22}$ was first observed in 1962 as one of the components in a mixture of isomers prepared by the hydrolysis of ethanolic solutions of $B_{20}H_{18}^{2-}$ [2] and has since been systhesized by several other methods with yields ranging from poor to moderate.[3] It's structure, see Figure 1, comprises two decarborane-like structural units fused along the common B(5)–B(6) edge.[4] i-$B_{18}H_{22}$ exhibits
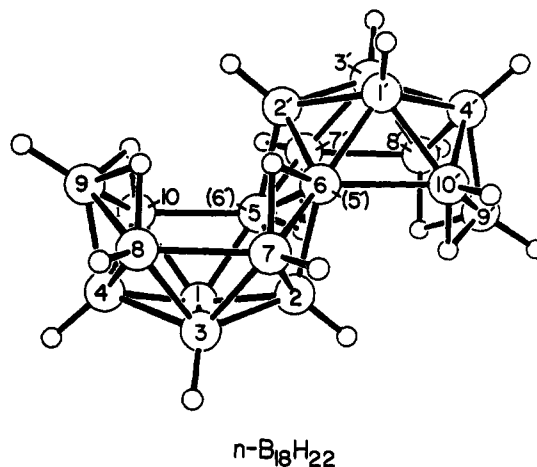
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n-B₁₈H₂₂

Figure 1. Structure and numbering scheme of n-$B_{18}H_{22}$.[4]

Table I. Yield of n-$B_{18}H_{22}$ as a Function of Salt

salt	% yield	salt	% yield
$HgCl_2$	47	Hg_2Cl_2	58
$HgBr_2$	68	$FeBr_2$	31
HgI_2	63	$SnCl_4$	low

a very similar structure in which the cages are also edge fused but twisted relative to each other.[5]

In our optimized synthesis of n-$B_{18}H_{22}$, 0.70 g (1.9 mmol) of $HgBr_2$ was added with stirring to 0.34 g (1.8 mmol) of $Me_4NB_9H_{12}$,[6] which had been dissolved in 50 mL of freshly distilled CH_2Cl_2. A grey precipitate as well as minute droplets of elemental mercury began to appear within 5 min. Stirring was continued at room temperature overnight, after which the reaction mixture was filtered and the CH_2Cl_2 removed in vacuo. The resulting residue was extracted with toluene, and this solution was, in turn, filtered and the solvent removed to yield 0.13 g (0.60 mmol) n-$B_{18}H_{22}$, a 68% yield. All manipulations were performed under a nitrogen atmosphere using standard Schlenk line techniques. The light yellow product was identified by comparison of its ^{11}B NMR to that reported by Todd.[7]

The highest yield preparations of n-$B_{18}H_{22}$ have resulted from the use of $HgBr_2$ as in the synthesis described above. This reaction has been directly scaled up to yield 10 mmol of product without significant variation in yield. Analogous reactions using $HgCl_2$ and HgI_2 as well as salts of Hg(I), Sn(IV), and Fe(I) also resulted in the production of n-$B_{18}H_{22}$ but at significantly reduced yields, see Table I. Attempts to run the reaction in more basic solvents only resulted in reduced yields or the production of $B_9H_{13}\cdot L$ species.

Besides the n-$B_{18}H_{22}$, we find the only other boron-containing products of these reactions to be a mixture of two compounds we have tentatively identified as mono- and dihalogenated nonaboranes. We also observe the production of hydrogen gas but in a significantly smaller quantity than would be expected if the simplest view of this reaction is considered, see eq 1.

$$3HgBr_2 + 4Me_4NB_9H_{12} \rightarrow$$
$$2B_{18}H_{22} + Hg + Hg_2Br_2 + 2H_2 + 4Me_4NBr \quad (1)$$
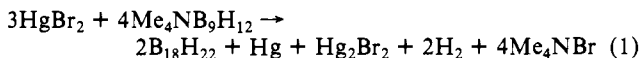
The reaction we describe represents a straightforward synthesis of n-$B_{18}H_{22}$ in good yield with only the simplest precautions necessary to exclude gross amounts of air and water. We have not yet observed any metal-containing intermediates of the type suggested by the oxidative fusion work of Grimes.[1] Any serious

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consideration of the reaction's mechanism, then, will necessarily await the unambiguous identification of the boron-containing byproducts.

Dimethylsilylene: Its Optical Absorption Spectrum and Reaction Kinetics[1]

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Photolysis of dodecamethylcyclohexasilane[2] (I) has been used as a convenient source of dimethylsilylene (II) in solution[3-9] and in the gas phase[10] (eq 1). The reaction has also been used to

$$c\text{-}(Me_2Si)_6 \xrightarrow{h\nu} c\text{-}(Me_2Si)_5 + Me_2Si: \qquad (1)$$
$$\text{I} \qquad\qquad\qquad \text{II}$$
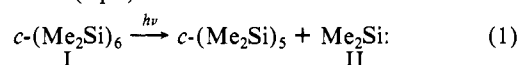
generate the silylene in hydrocarbon and argon matrices so that its infrared,[11] UV–visible[12] (λ_{max} = 450 nm), and fluorescence spectra[12] could be recorded. In fact, irradiation in the UV–visible band at 450 nm has been used to induce rearrangements of II which have been monitored by infrared spectroscopy.[11] We report results which show that this system is more complicated than the current literature suggests and which demonstrate that the UV–visible spectrum of II has been incorrectly assigned or that there is a substantial shift ($\sim$100 nm) in its absorption maximum in going from matrices to solution.

Laser flash photolysis[13] (λ = 308 nm, pulse width 8 ns, power 80 mJ per pulse) of I (10^{-4} M), in 3-methylpentane or cyclopentane solvent at 293 K, gave an absorption band at 350 nm. This transient grew with a lifetime of 74 ns and decayed in 8 μs. No band was detected at 450 nm.

Quenching experiments suggest that the transient absorption at 350 nm was due to dimethylsilylene (II). Addition of triethylsilane, an effective silylene scavenger,[4,9] quenched the transient absorption (eq 2). The rate constant for this reaction, k_2, was

$$Me_2Si: + Et_3SiH \rightarrow Et_3SiSi(Me)_2H \qquad (2)$$
$$\text{III}$$
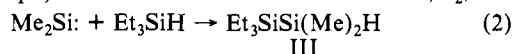
measured by monitoring the pseudo-first-order rate constant, k_{obsd}, for the disappearance of the transient as a function of substrate concentration, eq 3, where k_0 describes the decay of the transient

$$k_{obsd} = k_0 + k_2[Et_3SiH] \qquad (3)$$

in the absence of the quencher. It was found that k_2 = 2.0 × 10^6 M^{-1} s^{-1} in cyclopentane solvent.

In similar vein, methanol quenched the absorption spectrum at 350 nm (eq 4), although the reaction kinetics were a little

$$Me_2Si: + MeOH \rightarrow MeOSi(Me)_2H \qquad (4)$$
$$\text{IV}$$
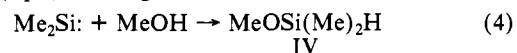
unusual. In cyclopentane as solvent and at methanol concentrations below 0.05 M, the rate constant for quenching, k_4, was found to be 3.1 × 10^7 M^{-1} s^{-1} while above this concentration it was 5.7 × 10^6 M^{-1} s^{-1}. Similar effects have been observed in competition studies of the insertion reactions of dimethylsilylene into Si–H and O–H bonds.[9] They are presumably related to changes in the distribution of methanol monomers and oligomers that occur when the alcohol concentration is varied. However, we were unable to account for the sharp change in reaction kinetics by quantitative analysis of the data in these terms, although such an approach was successful for arylchlorocarbenes.[14]

The methanol quenching experiment was repeated in tetrahydrofuran as solvent, which was chosen for its ability to prevent oligomerization of the methanol.[15] The absorption spectrum was "blue shifted" by the solvent such that λ_{max} = 300 nm. In the absence of methanol the absorption grew with a lifetime of 30 ns and decayed with one of 8 μs. The rate constant for reaction with methanol was found to be 3.1 × 10^7 M^{-1} s^{-1}. As expected, tetrahydrofuran eliminated the unusual kinetic behavior, and the rate constant measured in this solvent was quite similar to that observed at low methanol concentrations in cyclopentane.

Product studies were carried out by photolyzing I (0.05 M) and triethylsilane (2.5 M) in cyclopentane in a photochemical reactor (300 nm). Analysis by GC/MS showed that III had been formed in 85% yield at 64% conversion of I. In addition, product studies were carried out in cyclopentane solution with methanol (0.38 M) as substrate. While the simple insertion product IV was formed in >95% yield V and VI were detected in yields of 1% and 2%,

$$MeO(Me_2Si)_3H \qquad MeO(Me_2Si)_4H$$
$$\text{V} \qquad\qquad\quad \text{VI}$$

respectively, at 43% conversion of I. Similar results were obtained when decamethylcyclopentasilane was used as the dimethylsilyene source.[16]

To confirm that the absorption spectrum at 350 nm was indeed due to dimethylsilylene, we carried out a competition study by photolyzing a mixture of I (0.04 M), methanol (0.27 M), and triethylsilane (0.22 M) in cyclopentane to 80% conversion of I. Product analysis indicated that the ratio k_4/k_2 was 2.1 whereas the laser flash photolysis results (vide supra) gave 2.4.

While we were unable to detect the 450-nm absorption previously assigned[12] to dimethylsilylene by photolysis at 308 nm, we were able to detect an absorption at a similar wavelength by photolysis with much higher energy radiation (249 nm, pulse width 8 ns, power up to 250 mJ per pulse). Under these conditions, a band at 470 nm was detected along with the 350-nm band. The former was present immediately after the laser flash and decayed in 192 ns and could not be quenched by methanol (0.2 M) or triethylsilane (0.15 M).

Product studies carried out in methanol as solvent, with photolysis of I at 250 nm, revealed no new products, which was consistent with this observation and suggests that the 470-nm transient was a species, present in low concentration, that gave insignificant yields of chemical products *or* that it decomposed to give dimethylsilylene.

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