

ligand and away from O2 and that the other two fluorines bifurcate this oxygen, O2 (*i.e.*, take positions as far as possible from O2).

A close inspection of Figure 2 reveals that, since no. 2 TTA has its terminal groups (thienyl and CF₃) reversed, the over-all idealized (*i.e.*, neglecting the ring folding and the nonplanarity) symmetry including the total ligand is the minimum trivial symmetry of C₁. Considering only the eight oxygens of the four TTA

ligands, the symmetry is very nearly S₄ $\bar{4}$, and not D_{2d}. The displacements, normal to the trapezoidal planes, amount to 0.06 Å.

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dπ-pπ Bonding and Conjugation Involving Group IV Elements

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The possibility of conjugation between aromatic residues linked by tetrahedral silicon, germanium, and tin atoms has been investigated. The experimental method used involved the measurement of the nmr contact shifts of suitably substituted paramagnetic nickel chelates. The results show that there is a negligible amount of conjugation. The significance of this result relative to the evidence for dπ-pπ bonding involving group IV elements obtained by other experimental methods is discussed. In contrast to pπ-pπ bonding, dπ-pπ bonding with a central atom does not necessarily lead to conjugation. The synthesis of a five-coordinated tin chelate is also described, and nmr evidence for analogous germanium and silicon compounds is reported.

Introduction

The electronic structures of the second-, third-, and fourth-row elements—Si, Ge, and Sn—differ from that of their first-row analog C in that they have valence-shell d orbitals available for bond formation. The utilization of these orbitals to form σ bonds is well established. Thus, in an ion such as SiF₆²⁻ the coordination number six can only be attained by involving the Si 3d orbitals in the bonding process. The situation with respect to π bonding is less clear, although evidence for such interactions has been sought by a large number of physical techniques. Thus at various times bond length determinations,¹ dipole moment determinations,² infrared spectroscopy,³ nuclear magnetic resonance,⁴⁻⁶ chemical reactivity,⁷ electronic spectroscopy,^{8,9} and electron spin resonance¹⁰⁻¹⁵

have all been utilized to obtain information bearing on this problem. Much of the earlier work has been summarized in a review by Stone and Seyferth.¹⁶ These various investigations have not led to uniform conclusions regarding dπ-pπ bonding—in some cases the results have indicated important contributions from such interactions (*e.g.*, see ref 8) while in other cases the effects appear to be negligible (*e.g.*, see ref 6). Part of this lack of uniformity can no doubt be ascribed to the use of different compounds in different experiments. It is certainly very possible that dπ-pπ bonding may be important in one bonding situation but negligible in another. However, it also appears that some degree of confusion has arisen from drawing too close an analogy between dπ-pπ bonding and pπ-pπ bonding. In particular, the latter bonding is closely associated with conjugation, whereas the former may not be. There have been several theoretical papers in which this distinction has been pointed out, such as that of Craig and Mitchell¹⁷ on "island" and cyclic delocalization in pπ-dπ systems and the more general theoretical treatment of Jaffé¹⁸ on multiple bonds involving d orbitals. In this latter paper the case of a tetrahedral central atom has been specifically treated. In concurrence with the theory, there is a variety of experimental evidence suggesting that when the central atom is one of the group IV elements—Si, Ge, or Sn—dπ-pπ bonding is of some significance. Whether there

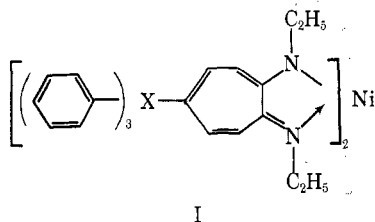
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is conjugation between different π systems attached to such a central atom is, however, much less clearly established, and Jaffé's analysis indicates that it is unlikely to occur. Kabachnik¹⁹ has suggested that although the normal spectroscopic manifestations of conjugation are lacking, conjugative effects may still be sufficiently important to have chemical significance. The observation of Cowell, Urry, and Weissman¹⁵ that the dianion of bis(2,2'-biphenylene)silane has a singlet ground state in contrast to the triplet ground state of the carbon analog has been interpreted as evidence for conjugation. The present experiments were designed to be a rather direct test for such conjugation. Unpaired electron spin density is introduced into the π system of one substituent R' of a molecule MR₃R' where all of the R radicals possess π electrons. The presence or absence of spin density in the other π systems is then probed by the observation of nmr contact shifts.

Results

In previous publications^{20,21} we have utilized the Ni(II) aminotroponimineates to study problems involving bonding and conjugation in π systems. In the present work contact shifts have been measured for chelates of structure I, where X = Si, Ge, or Sn.



In Ni(II) aminotroponimineates of this type there exists an equilibrium between a planar, diamagnetic and a tetrahedral, paramagnetic form of the complex.²² In solution at room temperature N-ethyl-substituted derivatives are predominantly in the paramagnetic configuration. In this form about 10% of the unpaired spin density, formally resident in the Ni d orbitals, is delocalized to the π system of the aminotroponimineate ligand and is manifested by large contact shifts in the proton magnetic resonance spectrum. If the ligand π system is extended by conjugation with a substituent group, contact shifts are observed for protons on the substituent group. This effect has been observed for a variety of substituents and has been used to evaluate the conjugative abilities of various linking groups.²⁰ The complexes chosen are particularly favorable for this type of study. Previous results have shown that there is a π spin density of $\sim +0.055$ at the γ position of the aminotroponimineate ligand which at 60 Mc/sec and room temperature gives rise to a contact shift of more than 7000 cps. Since, even allowing for some uncertainty in the diamagnetic reference frequencies,

contact shifts as small as 20–30 cps can be measured with some confidence, the experiment is easily capable of detecting a leakage of less than 1% of the spin from the γ position to the substituent π system. Further, the pattern of the shifts in the π system of a phenyl group is quite characteristic—the *ortho* and *para* positions have positive spin densities and give rise to high-field shifts with the *para* shift usually larger than the *ortho*, while the *meta* position has a negative spin density which is accompanied by a low-field shift. On the other hand, shifts arising from spin in the σ system are usually small and attenuate rapidly with distance from the spin-bearing atom.

Nmr data for the Ni chelates I and for the corresponding ligands are given in Table I. The contact shifts are taken to be the difference between the ligand and chelate frequencies. This is justified by previous results with Zn and other diamagnetic chelates which demonstrated that complex formation per se has only a minor effect on the proton chemical shifts.²⁰ The contact shifts for the α and β protons of the aminotroponimineate ring and for the ethyl group of I are quite typical of those found for a large variety of analogous compounds and demonstrate that the normal amount of spin delocalization ($\sim 10\%$) has occurred. The contact shifts of the protons of the substituent phenyl groups are small and all to high field. In each case, two multiplets were observed in approximate intensity ratios 3:2. The higher field resonance (intensity 2, contact shift ~ 100 cps) is a simple doublet (splitting constant ~ 7 cps). This must arise from the *ortho* protons since the *meta* protons would give rise to a triplet. The lower field resonance (intensity 3, contact shift ~ 30 cps) is a more complex multiplet arising from a superposition of the *meta* and *para* protons. The shape of the pattern indicates the *para* proton is shifted rather less than the *meta* protons. These contact shifts are not consistent with the presence of spin density in the aromatic π system. They most probably arise from a small amount of negative spin density in the σ system. (Contact shifts arise from spin density at the nucleus which can only occur if the odd-electron density is in an s orbital. If the spin is distributed in the σ system, the s orbitals can participate directly and positive spin gives rise to low-field shifts. If the spin is in the π system, McConnell's²³ indirect mechanism is required and positive spin causes high-field shifts.) This result is readily interpretable in terms of the spin polarization mechanism first proposed by Levy and Orgel²⁴ to account for the contact shift of the vanadocene protons. In essence, they suggested that if there is a strongly bonding metal–ligand orbital of different symmetry to the spin-containing orbital (so that direct mixing of the two orbitals does not occur), the electron pair in the bonding orbital will be polarized in the sense that the α spin is found to a greater extent on the metal leaving an excess of β spin (negative spin density) on the ligand.

During the course of the synthesis of these compounds

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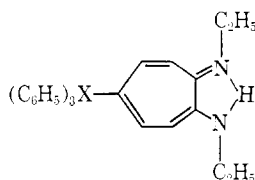
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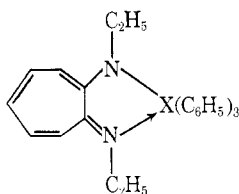
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TABLE I
NMR DATA

Compound	α	β	CH ₂	CH ₃	Aromatic
Si ligand	-375	-417	-201	-79	-445
Si Ni chelate	+5322	-3144	-10,185	-825	-405 (<i>m</i> + <i>p</i>), -335 (<i>o</i>)
Ge ligand	-373	-413	-200	-78	-442
Ge Ni chelate	+5429	-3264	-10,290	-810	-408 (<i>m</i> + <i>p</i>), -345 (<i>o</i>)
Sn ligand	-375	-420	-202	-80	-445
Sn Ni chelate	+5249	-3219	-10,252	-795	-414 (<i>m</i> + <i>p</i>), -364 (<i>o</i>)

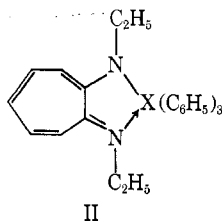
a second series of diamagnetic N-bonded Si, Ge, and Sn chelates was formed (see below). Nmr data for this series of compounds are given in Table II. Their structure follows from the analytical data and the nmr spectra. The seven-membered ring aromatic region of the proton nmr is complex as opposed to the apparent simple AB pattern observed for γ -substituted amino-

TABLE II
NMR DATA

X	α	β	γ	CH ₂ ^a	CH ₃ ^a	Aromatic
Si Complex	-420	-360	-174	-30	-430	
Ge Complex	-420	-360	-176	-34	-435	
Sn Complex	-426	-370	-192	-43	-437	

^a A spin-spin coupling constant of $J = 7$ cps was determined for all of these compounds from the splitting of the CH₂ and CH₃ resonances.

troponimines. The resonances of the N-ethyl groups are shifted significantly to high field as would be expected for a nitrogen-bonded complex. Further, only a single triplet is observed for the CH₃ group and a single quartet for the CH₂ protons, indicating a symmetric chelate. They have therefore been assigned structure II, where X = Si, Ge, or Sn. Such a structure



involves a five-coordinated central atom, and, as might have been anticipated, the stability decreases in the order Sn > Ge > Si. Analogous chelates involving dipyriddy ligands rather than aminotroponimineate ligands have been reported by Corey and West.²⁵ In the latter case a positive siliconium ion results.

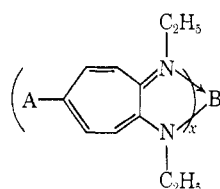
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Discussion

The data of Table I provide rather unambiguous evidence for the lack of conjugation between the aminotroponimineate π system and the π systems of the phenyl groups. It is of interest to discuss this result in relation to the various other experimental methods which have been used to probe $p\pi-d\pi$ bonding. Perhaps most closely related are various studies involving electron spin resonance. The most elegant of these is the work of Bedford, Bolton, Carrington, and Prince¹⁴ on the radical anions of $(\text{CH}_3)_3\text{MC}_6\text{H}_5$ where M = Si or Ge. These radicals are best regarded as perturbed benzene negative ions, the perturbation being sufficient to split the orbital degeneracy found in the unsubstituted C_6H_6^- ion. Whether the splitting results in the antisymmetric orbital or the symmetric orbital being lower depends on whether the substituent group tends to donate electrons to the π system or accept electrons from the π system. The results are quite unambiguous in showing that the Si or Ge are accepting π electrons. There would seem to be no plausible alternative to the proposition that the acceptor orbitals are the empty Si and Ge d orbitals. However, two points may be noted. First, the interaction is between Si or Ge d orbitals and the π -antibonding orbital. It might be anticipated that there would be a better energy match of Si d orbitals with π^* than with π aromatic orbitals, and since stronger donation is to be expected from a negative ion than from a neutral species, this situation is perhaps the most favorable possible for $p\pi-d\pi$ interaction. Second, it should be noted that the above result does not imply that the Si or Ge is part of an extended π system; *i.e.*, it says nothing about through conjugation. This result is therefore not inconsistent with the conclusions drawn from this work. The same statement holds for a variety of esr studies involving heteroaromatic atoms. These have provided no clear evidence that the d orbitals participate in the conjugation.

There remains the work of Cowell, Urry, and Weissman¹⁵ on biphenylenesilane anions. The monoanion is a free radical with hyperfine splitting from both phenylene rings. The same is true, however, for the carbon analog,²⁶ and the result does not necessarily imply that

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TABLE III
ANALYTICAL DATA

A	B	x	Mp, °C	% Ni		% Sn, Ge, or Si		% N		% C		% H	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
(C ₆ H ₅) ₃ Sn	H	1	151			22.6	22.3	5.3	5.3	66.3	66.45	5.8	5.5
(C ₆ H ₅) ₃ Ge	H	1	186			15.1	14.9	5.8	5.7	72.7	72.7	6.3	6.5
(C ₆ H ₅) ₃ Si	H	1	189			6.5	6.3	6.5	6.6	80.1	80.0	6.95	6.8
(C ₆ H ₅) ₃ Sn	Ni	2	298										
(C ₆ H ₅) ₃ Ge	Ni	2	304	5.8	5.9	14.2	13.9	5.5	5.4	68.6	68.7	5.8	6.0
(C ₆ H ₅) ₃ Si	Ni	2	326					6.05	6.05	75.2	75.0	6.3	6.4
H	(C ₆ H ₅) ₃ Sn	1	130			22.6	23.45	5.3	5.0	66.3	66.3	5.8	5.8
H	(C ₆ H ₅) ₃ Ge	1 ^a											
H	(C ₆ H ₅) ₃ Si	1 ^a											

^a Compound not isolated; nmr evidence for its presence in crude product.

there is a single continuous π system. It is sufficient if the rate of electron exchange between two independent π systems is $\omega_e \geq 10^8 \text{ sec}^{-1}$. It is, however, significant that the total spread of the esr spectrum of the silicon compound is substantially less than that of the carbon compound, indicating that a significant fraction of the spin resides in the five-membered rings containing the silicon. This is evidence for silicon d π -p π interaction but not necessarily for conjugation between the perpendicular π systems. The diamagnetism of the silane dianion was taken as evidence for such conjugation between the two π systems. However, calculation shows²⁷ that the lowest antibonding π orbital in which the last two electrons of the dianion must be placed is of E symmetry in the D_{2d} point group corresponding to the molecular symmetry. This orbital can indeed interact with Si d orbitals of the same symmetry, but this interaction cannot lead to any splitting of the orbital degeneracy; *i.e.*, the d π -p π bonding cannot affect the triplet ground state of the dianion. The observed diamagnetism must therefore be attributed to some more indirect mechanism, possibly of the superexchange type, and does not provide evidence for conjugation.

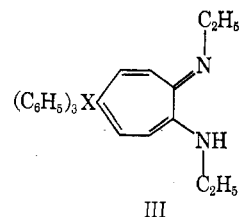
There is a variety of other experimental evidence, such as, for example, the elegant optical experiments of Goodman, Konstam, and Sommer⁸ and the more recent work of Nagy, *et al.*,⁹ all demonstrating the interaction of unfilled d orbitals on Si, Ge, and Sn with neighboring π orbitals. These do not, however, provide evidence of "through" conjugation. The present results therefore support the theoretical analyses of Jaffé¹⁸ and of Craig and Mitchell¹⁷ to the effect that the directional properties of d orbitals lead to significant differences between p π -p π and p π -d π bonding and that the latter type of bonding does not necessarily lead to conjugation in the accepted sense of the word. Indeed, bearing in mind the sensitivity of the contact shift method, it can be concluded that conjugative

effects arising from p π -d π bonding in tetrahedral Si, Ge, and Sn are negligible. This result may be contrasted with the previous findings²⁰ that oxide, sulfide, and amine linkages, in which the central atom is again approximately tetrahedral but has unshared electron pairs in at least one of the sp³ orbitals, do transmit a significant amount of spin density and so behave as conjugating groups.

Experimental Section

In the preparation and isolation of the triphenyltin (-germanium, -silicon) derivatives of N,N'-diethylaminotroponimine, all operations were carried out under nitrogen, and sodium-dried solvents were used.

The compounds III (X = Sn, Ge, Si) were air and moisture



stable but the compounds II were moisture sensitive. Analytical data for these compounds and for the nickel chelates I are given in Table III.

Nmr data were determined using Varian Associates A-60 and HR-60 spectrometers for the diamagnetic and paramagnetic compounds, respectively, at 60 Mc/sec with tetramethylsilane as an internal reference. Nmr data are given in Tables I and II.

γ -Triphenyltin N,N'-Diethylaminotroponimine.—A solution of 2.55 g (0.01 mole) of γ -bromo-N,N'-diethylaminotroponimine (γ -BrEt₂ATI) in 50 ml of ether was stirred at 0°. A solution of 13 ml of 1.6 N n-butyllithium (0.02 mole) in hexane was added dropwise and the reaction mixture was kept under reflux for 15 min to give a solution of N- γ -dilithio-N,N'-diethylaminotroponimine.²⁸ After cooling this to -80°, 3.86 g (0.01 mole) of triphenyltin chloride in 30 ml of ether was added with stirring. The reaction mixture was brought to room temperature over a period of 1 hr, was heated under reflux for 15 min, and was then filtered. After adding 1 ml of water to the filtrate to liberate the free amine from its N-lithio derivative, the reaction mixture was cooled to 0° and filtered. The solid obtained was recrystal-

(27) H. E. Simmons, private communication.

(28) A. D. Josey unpublished work.

lized from cyclohexane to give 2.8 g (59% yield) of yellow crystals of γ -triphenyltin Et_2ATI .

γ -Triphenylgermanium and γ -Triphenylsilicon Et_2ATI .—These were prepared in a similar manner excepting that triphenylgermanium bromide and triphenylchlorosilane, respectively, were used in place of triphenyltin chloride.

Ni(II) Chelates of γ -Triphenyltin(-silicon, -germanium) Et_2ATI .—These chelates were prepared by the same procedure as detailed below for the germanium derivative.

A solution of 0.30 g (0.0012 mole) of hydrated nickel acetate in a mixture of 4 ml of water and 12 ml of ethanol was added dropwise to a stirred solution of 0.96 g (0.002 mole) of γ -triphenylgermanium Et_2ATI in 15 ml of benzene and 30 ml of ethanol. The reaction mixture was heated under reflux for 30 min and then cooled overnight at 0°. The solid obtained was recrystallized from cyclohexane to give 0.65 g (65% yield) of black crystals of the Ni(II) chelate of γ -triphenylgermanium Et_2ATI .

Triphenyltin(IV) N,N' -Diethylaminotroponimineate.—A solution of 1.76 g (0.01 mole) of Et_2ATI in 35 ml of ether was stirred at 0° while 6 ml of 1.6 *N*-butyllithium (0.01 mole) in hexane was added dropwise. It was then stirred at -80° with the dropwise addition of 3.86 g (0.01 mole) of triphenyltin chloride in 40 ml of ether. The reaction mixture was warmed to room temperature over a period of 1 hr and then held under reflux for

10 min. The reaction mixture was filtered and then concentrated. The yellow product that separated at 0° was recrystallized from ether to give 3.2 g (55% yield) of yellow crystals of triphenyltin(IV) N,N' -diethylaminotroponimineate.

This compound can be sublimed unchanged at 200° (0.5 mm), but it is extremely sensitive to moisture. By nmr it was shown that about two-thirds of the tin chelate in a CDCl_3 solution was decomposed on simple filtration through a layer of cotton. Presumably, the action was from the small amount of water of hydration in the cotton.

Triphenylgermanium(IV)[-silicon(IV)] N,N' -Diethylaminotroponimineates.—In attempts to prepare the corresponding pentavalent germanium(IV) and silicon(IV) chelates by a similar procedure, crude products were obtained whose nmr spectra indicated the presence of the desired chelates. Data are given in Table II. Attempts to purify these germanium and silicon chelates by recrystallization were unsuccessful because of their instability. The silicon chelate appeared the less stable of the two.

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Kinetics and Mechanism of the Chromium(II)-Catalyzed Substitution of Iodide Ion in the Iodopentaaquochromium(III) Ion by Water and by Fluoride, Chloride, and Bromide Ions^{1a,b}

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The substitution of iodide ion in the iodopentaaquochromium(III) ion by water is catalyzed by chromium(II). The catalyzed path obeys the rate law $-\text{d}[\text{CrI}^{2+}]/\text{dt} = k_3[\text{Cr}^{2+}][\text{CrI}^{2+}]/[\text{H}^+]$, with $k_3 = 2.66 \times 10^{-2} \text{ sec}^{-1}$ at 25° and $[\text{ClO}_4^-] = 2.0 \text{ M}$. Chromium(II) also catalyzes the substitution of iodide by fluoride, chloride, and bromide ions. The dominant paths for these catalyzed reactions have the form $-\text{d}[\text{CrI}^{2+}]/\text{dt} = k_X[\text{Cr}^{2+}][\text{CrI}^{2+}][\text{X}^-]$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$). At 25°, $[\text{ClO}_4^-] = 2.0 \text{ M}$, and $[\text{HClO}_4] = 1.0 \text{ M}$, the values of k_X are 5.3×10^4 , 2.7×10^2 , and $63 \text{ M}^{-2} \text{ sec}^{-1}$ for fluoride, chloride, and bromide ions, respectively. The mechanistic implications of these results are discussed. It is suggested that the $\text{CrI}^{2+} \rightarrow \text{Cr}^{2+}$ reaction proceeds *via* the transition state $[\text{ICrOHCr}^{3+}]^\ddagger$. Intermediates of the type CrIX^+ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) are postulated to account for the halide ion effects.

Introduction

Following the discovery of the bridged activated complex in electron-transfer reactions,² many studies have been performed to elucidate the role of bridging ligands in such reactions.⁸ More recently, the effects of nonbridging ligands directly bound to the oxidant have been examined systematically.⁴⁻⁷ Extremely useful information regarding these effects has been obtained from

studies of the reductions of cobalt(III) and chromium(III) complexes by the hexaaquochromium(II) ion because, for these systems, it is possible to ascertain the nature of the bridging ligand and the positions (*cis* or *trans*) of the nonbridging ligands with respect to the bridge. It must be noted, however, that, for an inner-sphere mechanism involving a single bridging ligand, there are five additional coordinating positions on the reducing agent. Nonbridging ligand effects in these positions are difficult to evaluate because substitution lability of the reducing agent is necessary to make the bridged transition state readily accessible. Furthermore, it has been tacitly assumed that reductions by hexaaquochromium(II) ion that proceed *via* an inner-sphere mechanism may be rather insensitive to the replacement of perchlorate ion by other simple anions.

(1) (a) This work was supported by Grants GP-2001 and GP-6528 from the National Science Foundation; (b) abstracted in part from the Ph.D. dissertation of D. E. Pennington, the Pennsylvania State University, June 1967; (c) Fellow of the Alfred P. Sloan Foundation.

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