The Si-Si bond length of 2.606 (2) Å is within the range of various estimates of the Si and W covalent radii (2.47-2.77 Å). The experimental range for Si-W and Mo-Si bonds in seven structurally characterized silyl complexes is 2.389-2.669 Å. The Si-Si bond distance in 1b is 2.260 (2) Å, a value that falls midway between the expected values for a single bond (2.35 Å) and a double bond (2.14 Å). However, unusual Si-Si distances have also been observed in other ESi2 ring systems: E = O (2.227 (2) Å), NR (2.232 (2) Å), CH2 (2.272 (2) Å), S (2.289 (2) Å), Te (2.32 Å), and SiR2 (2.40 Å). Among these main-group rings, however, the Si–Si distance decreases with increasing electronegativity and smaller size of the non-silicon atom. The extensively short Si–Si bond in 1b, which contains a large endopropositive tungsten center, does not fit this trend and most probably results from partial Si–Si double bond character as described by the Dewar–Chatt–Duncanson model.

Another measure of disilene character in 1b is the extent of pyramidalization at silicon. The angles subtended at each silicon by the methyl groups and the other silicon total 348.3°. Between the 360° and 329.1° values expected for sp3 and sp2 hybridization, the planes containing the SiMe2 fragments are bent away from the tungsten center by 30.2° from the “olefin” plane containing the two silicon atoms and perpendicular to the WSi2 plane. Thus the silicones are somewhat pyramidal, but less so than found for carbonyl in ethylene complexes of low-valent early-transition metals (Crp5, Ti(CH3)2, 35°; Crp5Ta(CHCMe3)(PMe3)(C2H4), 34°). Adverse nonbonded interactions with the Cp rings may increase the degree of nonplanarity at the silicon atoms. The C7–C3 (Cp–Me) separation is 3.30 Å, within the sum of the van der Waals radii (3.40 Å), and the calculated closest H–H contact is ~2.0 Å. Steric interactions with the Cp rings may also be responsible for the small C7–Si–C8 angle of 104.0° (4). Although 1b is the first structurally characterized complex of its type, there have been two previous reports of mononuclear transition-metal disilene complexes. In 1987, West briefly described a compound formed by reaction of the stable disilene [D(Mo–Si)2]2 with Cp*Ta(CHCMe3)(PMe3)(C2H4), 2.513 (2) Å.12

were prepared from $P$.

Spectroscopic data complementary to the sequence $5'-$CAAAAAAAG$-3'$ and nucleotides incorporating the flexible nucleoside analogue containing one or more building blocks constructed, for the first time, from an optically active glycerol derivative (a flexible nucleoside), incorporation of the oligonucleotide into duplex DNA, and measurements of the strength of the duplex formed between flexible and natural oligonucleotides.

Optically active flexible nucleoside analogues bearing thymine were prepared from (S)-3-(benzoxyl)-1,2-propanediol (Fluka) by the route shown in Scheme I, which yielded 2 with $[\alpha]_D^{346} = -4.4^\circ$ ($c = 1.76$, acetone). The pivaloyl protecting group used to protect selectively the primary hydroxyl group was only partly satisfactory, as it undergoes migration during chloromethylation. However, considerations of cost and synthetic flexibility made it the optimal solution to the synthetic problem. Spectroscopic data on detritylated 2 were identical with those reported in the literature.

The melting temperatures of a series of duplexes of oligonucleotides incorporating the flexible nucleoside analogue complementary to the sequence 5'-CAAAAAAAG-3' and 5'-CTTTATTTG-3' were determined (Table I). The melting temperature of duplex DNA is lowered by 9-15 $^\circ$C for each flexible nucleoside incorporated into a strand (Table I). The effect is not precisely additive; the melting temperature of a strand containing two adjacent residues is slightly lower than the melting temperature of a strand containing the two separated by a natural nucleoside. However, the destabilization is similar to that created by a GT mismatch.

First principles suggest that incorporation of flexible nucleoside analogues into an oligonucleotide chain decreases its ability to form duplex structures, as the entropy lost upon going from two separated by a natural nucleoside than in one containing natural oligonucleosides. We did not, however, anticipate that the decrease in stability would be so great. From these results, it seems unlikely that oligonucleotides of moderate length (shorter than 15 bases) composed entirely of flexible nucleosides will form stable duplex structures with complementary natural oligonucleotides in aqueous solution.

This result is disappointing for those hoping to use flexible oligonucleotide analogues as antisense compounds or as probes. Further, this result diminishes the likelihood that the first self-replicating systems used flexible oligonucleotide analogues. However, it should be emphasized that it is not yet known what amount of stability in duplex structures is desirable to create a primitive self-replicating system.

The ubiquity of ribose in modern biochemistry strongly suggests a central role for ribose at the time in natural history when modern metabolism was emerging. However, modern biochemistry cannot be extrapolated back to organisms more ancient than the first that contained a genetically encoded messenger RNA. Thus, the question as to whether RNA was first can be resolved only by chemical experiments such as those reported here. By raising doubts about the suitability of flexible

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**Table I. Melting Temperatures of Duplexes Containing Flexible Analougues**

<table>
<thead>
<tr>
<th>Oligonucleotide</th>
<th>$T_m$, $^\circ$C</th>
<th>$T_m$, $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5'TTTTTTGG'</td>
<td>40</td>
<td>5'CAAAAAAAG'</td>
</tr>
<tr>
<td>3'GAAAAAGG'</td>
<td></td>
<td>3'GTTATTTG'</td>
</tr>
<tr>
<td>5'C'TTTTTTGG'</td>
<td>25</td>
<td>5'CAAAAAAAG'</td>
</tr>
<tr>
<td>3'GAAAAAGG'</td>
<td></td>
<td>3'GTTATTTG'</td>
</tr>
<tr>
<td>5'C'TTTTTTGG'</td>
<td>13</td>
<td>5'CAAAAAAAG'</td>
</tr>
<tr>
<td>3'GAAAAAGG'</td>
<td></td>
<td>3'GTTATTTG'</td>
</tr>
<tr>
<td>5'C'TTTTTTGG'</td>
<td>11</td>
<td>5'CAAAAAAAG'</td>
</tr>
<tr>
<td>3'GAAAAAGG'</td>
<td></td>
<td>3'GTTATTTG'</td>
</tr>
<tr>
<td>5'C'TTTTTTGG'</td>
<td>21</td>
<td>5'CAAAAAAAG'</td>
</tr>
<tr>
<td>3'GAAAAAGG'</td>
<td></td>
<td>3'GTTATTTG'</td>
</tr>
<tr>
<td>5'C'TTTTTTGG'</td>
<td>55</td>
<td>5'CAAAAAAAG'</td>
</tr>
<tr>
<td>3'GAAAAAGG'</td>
<td></td>
<td>3'GTTATTTG'</td>
</tr>
</tbody>
</table>

*Upper-case letters refer to deoxyribonucleotides, while lower-case letters refer to glyceronucleosides. Melting temperature ($T_m$) were determined by measuring change in absorbance at 260 nm (cuvette, 1-mm path length) as a function of temperature at 0.050 mM of each strand in sodium phosphate buffer (10 mM, pH 7.0) containing NaCl (1 M) and EDTA (10$^{-4}$ M). For the duplex of CTTTTTTTTG and CAAAAAAAAG, and additional measurement was performed in Tris buffer (10 mM, pH 7.0) containing MgCl$_2$ (100 mM); no transition was observed under these conditions. When a base line at low temperatures was observed, the $T_m$ was calculated by using sloping base lines. For duplexes with $T_m < 20$ $^\circ$C, such a base line could not be observed in water, and $T_m$ values were calculated by using a flat base line.

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(7) Of course, these results do not exclude the possibility that an oligonucleotide composed entirely of flexible building blocks will not form a stable duplex with a second strand also entirely composed of flexible building blocks.


(10) We are indebted to L. Orgel for making this point clearly.


sugars as building blocks for replicating systems, these results direct thinking once again toward ribose itself, and chemical work seeking an improved abiotic synthesis of ribose would be most desirable.

(16) Note Added in Proof: In the synthesis of these oligomers, coupling yields were ca. 90% for glycerothymine and >99% for natural nucleotides. The product oligonucleotides were purified by reversed phase HPLC (Nucleosil C-4 column, gradient from 15% to 30% acetonitrile in 0.1 M triethylammonium acetate) prior to the removal of the 5'-trityl groups and deuterolysis (80% acetic acid). Samples of the oligonucleotides containing the flexible base were digested with spleen phosphodiesterase, snake venom phosphodiesterase, and bacterial alkaline phosphatase. HPLC of the digests showed the expected nucleotides in their expected ratios.

A New Access to Acyl- and Aroyllithiums via Lithium-Tellurium Exchange

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The most straightforward method for nucleophilic introduction of acyl and aroyl groups into organic molecules is the use of carboxylic anions, represented by acyl- and aroyllithiums, as nucleophiles. Their synthetic utility, however, has been severely limited for a long time because of difficulty both in their generation and in control of their reaction courses. Notable advances in this chemistry appeared in the 1980s.

In 1982, Seyferth et al. succeeded in an efficient intermolecular trapping of acylithiums under carefully controlled reaction conditions. Shortly after, Murai and we disclosed a unique intramolecular conversion of acylithiums into lithium enolates based on 1,2-silicon shift. As for the methodology for generation of acyl- and aroyllithiums, there are only two methods available so far. One is the reaction of acylsilanes with fluoride ion, where corresponding adducts were reaction of acylsilanes with fluoride ion, where corresponding adducts were obtained in the presence of electrophiles. Alternative mechanisms have been also postulated. (a) Schinzer, D.; Heathcock, C. H. Tetrahedron Lett. 1981, 22, 1881. (b) Degi-Iannuzzi, A.; Pika, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. J. Chem. Soc., Chem. Commun. 1980, 1201. (c) DePuy, C. H.; Bierbaum, V. M.; Davis, R. J.; Dwyer, M.; Sonoda, N. J. Am. Chem. Soc. 1985, 107, 3385. (d) Page, P. C. B.; Rosenthal, S.; Williams, R. V. Tetrahedron Lett. 1987, 28, 4455.


Under similar conditions, [p-(trifluoromethyl)benzoyl]lithium and (2,6-difluorobenzoyl)lithium (2b,c) can be generated from the corresponding telluroesters (1b,c) in good yields (entries 3 and 4). Efficient generation of acyllithiums bearing no α-hydrogen, e.g., pivaloyllithium and (1-adamantylcarbonyl)lithium (2d,e), has been attained also (entries 5–11). In the case of acyllithiums, reactions at –78 °C using tert-butyllithium gave favorable results when pinacolone was used as an electrophile (entries 5–7 and 11). Chloroacetyltrimethylsilane is also suitable electrophile, and the desired product, acylsilane 4, was formed in good yield by using butyllithium at –105 °C (entry 8). Use of pivaldehyde as an electrophile afforded a poor yield of α-hydroxy ketone 5 due to rapid addition of tert-butyllithium to the aldehyde (entry 10). Although tert-butyl octanetelluroate gave octanoyltrimethylsilane in only ca. 10% yield under conditions similar to those of entry 8, the exchange reaction might have proceeded efficiently because an almost quantitative amount of dibutylltelluride was obtained from the resulting mixture.

In order to test the stability and the reactivity of benzoyllithium, we subsequently added pinacolone to the mixture obtained by the reaction of 1a with butyllithium performed at –105 °C in THF/Et3O for 1 min. The result that 3a (16%), benzoin [34%, via dimerization of in situ formed benzoyllithium (2a)], and benzil (21%, probably derived by the reaction of 2a with 1a) were formed, together with 81% of dibutyl telluride, indicates that benzoyllithium is extremely reactive, having a lifetime much shorter than 1 min, even at –105 °C. The fact that benzene and alcohol 6 were not detected from the resulting mixture suggests that elimination of carbon monoxide from 2a leading to phenyllithium may be ruled out under these conditions.  


(11) The result clearly indicates that butyllithium attacked Te atom exclusively affording benzoyllithium (2a), which then reacted with pinacolone to give 3a. For other byproducts formed, see supplementary material.