

free energies.¹² These two conformations are due to the presence of diastereoisomers. The complex (m.p. 153–154.5°) prepared from optically inactive *sec*-butylamine contains equimolar amounts of a racemic [(+, +) and (–, –)] and a meso [(+, –)] form. The two optically active complexes (m.p. 192–193°) prepared from (+)-amine ($[\alpha]_D^{23} + 7.53^\circ$) or (–)-amine ($[\alpha]_D^{23} - 7.50^\circ$)¹³ are accordingly (+, +) or (–, –) and give identical spectra corresponding to the outer set of lines (Fig. 1b). These active complexes therefore possess a slightly more stable tetrahedral form than does the meso complex, which produces the smaller set of contact shifts. The intrinsically dissimilar tetrahedral forms are possibly further differentiated by a lack of free rotation of the *sec*-butyl groups about the C–N bond. Two distinct sets of interactions between these groups are possible through the agencies of direct steric interference or a correlation type solvent effect. Evidence that solvent does not interact equivalently with the two diastereoisomers is given by the inequality of the following contact shift ratios for the (+, +) and (+, –) complexes, respectively: $(\Delta H_i)_{\text{CDCl}_3}/(\Delta H_i)_{\text{CS}_2} = 2.37 \pm 0.02, 2.52 \pm 0.04$.

Facile ligand exchange is uniquely demonstrated by use of the active complexes. Equimolar solutions of the (+, +) and (–, –) species in CS₂ or CDCl₃ when mixed develop within 7 min. the spectrum of Fig. 1a. Integration shows the ratio of active and inactive products is the same from both direct reaction and ligand exchange and is 1.10 ± 0.05 in CS₂ solution.

Although attempts to detect geometrical isomers of metal complexes by nuclear resonance have recently been successful,¹⁶ these results represent the first detection by such means of diastereoisomeric complexes or, to our knowledge, of any diastereoisomeric pair. Full details of resonance studies of type I complexes will be reported subsequently.

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(12) The possibility that the two tetrahedral forms could also differ in their intrinsic *g*-values and thereby contribute partially to the distinguishability of the two sets of resonances cannot be excluded at present.

(13) The amines were resolved with (+) and (–)-tartaric acids according to Thome¹⁴ and Bruck, *et al.*¹⁵ The latter obtained $[\alpha]_D^{25} + 7.48^\circ, -7.64^\circ$.

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ELECTRON DELOCALIZATION INVOLVING SILICON IN IONS DERIVED FROM BIS(2,2' BIPHENYLENE) SILANE¹

Sir:

The participation of the 3d orbitals of silicon to effect enhanced bonding in various covalently bonded silicon compounds has long been a subject of speculation. Participation of this kind has been used to explain such diverse anomalies as the trigonal planar structure of trisilylamine² and the unexpectedly low +*I* effect of a trimethylsilyl substituent in aromatic molecules.³

Recently, Townsend has reported electron spin resonance results for ions derived from various arylsil-

anes.⁴ He was prevented from making any meaningful estimate of silicon involvement in electron delocalization by the nature of arylsilane ions studied.

We have found that ions produced by the potassium reduction of bis(2,2'-biphenylene) silane, a compound first prepared by Gilman and Gorsich,⁵ possess magnetic and chemical properties which afford direct evidence of silicon participation in electron delocalization.

When a dilute solution of bis(2,2'-biphenylene) silane in 1-methyltetrahydrofuran or in 1,2-dimethoxyethane is treated briefly at –60° with pure potassium metal, a wine red solution is obtained. This solution appears to be reasonably stable in the absence of excess potassium metal. At –60° the wine red solution exhibits an intense paramagnetic resonance absorption centered at approximately the position for a free electron. At this temperature the absorption is resolved into nine lines. At higher temperatures, near room temperature, a five line spectrum is obtained. From the nature of the hyperfine structure we deduce that this uninegative ion radical probably involves complete delocalization of the electron spin over both biphenyl ring systems. In the case of the uninegative ion radical of the carbon analog, bis(2,2'-biphenylene) methane, the hyperfine structure has been completely resolved and the results would support this conclusion.⁶

Of particular interest is the narrowness of the total splitting in the uninegative bis(2,2'-biphenylene) silane ion radical, the line breadth being 11.5 gauss compared with a line breadth of 24.2 gauss observed for the biphenyl.⁷

A comparison of these two line breadths indicates that approximately 50% of the spin resides in the two 5 membered hetero rings. For the analogous uninegative bis(2,2'-biphenylene) methane the line breadth is 21 gauss. Thus silicon in the spiro position has a very large effect in increasing spin density in the five membered rings.

When the wine-red solution of the uninegative bis(2,2'-biphenylene) silane ion radical is treated with excess potassium metal for several minutes, even at temperatures as low as –79°, a royal purple solution of the dinegative ion is obtained. This species is diamagnetic in contrast with the dinegative ion of bis(2,2'-biphenylene) methane which is a triplet in its ground state.⁸

The dimagnetism of the dinegative bis(2,2'-biphenylene) silane ion can be explained by assuming a 26 electron closed shell aromatic π structure. Such a structure would involve conjugation of the two biphenyl ring systems through the silicon atom. Such conjugation does not require coplanarity of the molecule since in the D_{2d} symmetry of the parent compound the π functions transform as A₂, B₁, and E and the silicon d orbitals transform as A₁, B₁, B₂ and E. Thus the p π d π B₁ and E m.o.'s afford conjugation for this symmetry. The presence of the low lying d orbitals of the silicon would account for the observed difference in ground states for the dinegative bis(2,2'-biphenylene) silane and its carbon analog.

We are continuing our study of these and closely related ions and ion radicals.

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