

than the frequency kT/h which, according to transition-state theory, represents translation along the reaction coordinate in the transition state. Thus, this calculation indicates that the lifetime of the ion pair that is depicted as an intermediate in the two-step mechanism would have to be comparable to that of a transition state.

In conclusion, we believe that the transition state for proton exchange between an alcohol and a carboxylic acid has considerable polar character because of the peculiar value of the Brønsted slope. Furthermore, we believe that the configuration of the reacting system that most nearly resembles an ion pair is extremely short-lived—too short-lived to respond to any of the usual kinetic methods for detecting metastable reaction intermediates.

Appendix

K_i for the neopentyl alcohol was estimated by two independent methods that agreed to better than one order of magnitude. The first method relates K_i solely to data for electrolytes in glacial acetic acid. The relation is given in eq. 7. In this equation, the K_D values

$$K_i = \frac{[\text{ROH}_2^+\text{OAc}^-]}{[\text{ROH}]} = K^{\text{ROH}_2^+\text{ClO}_4^-} \times \frac{K_D^{\text{ROH}_2^+\text{ClO}_4^-}}{K_D^{\text{ROH}_2^+\text{OAc}^-}} \frac{K_{\text{auto}}}{K_A^{\text{HClO}_4}} \quad (7)$$

every collision. Since the lifetime of the collision complex is almost certainly less than 10^{-11} sec. and probably less than 10^{-12} sec., the time required for proton transfer appears to be less than 10^{-12} sec.: K. R. Ryan and J. H. Futrell, *J. Chem. Phys.*, **42**, 824 (1965).

are ion-pair dissociation constants, $K_{\text{auto}} = [\text{AcOH}_2^+] \times [\text{AcO}^-]$, K_A is the formal acid dissociation constant, and $K^{\text{ROH}_2^+\text{ClO}_4^-}$ is the equilibrium constant for reaction of a primary alcohol with perchloric acid (eq. 8).

$$K^{\text{ROH}_2^+\text{ClO}_4^-} = \frac{[\text{ROH}_2^+\text{ClO}_4^-]}{[\text{ROH}][\text{HClO}_4]} \quad (8)$$

Values of the latter at 25° are 4.4 for methanol and 7.4 for ethanol,²¹ for an average value of 6. Since perchloric acid is a strong acid in HOAc, $K_A^{\text{HClO}_4} \approx K_D^{\text{AcOH}_2^+\text{ClO}_4^-}$, which in turn should be approximately equal to $K_D^{\text{ROH}_2^+\text{ClO}_4^-}$. The value of $K_D^{\text{ROH}_2^+\text{OAc}^-}$ should be at least approximately equal to K_D for other hydrogen-bonded acetate ion pairs such as pyridium acetate, for which the value is 1×10^{-6} .²² The value for K_{auto} is 3.5×10^{-15} .²³ As a result, pK_i is estimated as 7.7.

The second method¹⁵ involves the use of the approximate relationship

$$K_i \text{ (in HOAc)} \approx 1 \times 10^9 K_B \text{ (in H}_2\text{O)} \quad (9)$$

Reported values of K_B for primary alcohols in water^{24,25} range from 10^{-15} to 10^{-17} , a plausible average being 5×10^{-17} . As a result, pK_i is estimated as 7.0.

The average estimate for pK_i , based on both methods, is 7.3.

(21) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956).

(22) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 10 (1956).

(23) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2974 (1956).

(24) For a recent review, see E. M. Arnett in "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. Taft, Ed., Interscience Publishers, New York, N. Y., 1963, pp. 223-403.

(25) G. D. Giles and C. F. Wells, *Nature*, **201**, 606 (1964).

Electron Spin Resonance Spectra of Some Group IV-B Substituted Biphenyl Anion Radicals. Dative π -Bonding

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Contribution from the Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois. Received January 6, 1965

The preparation of the previously unreported compounds, $4\text{-(CH}_3)_3\text{MC}_6\text{H}_4\text{C}_6\text{H}_5$ and $4,4'\text{-(CH}_3)_3\text{MC}_6\text{H}_4\text{C}_6\text{H}_4\text{M}$ ($\text{M} = \text{Si, Ge, Sn}$), and their reduction with alkali metals and with a dropping mercury electrode are described. The uninegative radical anions thus produced give well-resolved electron magnetic resonance spectra, which are interpreted and discussed in terms of a simple molecular orbital model involving the d -orbitals of the substituent. For the carbon-silicon and carbon-germanium bonds, the calculated π -bond orders are approximately 0.18 and 0.13, respectively. The Coulomb and resonance integrals, which are consistent with the correct spin densities, suggest that silicon is more electropositive than germanium.

(1) (a) National Science Foundation Predoctoral Fellow, 1961-1963; (b) Alfred P. Sloan Research Fellow.

Introduction

The role of dative π -bonding ($d\pi$ - $p\pi$ bonding) in the chemistry of the higher analogs of carbon (Si, Ge, Sn, Pb) has received a great deal of attention. Stone and Seyferth have presented a review of some physical and chemical evidence for the existence of π -bonding in silicon compounds²; and, on the basis of the high C-M overlap integrals ($\text{M} = \text{Si, Ge, Sn, Pb}$), Craig, *et al.*, concluded that π -bonding should be important in the chemistry of unsaturated derivatives of these elements.³

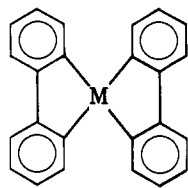
Since Stone and Seyferth's review, several papers dealing with dative π -bonding in group IV-B compounds

(2) F. G. A. Stone and D. Seyferth, *J. Inorg. Nucl. Chem.*, **1**, 112 (1955).

(3) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

have appeared. Thus, multiple bonding has been used to explain anomalous trends in the chemical shifts and coupling constants obtained in nuclear magnetic resonance (n.m.r.) spectra of silicon compounds,⁴ the ultraviolet spectra of the trimethylazido and triphenylacetyl derivatives of the group IV-B elements,⁵ and the infrared spectra and acidities of the corresponding triphenylhydroxy derivatives.⁶ From these studies, it was concluded that the relative order of π -bonding is $\text{Si} > \text{Ge} \gg \text{Sn}, \text{Pb}$. On the other hand, the Hammett σ -constants of the $(\text{CH}_3)_3\text{Si}$ group indicate that its effect on an aromatic system is primarily $+I$, although when conjugated to an electron-releasing substituent the group exerts a slight $-R$ effect.^{7a} A comparison of the σ -constants of the $(\text{C}_6\text{H}_5)_3\text{Ge}$ and $(\text{C}_6\text{H}_5)_3\text{Si}$ groups indicates that both groups have approximately the same effect ($-I, -R$).^{7b}

Recently the electron spin resonance (e.s.r.) spectra of some anion radicals containing silicon or germanium have been reported. Townsend reduced several tetraarylsilanes and obtained the corresponding uninegative ions, but the complicated nature of their spectra prevented any but the most general conclusions.⁸



I, M=Si; II, M=C

Cowell, Urry, and Weissman found that the dinegative anion of I is diamagnetic, in contrast to the paramagnetic dinegative anion of II, thus proving that the two extra electrons are delocalized over both ring systems in the silicon compound.⁹ Bedford, *et al.*, compared the e.s.r. spectra of the anions formed from the reduction of $(\text{CH}_3)_3\text{MC}_6\text{H}_5$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}$) and concluded that the trimethylsilyl and trimethylgermyl groups are electron withdrawing, in contrast to the *t*-butyl group, and that the resonance effect of silicon was greater than that of germanium.¹⁰

Although these e.s.r. experiments prove that the odd electron in group IV substituted anion radicals is delocalized through the d-orbitals of the substituent, the actual magnitude of the resonance interaction was not estimated in the previous work. Since simple molecular orbital theory has enjoyed great success in explaining the e.s.r. spectra of anion radicals,¹¹ it was decided to investigate the e.s.r. spectra of some group

(4) (a) H. Schmidbaur, *J. Am. Chem. Soc.*, **85**, 2336 (1963); (b) C. H. Van Dyke and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 1071 (1964); (c) E. A. V. Ebsworth and J. J. Turner, *J. Phys. Chem.*, **67**, 805 (1963); *J. Chem. Phys.*, **36**, 2628 (1962).

(5) (a) J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 889 (1964); (b) D. F. Harnisch and R. West, *ibid.*, **2**, 1082 (1963).

(6) (a) R. West and R. H. Baney, *J. Phys. Chem.*, **64**, 822 (1960); (b) R. West, D. H. Baney, and D. L. Powell, *J. Am. Chem. Soc.*, **82**, 6269 (1960).

(7) (a) R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953); J. L. Speier, *ibid.*, **75**, 2930 (1953); (b) R. A. Benkeser, C. E. DeBoer, R. E. Robinson, and D. M. Sauve, *ibid.*, **78**, 682 (1956).

(8) M. G. Townsend, *J. Chem. Soc.*, 51 (1962).

(9) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Am. Chem. Soc.*, **85**, 822 (1963); *J. Chem. Phys.*, **38**, 2028 (1963).

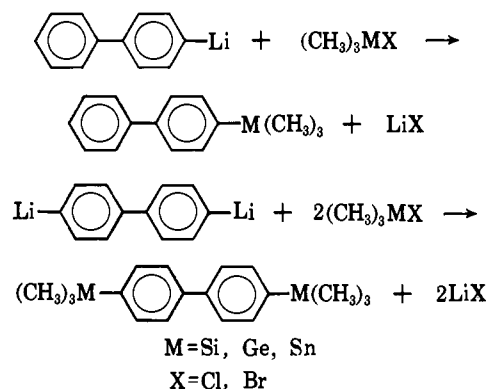
(10) J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963).

(11) A. Carrington, *Quart. Rev. (London)*, **17**, 67 (1963), and references therein.

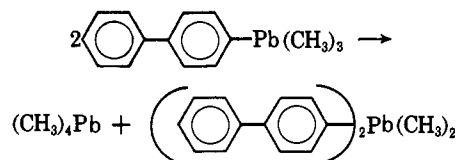
IV substituted biphenyl anions in order to obtain quantitative estimates, *via* LCAO-MO calculations, of the π -bonding effects of silicon, germanium, and tin.

Results and Discussion

For the most part, the preparation of the biphenyl compounds used in this work was straightforward and good yields were obtained by the reactions



In the attempted preparation of 4-trimethylplumbylbiphenyl, only bis(4-biphenyl)dimethylplumbane was isolated. The latter compound probably arises from a disproportionation of the trimethylplumbylbiphenyl initially formed from biphenyllithium and trimethyllead chloride. Such redistribution reactions are common in



organolead chemistry, but random mixtures are usually obtained when only alkyl groups are bonded to lead.¹² Although a small amount (*ca.* 15%) of the corresponding tin derivative, bis(4-biphenyl)dimethylstannane, was recovered from the reaction of 4-lithiobiphenyl with commercial trimethyltin chloride, the possibility of this arising from some dimethyltin dichloride impurity in the starting material cannot be excluded. The attempted preparation of 4,4'-bis(trimethylplumbyl)biphenyl gave only ill-defined products, as would be expected if redistribution also occurs with this compound.

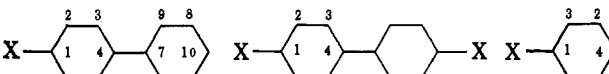
Analysis of Spectra. Likewise, the alkali metal reduction of the substituted biphenyls proceeded smoothly in tetrahydrofuran (THF) at -23 or -63° to give the corresponding uninegative anion, except when the substituent was trimethylstannyl (see below). The e.s.r. spectra of the biphenylate radicals are shown in Figures 1-10 and are discussed individually below. Beneath each observed spectrum (presented as the first derivative of the absorption spectrum) is the spectrum calculated from the assigned hyperfine coupling constants. The splittings, summarized in Table I, were assigned to the various protons on the basis of theory and by analogy with the assignments in the unsubstituted biphenylide radical.

Sodium 4-trimethylsilylbiphenylide gave the spectrum shown in Figure 1 at -50° . At room temperature,

(12) G. Calingaert and H. A. Beatty in "Organic Chemistry, An Advanced Treatise," Vol. II, H. Gilman, Ed., 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., p. 1810 ff.

Table I. Coupling Constants and Calculated and Experimental Spin Densities in Some Group IV-B Substituted Anion Radicals

Anion	Atom ^a	a_i^H , gauss	ρ_i (obsd.) ^b	ρ_i (calcd.)	
				McLachlan	Hückel
Trimethylsilylbiphenylide	1	0.196	0.151
	2	0.16	0.006	-0.002	0.032
	3	2.08	0.074	0.077	0.073
	4	0.142	0.128
	7	0.091	0.092
	8	2.72	0.097	0.096	0.078
	9	0.48	0.017	-0.026	0.014
	10	4.96	0.177	0.174	0.128
	Si	0.108	0.106
	CH ₃	0.16	0.006
Bis(trimethylsilyl)-biphenylide	1	0.170	0.130
	2	0.14	0.005	-0.008	0.024
	3	2.24	0.080	0.077	0.069
	4	0.110	0.103
	Si	0.082	0.081
	CH ₃	0.14	0.005
Trimethylgermylbiphenylide	1	0.196	0.149
	2	0.00	0.00	-0.013	0.025
	3	2.38	0.085	0.086	0.077
	4	0.130	0.121
	7	0.102	0.101
	8	2.70	0.096	0.096	0.080
	9	0.52	0.019	-0.025	0.016
	10	5.08	0.181	0.183	0.135
	Ge	0.100	0.099
	CH ₃	0.00	0.00
Bis(trimethylgermyl)-biphenylide	1	0.175	0.132
	2	0.20	0.007	-0.015	0.021
	3	2.41	0.085	0.083	0.072
	4	0.109	0.104
	Ge	0.089	0.080
	CH ₃	0.00	0.00
Trimethylsilylbenzenide ^c	1	0.244	0.205
	2	2.66	0.095	0.075	0.084
	3	1.06	0.038	-0.004	0.040
	4	8.13	0.290	0.279	0.216
	Si	0.336	0.330
	CH ₃	0.40	0.014
Trimethylgermylbenzenide ^c	1	0.197	0.164
	2	2.33	0.083	0.057	0.066
	3	1.46	0.052	-0.003	0.033
	4	7.61	0.272	0.222	0.173
	Ge	0.472	0.465
	CH ₃	<0.10	<0.004
Biphenylide	1	5.40	0.193	0.213	0.158
	2	0.44	0.016	-0.027	0.020
	3	2.70	0.097	0.106	0.090
	4	0.128	0.123
Di- <i>t</i> -butyldiphenylide ^e	1	0.214	0.159
	2	0.60	0.021	-0.030	0.018
	3	2.64	0.095	0.109	0.091
	4	0.128	0.123
<i>t</i> -Butylbenzenide ^{d,e}	CH ₃	0.10	0.004
	1	-0.089	0.000
	2	4.66	0.166	0.294	0.250
	3	4.66	0.166	0.294	0.250
	4	1.74	0.062	-0.089	0.000
<i>t</i> -Butylbiphenylide ^e	CH ₃	<0.1	<0.004
	1	0.210	0.155
	2	(?)	...	-0.030	0.017
	3	2.7	0.10	0.109	0.091
	4	0.122	0.119
	7	0.133	0.127
	8	2.7	0.10	0.106	0.090
	9	0.6	0.02	-0.026	0.020
	10	5.6	0.20	0.217	0.161
	CH ₃	(?)
Bis(trimethylstannyl)-biphenylide	2	(?)
	3	2.36	0.084
	CH ₃	(?)

^a The numbering system used is  ^b $Q = 28$ gauss. ^c Values of a_i^H taken from ref. 10. ^d Values of a_i^H taken from ref. 20. ^e Spin densities calculated with $\alpha(1) = \alpha_0 - 0.05\beta_0$.

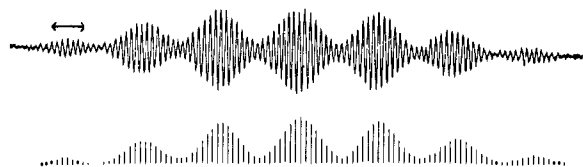


Figure 1. Sodium 4-trimethylsilylbiphenylide (0.001 *M* in tetrahydrofuran). In all spectra presented here, the applied magnetic field increases from left to right, and the lengths of the arrows indicate a field change of 1 gauss.

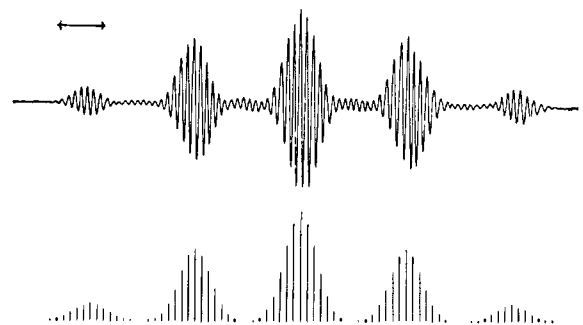


Figure 2. Sodium 4,4'-bis(trimethylsilyl)biphenylide (0.001 *M* in tetrahydrofuran at -50°).



Figure 3. Sodium 4,4'-bis(trimethylsilyl)biphenylide (0.001 *M* in tetrahydrofuran at room temperature).

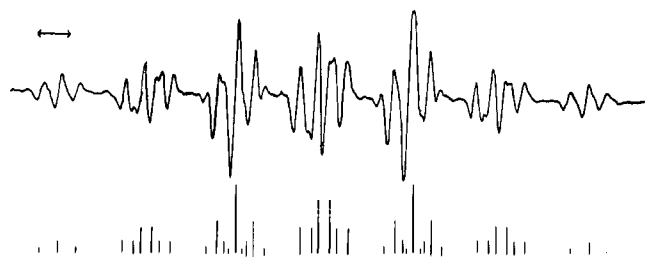


Figure 4. Sodium 4-trimethylgermylbiphenylide (0.001 *M* in tetrahydrofuran at room temperature).

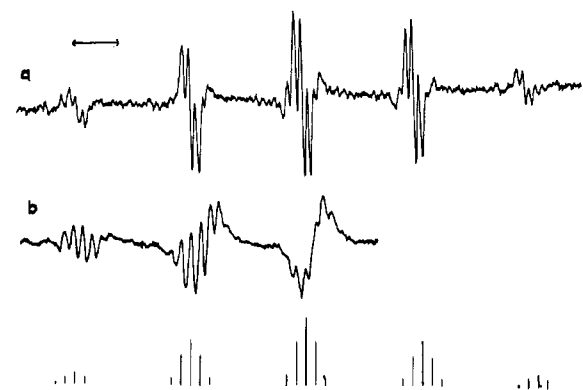


Figure 5. Potassium 4,4'-bis(trimethylgermyl)biphenylide (in tetrahydrofuran): (a) at -50° , (b) at 10° .

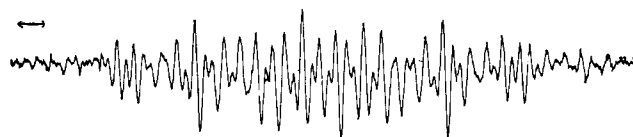


Figure 6. Spectrum of the decomposition product obtained from the reduction of 4-trimethylstannylbiphenyl (in tetrahydrofuran at room temperature).

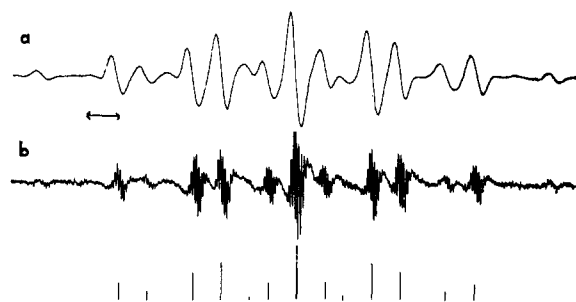


Figure 7. Spectra obtained from the prolonged reduction of 4,4'-bis(trimethylstannyl)biphenyl and the decomposition of sodium biphenylide: (a) high sensitivity, (b) high resolution (in tetrahydrofuran at room temperature).

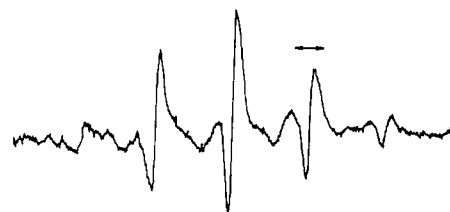


Figure 8. Spectrum from the radical believed to be potassium 4,4'-bis(trimethylstannyl)biphenylide (in tetrahydrofuran at -50°).

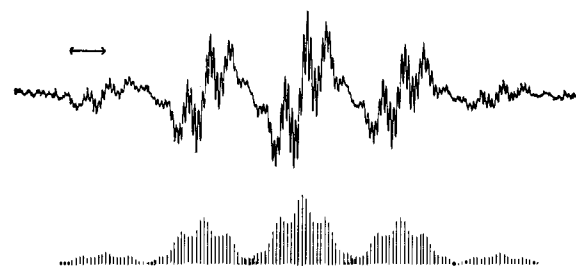


Figure 9. Potassium 4,4'-bis(*t*-butyl)biphenylide (in tetrahydrofuran at room temperature).

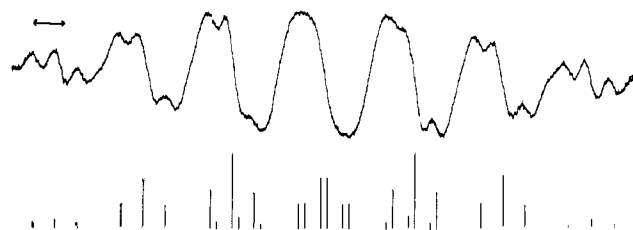


Figure 10. Potassium 4-*t*-butylbiphenylide (in tetrahydrofuran at -50°).

only seven broad bands with a spacing of *ca.* 2.3 gauss were observed. The increased resolution at the lower temperature may be due to decreased ion-pair formation with the sodium atom as a consequence of the higher dielectric constant of the solvent at the lower tempera-

ture, although other factors, *e.g.*, spin exchange at the higher temperature, may be responsible.¹³ The coupling constants at -50° were the same with either sodium or potassium as the counterion, showing that the splitting does not arise from an interaction of the odd electron with the nucleus of the metal atom.¹⁴ The spacing between each pair of adjacent lines is 0.16 ± 0.01 gauss (average deviation), and since the lines overlap, all the coupling constants must be an integral multiple of 0.16. The spectrum was then interpreted by a trial and error procedure in which a spectrum, calculated from assumed coupling constants, was superimposed on the observed spectrum. A nearly perfect fit for both positions and intensities was obtained using the coupling constants given in Table I. The total number of lines predicted is 103, of which 101 may be seen; the total width of the spectrum is 16.3 ± 0.1 gauss (calcd., 16.32).

Sodium 4,4'-bis(trimethylsilyl)biphenylide gave the spectra shown in Figures 2 and 3 at -50° and room temperature, respectively. The spectrum in Figure 2 was interpreted in the same manner as described above for trimethylsilylbiphenylide except that in this case, the splitting due to the proton at carbon 3 (see Table I for numbering system) could be measured from the spectrum taken at room temperature.¹⁵ The best fit for the intensities was obtained by assuming that the splitting caused by the proton at position 2 equals the splitting from the methyl protons. The small peaks between the five main groups may be attributed either to 4-trimethylsilylbiphenylide, present as an impurity, or to a splitting of approximately 2.24 gauss due to Si²⁹ although the experimental and calculated relative intensities differ slightly. The total width of the spectrum is 10.4 ± 0.1 gauss (calcd., 10.48).

Sodium 4-Trimethylgermylbiphenylide (Figure 4). In this case the coupling constants could be measured directly from the spectrum after the approximate splitting scheme was obtained. The spectrum of this compound remained essentially unchanged on lowering the temperature. Lines separated by 0.2 gauss may be just distinguished; the poor resolution may be due to broadening of the lines by small splittings from the methyl and 2-position protons. The total width is 16.1 ± 0.1 gauss (peak to peak) and 16.9 ± 0.2 gauss as measured from the points where the signal first becomes distinguishable from the noise (calcd., 16.28).

Potassium 4,4'-Bis(trimethylgermyl)biphenylide (Figure 5). The spectrum taken at -50° appears to be less resolved than the one recorded at 10° . This effect is possibly due to an anisotropic broadening at the lower temperature.¹³ The coupling constants given in Table I were obtained from the spectrum in Figure 5b. The radical decomposed rapidly at 10° , and the effects of the decomposition may be seen in the second and third groups of peaks. The decomposition product is diamagnetic. The total width of this signal is 10.4 ± 0.2 gauss (calcd., 10.44).

(13) J. G. Powles and M. J. Mosley, *Proc. Phys. Soc. (London)*, **78**, 370 (1961).

(14) F. C. Adam and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 1518 (1958).

(15) In the text and in Table I, a coupling constant is assigned to a particular position with the understanding that all protons in symmetrically equivalent positions have the same coupling constant. The numbering system applies only to spin densities, bond orders, etc.; the conventional numbering system is used in naming the compounds.

Reduction of 4-Trimethylstannylbiphenyl. The spectrum shown in Figure 6 was obtained at both -50° and at room temperature from the solution obtained by treating trimethylstannylbiphenyl with sodium-potassium alloy at -63° . The spectrum is much broader than the corresponding silicon and germanium derivatives (20.4 to *ca.* 16 gauss, respectively) and consists of about 49 lines. Also in contrast to the silicon and germanium derivatives, the radical appears to be stable at room temperature. These facts, together with the large amount of solids formed on the surface of the alloy during the reduction, indicate that the trimethylstannyl group was cleaved from the biphenyl. The spectrum was not analyzed in detail.

Potassium 4,4'-Bis(trimethylstannyl)biphenylide. Prolonged reduction of bis(trimethylstannyl)biphenyl gave a green solution, stable at room temperature, from which were obtained the spectra shown in Figure 7. The spectra are interpreted in terms of a triplet splitting of 2.98 gauss, a quintet splitting of 2.16 gauss, and a multiplet splitting of 0.08 gauss. The high-sensitivity spectrum is shown so that the peaks of unit intensity may be seen. Since a radical giving rise to an identical spectrum was isolated from the decomposition of sodium biphenylide at room temperature, it is evident that the trimethylstannyl groups were again cleaved from the molecule. Very brief treatment of a solution of bis(trimethylstannyl)biphenyl with sodium-potassium alloy at -63° gave a pale green solution, from which was obtained the spectrum shown in Figure 8. Five lines, with a spacing of 2.36 ± 0.04 gauss, are observed, thus indicating that the effect of the trimethylstannyl group is similar to that of the trimethylsilyl and trimethylgermyl groups.

Potassium biphenylide was prepared for the purpose of calibrating the Fieldial. The constants obtained from this work are: $a_p = 5.40$, $a_m = 0.44$, and $a_o = 2.70$ gauss; Carrington and dos Santos-Veiga report the values 5.46, 0.43, and 2.73 gauss, respectively, for the *para*, *meta*, and *ortho* coupling constants.¹⁶ The total width is 23.4 gauss.

*Potassium 4,4'-Di-*t*-butylbiphenylide and Potassium 4-*t*-Butylbiphenylide*. The spectra of the above *t*-butylbiphenylides (Figures 9 and 10) were obtained in order to compare the effect of the *t*-butyl group, in which electron-withdrawing resonance is absent, with the trimethyl derivatives of the heavier group IV-B elements. The coupling constants are very similar to those for the biphenyl anion itself. The total width of the spectrum of the di-*t*-butyl derivative is 12.8 ± 0.2 gauss (calcd., 13.0) and that of the monosubstituted compound is 18.8 ± 0.2 gauss (measured from the points where the signal is first observed) or 17.7 gauss (measured from the centers of extreme peaks) (calcd., 17.9). The total splitting of *p*-deuteriobiphenylide is 20.4 ± 0.1 gauss.^{17a}

Calculations. After the coupling constants are assigned to the protons, the splittings may be related to the spin densities on the corresponding carbon atoms in the π -system by the relation^{17b,18} $a_i = Q\rho_i$, where a_i is the observed coupling constant, ρ_i is the spin density,

(16) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

(17) (a) E. de Boer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958); (b) S. I. Weissman, *J. Chem. Phys.*, **25**, 890 (1956).

(18) H. M. McConnell and D. M. Chesnut, *ibid.*, **28**, 107 (1958).

and Q is a constant, taken to have the value 28 gauss in this work.¹⁹ The spin densities thus calculated are given in Table I under ρ_i (obsd.).

In order to calculate the spin density distribution in the group IV substituted biphenylides, the $(\text{CH}_3)_3\text{M}$ ($\text{M} = \text{Si}, \text{Ge}$) substituent was treated as a heteroatom possessing a vacant orbital which interacts with the π -system. The Hückel model was employed and σ - π orthogonality was assumed throughout (*i.e.*, hyperconjugation, if any, involving the $\text{M}-\text{CH}_3$ σ -bonds was ignored). This assumption seems to be justified by the spectra of the *t*-butylbiphenylides, since the observed coupling constants are nearly equal to those of the biphenyl anion itself. That there exists some σ - π interaction is shown by the small spin density at the methyl protons, but this interaction apparently has little effect on the coupling constants of the ring protons. To our knowledge, the mechanism responsible for the spin density at the methyl protons in a *t*-butyl group has not received a semiquantitative theoretical treatment, although Bolton, *et al.*, have qualitatively discussed the spectra of some alkylbenzenide radicals.²⁰

The parameters describing the heteroatom are the Coulomb integral, α_{M} , and the resonance integral, β_{CM} , which are then scaled in terms of the resonance integral of a "normal" aromatic carbon-carbon bond²¹: $\alpha_{\text{M}} = \alpha_0 + h_{\text{M}}\beta_0$; $\beta_{\text{CM}} = k_{\text{CM}}\beta_0$. It was also found necessary to include a measure of the inductive effect of the substituent on the contiguous ring carbon in order to account for the spin density distribution. In the model used, a substituent less electronegative than carbon decreases the Coulomb integral, α_{CM} , of the ring carbon to which the substituent is bonded; the degree of such perturbation is assumed to be proportional to h_{M} ²¹

$$\alpha_{\text{CM}} = \alpha_0 + \delta h_{\text{M}}\beta_0$$

where δ is known as the auxiliary inductive parameter. Wheland and Pauling found that the value, $\delta = 0.10$, gave reasonable results in explaining aromatic substitution reactions,²² and their value was adopted here.

In the Hückel model, the spin density on atom r is simply the probability amplitude of the odd electron on that atom, or $\rho_r = (C_{or})^2$, where the subscript, o , refers to the orbital to which the odd electron is assigned. However, if allowance is made for configuration interaction, the spin density is no longer equal to the probability amplitude of the odd electron. Using a perturbation treatment, McLachlan has derived an expression which corrects the Hückel spin densities for configuration interaction effects²³

$$\rho_r = C_{or}^2 - \lambda \sum_s \pi_{rs} C_{os}^2$$

where λ is a constant (1.2) and π_{rs} is the atom-atom polarizability.

(19) The value of Q is not strictly constant, for it depends on the charge density: see J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963); R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc.*, **86**, 3591 (1964).

(20) J. R. Bolton, A. Carrington, A. Foreman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

(21) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(22) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

(23) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

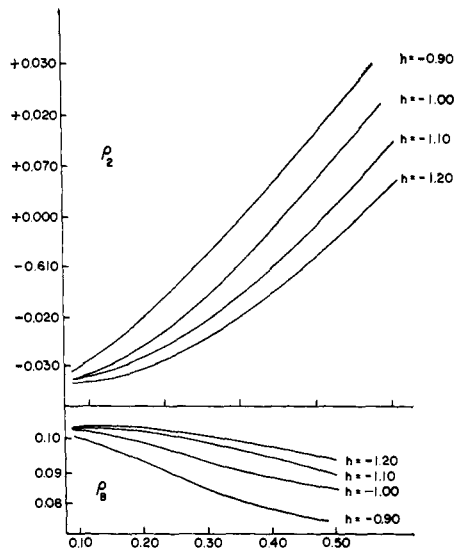


Figure 11. Ratios of calculated spin densities vs. k_{CM} assuming various h_{M} .

$$\pi_{rs} = 4 \sum_i^{\text{occ.}} \sum_j^{\text{vac.}} C_{ri} C_{sj} C_{sj} C_{ri} (\epsilon_j - \epsilon_i)^{-1}$$

The spin density distribution of the 4-substituted biphenylide were then calculated using McLachlan's expression for various values of the parameters h_{M} and k_{CM} . The ratios, ρ_{10}/ρ_8 and ρ_8/ρ_3 vs. k_{CM} , with several h_{M} constant, are shown in Figure 11; and the spin densities ρ_2 and ρ_8 vs. k_{CM} are likewise plotted in Figure 12. In Figure 13, the Hückel energy of the lowest un-

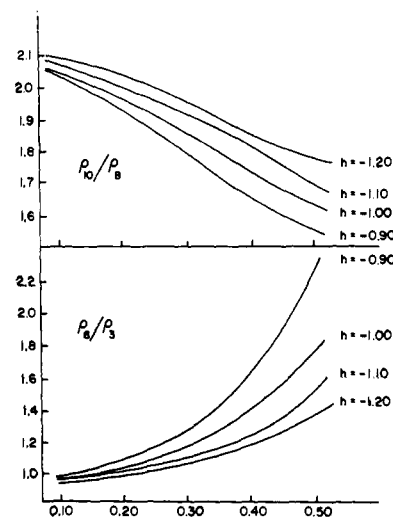


Figure 12. Spin densities vs. k_{CM} assuming various h_{M} .

occupied molecular orbital of the neutral 4-substituted biphenyl is shown as a function of k_{CM} for various h_{M} . The values of the heteroatom parameters which give the best fit of the calculated spin densities to the observed distribution were then obtained from the plots of ρ_i and ρ_i/ρ_j vs. k_{CM} . The values thus obtained are: $h_{\text{Si}} = -1.20$, $h_{\text{Ge}} = -1.05$, $k_{\text{CSi}} = 0.450$, $k_{\text{CGe}} = 0.300$. These values were then used to compute the spin densities in the 4,4'-disubstituted biphenylide and

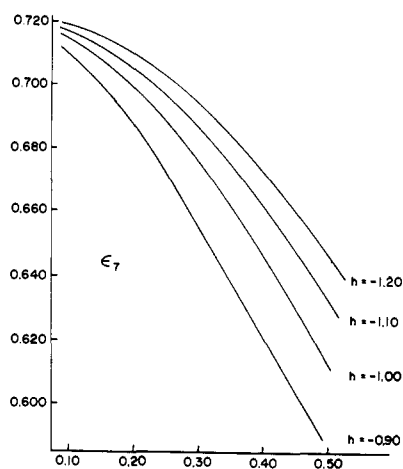


Figure 13. Calculated energy of the lowest unoccupied orbital in 4-substituted biphenyls vs. k_{CM} assuming various h_M .

the monosubstituted benzenide. The results of these calculations are entered in Table I under ρ_i (calcd.).

Comparison of ρ (obsd.) and ρ (calcd.) in Table I shows that excellent agreement was obtained for the biphenylide radicals using the parameters given above. The major discrepancies occur at the positions of negative spin density, where the McLachlan treatment tends to "overcorrect" the Hückel spin densities (this behavior was also observed in calculations on nitrile anion radicals).²⁴ However, the agreement in the case of the substituted benzenide radicals is very poor. In the McLachlan treatment, a high spin density on one carbon tends to induce a yet higher spin density on that carbon and negative spin density on its neighbors. Since the spin densities in the benzenide radicals tend to be higher than those in the biphenylide (the odd electron is not as delocalized), it may be that in this case the McLachlan treatment gives poorer results than the simple Hückel model. (It must be realized that if the Hückel spin densities were used throughout, a slightly different set of heteroatom parameters would be employed.) Indeed, as Table II shows, the Hückel (HMO)

Table II. Comparison of Spin Densities Calculated by Various Methods with the Observed Distribution in the Benzyl Radical

Position	HMO	SCF	VB ^a	Obsd. ^b
α	0.571	0.809	0.530	0.590 \pm 0.018
ortho	0.143	0.164	0.393	0.196
meta	0.000	-0.075	-0.221	0.00(?)
para	0.143	0.135	0.435	0.196

^a H. H. Dearman and H. M. McConnell, *J. Chem. Phys.*, **33**, 1877 (1960). ^b V. A. Tolkachev, I. I. Chkheidze, and N. Ya. Buben, *Dokl. Akad. Nauk SSSR.*, **147**, 643 (1962).

treatment gives better agreement with the observed spin densities in the benzyl radical than either the McLachlan treatment (SCF) or a simple valence bond approach (VB).

Since the derived values of the parameters, h_M and h_{CM} , give satisfactory agreement with observed spin densities, the bond orders and charge densities of the neutral molecule can be calculated. The bond order

(24) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2795 (1962).

and charge density are much less sensitive than the spin density to a small change in the parameters, since the former are given by a sum of terms and a change in one term tends to be cancelled by a change in another. Thus, the C-Si π -bond order was very close to 0.18 over a wide range of parameters, and the C-Ge π -bond order varied between 0.12 and 0.15 in a similar treatment. The results for the monosubstituted biphenyls and the monosubstituted benzenes are nearly identical with those of the disubstituted biphenyls, which are given in Table III. The bond orders and

Table III. Charge Densities and π -Bond Orders Calculated for the Disubstituted Biphenyls

Substituent	Atom ^a	q_i	Bond ^a	p_{lm}
(CH ₃) ₂ Si	1	0.970	1,2	0.649
	2	1.000	2,3	0.679
	3	0.999	3,4	0.617
	4	0.998	4,7	0.372
	Si	0.035	C-Si	0.177
(CH ₃) ₂ Ge	1	0.967	1,2	0.655
	2	1.007	2,3	0.678
	3	1.000	3,4	0.618
	4	1.003	4,7	0.371
	Ge	0.017	C-Ge	0.124

^a See Table I for numbering system.

charge densities are little changed from the parent hydrocarbon, a result consistent with the weak directive powers of these groups in aromatic electrophilic substitution reactions.⁷

Since the Coulomb integral, α , is a measure of the core potential of an atom in a molecule, it has been suggested that α is proportional to the electronegativity of that atom, since the electronegativity is a rough measure of the electron-attracting power of a bonded atom.²¹ If α_X is scaled in terms of β_0 , then $h_X = a(\chi_X - \chi_C)$.

In this work, it was found that $h_{Si} < h_{Ge}$; i.e., the core potential of germanium is greater than that of silicon. There is good evidence that the electronegativity of germanium is greater than that of silicon,^{25,26} and the effective nuclear charges as seen by a valence electron (calculated by Slater's rules)²⁷ are 4.15 for silicon and 4.45 for germanium. Although the core potentials of the *nd*-orbitals are probably not directly comparable to these quantities, one would expect a similar trend to be observed, whence α_{Si} is more positive than α_{Ge} .

Polarographic Reduction Potentials. Since there is a certain amount of arbitrariness in the choice of the values assigned to the heteroatom parameters, it is desirable to obtain independent justification of the values finally chosen. Such an independent check may be made by correlating the energy of the lowest unoccupied orbital (ϵ_{m+1}) with the polarographic half-wave reduction potentials of the hydrocarbons,²¹ provided that the reductions are electrochemically reversible. In this work, oscillopolarographic analyses showed that the one-electron reductions of the substituted biphenyls were reversible at the dropping mercury electrode in all cases. Streitwieser and Schwager have correlated the

(25) A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961); A. L. Allred and E. G. Rochow, *ibid.*, **5**, 264, 269 (1958); **20**, 167 (1961).

(26) M. A. Fineman and R. Daignault, *ibid.*, **10**, 205 (1959).

(27) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

half-wave reduction potentials of a number of hydrocarbons in dimethylformamide (DMF) with the energy of the lowest unoccupied orbital calculated from the Hückel model and obtained the least-squares equation²⁸

$$-E_{1/2} = (2.407 \pm 0.182)\epsilon_{m+1} - 0.396 \pm 0.093 \quad (1)$$

In this work, a silver nitrate-silver reference electrode was employed, whereas the potentials measured by Streitwieser and Schwager are referred to a mercury pool anode. A proportionality factor of 0.665, obtained from the half-wave potentials in both systems of biphenyl, was used to compensate for the difference in reference electrodes; these adjusted potentials are given in Table IV. The energy of the lowest unoccupied or-

Table IV. Comparison of the Energy of the Lowest Unoccupied MO Calculated from Reduction Potentials and the Secular Equation for Some Group IV Substituted Biphenyls

Substituent	$E_{1/2}$ (DMF) ^a	ϵ_7 ($E_{1/2}$)	ϵ_7 (e.s.r.)
4,4'-Di- <i>t</i> -butyl	-2.14	-0.722 ± 0.035	-0.720 ^b
4- <i>t</i> -Butyl	-2.10	-0.705	-0.712 ^b
4-Trimethylstannyl	-2.07	-0.693	...
None	-2.05	-0.685	-0.705
4-Trimethylgermyl	-2.05	-0.685	-0.682
4-Trimethylsilyl	-2.03	-0.676	-0.662
4,4'-Bis(trimethylgermyl)	-2.03	-0.676	-0.664
4,4'-Bis(trimethylsilyl)	-1.94	-0.640	-0.631

^a Adjusted to refer to a mercury pool reference electrode as discussed in the text. ^b Calculated with $\alpha(1) = \alpha_0 - 0.05\beta_0$; see Table I for the numbering system used in calculations.

bital, calculated from eq. 1, is entered under $\epsilon_7(E_{1/2})$ in Table IV. As can be seen, the values agree well with the energies calculated from the secular equation using the quantities h_M and k_{CM} derived from the e.s.r. spectra. The good agreement certainly indicates that the choice of parameters is not at all unreasonable.

Nuclear Magnetic Resonance. The n.m.r. spectra (see Table V) of the group IV substituted biphenyls are

Table V. Chemical Shifts (δ) of the Ring and Methyl Protons in Some Group IV-B Substituted Biphenyls

Substituent	δ (=CH) ^a	δ (CH ₃) ^a
4- <i>t</i> -Butyl	-359 ± 1	4.7 ± 0.2
4,4'-Di- <i>t</i> -butyl	-358	4.7
4-Trimethylsilyl	-365	67.4
4,4'-Bis(trimethylsilyl)	-366	67.4
4-Trimethylgermyl	-363	60.5
4,4'-Bis(trimethylgermyl)	-363	60.9
4-Trimethylstannyl	-363	66.4
4,4'-Bis(trimethylstannyl)	-364	66.6

^a Cycles per second relative to 2% cyclohexane internal standard in carbon tetrachloride. The concentration of the compounds was 0.05 mole fraction.

also consistent with the above conclusions. The order of shielding of the methyl protons is Si > Sn > Ge >> C, which is the same order found by Allred and Rochow for the tetramethyl derivatives of these elements.²⁵ The ring protons were found to be nearly equivalent

(28) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

(only one fairly sharp peak is observed), and their order of shielding is reversed from that of the methyl protons and is Si < Ge ~ Sn < C. The latter trend is consistent with the relatively large negative resonance integral, β_{C-Si} , and consequent electron-withdrawing resonance effect of silicon.

Summary

The e.s.r. spectra of some group IV substituted biphenyl anions were obtained and interpreted. The observed spin densities could be adequately explained on the basis of a Hückel model in which the spin densities are corrected for configuration interaction. The final values obtained for the Coulomb and resonance integrals suggest that silicon is more electropositive than germanium, but the former is more effective in an electron-withdrawing resonance capacity. The C-M π -bond orders were found by this model to be approximately 0.18 and 0.13 for silicon and germanium, respectively. These conclusions are consistent with polarographic data, n.m.r. chemical shifts, and chemical observations.

Experimental²⁹

Preparation of the Substituted Biphenyls. The biphenyls substituted with the (CH₃)₃M (M = Si, Ge, Sn) groups were prepared by the standard procedure of allowing a trimethylhalo derivative of the group IV element to react with either 4-lithiobiphenyl or 4,4'-dilithiobiphenyl. The lithiobiphenyls were prepared by adding *n*-butyllithium (15% in hexane, purchased from the Foote Mineral Co.) to the appropriate bromobiphenyl in ether at room temperature; the lithium-exchange reaction was essentially complete after stirring at room temperature for 0.5 hr. The trimethylchlorosilane was purchased from Metallomer Laboratories, and trimethyltin chloride was obtained from M & T Chemicals Co. Trimethylbromogermane was prepared by brominating tetramethylgermane,³⁰ made from methylmagnesium iodide and germanium tetrachloride in *n*-butyl ether.

Trimethyllead chloride was prepared from tetramethyllead (gift from the Ethyl Corp.) and anhydrous hydrogen chloride in hexane according to the directions of Calingaert, *et al.*³¹ In an evacuated capillary, the sample darkened at 280°.

Anal. Calcd. for C₃H₉PbCl: C, 12.52; H, 3.15. Found: C, 12.63; H, 3.15.

The preparation of 4-trimethylsilylbiphenyl is illustrative of the experimental procedure. Under an atmosphere of dry nitrogen, 50 ml. (0.078 mole) of *n*-butyllithium solution was added dropwise with stirring to 17.5 g. (0.075 mole) of 4-bromobiphenyl in anhydrous ether. After stirring the reaction mixture for 30 min., 5.8 g. (0.05 mole) of trimethylchlorosilane, dissolved in ether, was added dropwise with stirring. After the addition of the halide was complete, the mixture was then either refluxed gently for 1 hr. or stirred overnight at room temperature. The resulting mixture was then hydrolyzed with dilute sulfuric acid (*ca.* 1 *M*), and the aqueous and ether layers were then separated. After drying the

(29) Melting points are uncorrected; carbon-hydrogen analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(30) M. P. Brown and G. W. A. Fowles, *J. Chem. Soc.*, 2811 (1958).

(31) G. Calingaert, F. J. Dykstra, and H. Shapiro, *J. Am. Chem. Soc.*, **67**, 190 (1945).

ether layer with anhydrous Na_2SO_4 , the ether was stripped at reduced pressure, and the oily product dissolved in methanol. Cooling the methanol solution to -10° gave white crystals, which, after recrystallization from methanol, melted at 54° (55%).

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{Si}$: C, 79.58; H, 8.02. Found: C, 79.27; H, 7.92.

4-Trimethylgermylbiphenyl was produced in 74% yield from 5.0 g. (0.025 mole) of trimethylbromogermane in an analogous reaction. The product was recrystallized from methanol and melted at 55° .

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{Ge}$: C, 66.51; H, 6.70. Found: C, 66.55; H, 6.71.

Two products were obtained from the reaction of trimethylchlorostannane with 4-lithiobiphenyl. The first crop of crystals obtained after stripping the ether was only slightly soluble in methanol. Recrystallization from benzene-methanol mixture gave feathery, white needles, m.p. $173-175^\circ$; the product was identified from the analysis as bis(4-biphenyl)dimethylstannane (~15%).

Anal. Calcd. for $\text{C}_{26}\text{H}_{24}\text{Sn}$: C, 68.61; H, 5.32. Found: C, 68.15; H, 5.19.

The methanol mother liquor gave ca. 2 g. of pasty solid on cooling to -20° . Recrystallization from methanol-water afforded 1.5 g. (11%) of white flakes, m.p. 53° .

Anal. Calcd. for $\text{C}_{15}\text{H}_{18}\text{Sn}$: C, 56.83; H, 5.72. Found: C, 56.80; H, 5.73.

The reaction of trimethyllead chloride with 4-lithiobiphenyl gave only bis(4-biphenyl)dimethylplumbane, m.p. $178-180^\circ$, in nearly quantitative yield.

Anal. Calcd. for $\text{C}_{26}\text{H}_{24}\text{Pb}$: C, 57.44; H, 4.45. Found: C, 57.34; H, 4.50.

4,4'-Dilithiobiphenyl, prepared from the interaction of 0.075 mole of *n*-butyllithium and 10.5 g. (0.034 mole) of 4,4'-dibromobiphenyl in ether, gave 4,4'-bis(trimethylsilyl)biphenyl in 55% yield when allowed to react with 7.3 g. (0.067 mole) of trimethylchlorosilane. The product from methanol melted at $84-85^\circ$.

Anal. Calcd. for $\text{C}_{18}\text{H}_{26}\text{Si}_2$: C, 72.40; H, 8.78. Found: C, 72.51; H, 8.88.

The corresponding germanium derivative, m.p. 86° , was obtained in 80% yield from the reaction of dilithiobiphenyl, prepared as above, with trimethylbromogermane.

Anal. Calcd. for $\text{C}_{18}\text{H}_{26}\text{Ge}_2$: C, 55.78; H, 6.76. Found: C, 55.71; H, 6.64.

Trimethylchlorostannane was allowed to react with dilithiobiphenyl in the manner described above. The disubstituted tin compound, m.p. $125-126^\circ$, was obtained in 70% yield.

Anal. Calcd. for $\text{C}_{18}\text{H}_{26}\text{Sn}_2$: C, 45.06; H, 5.46. Found: C, 45.83; H, 5.56.

In the attempted preparation of 4,4'-bis(trimethylplumbyl)biphenyl, 9.2 g. (0.032 mole) of trimethyllead chloride was added as a slush in diethyl ether to 0.035 mole of 4,4'-dilithiobiphenyl. After hydrolysis, the ether was stripped at reduced pressure and replaced by methanol. Gentle heating ($<40^\circ$) on a steam bath dissolved the oily product giving a light yellow solution. Only yellow ill-defined products, m.p. $\sim 140-190^\circ$ dec., were obtained.

4-*t*-Butylphenyl and 4,4'-di-*t*-butylbiphenyl were prepared by a Friedel-Crafts reaction using 26.3 g. (0.284

mole) of biphenyl, 6.0 g. (0.045 mole) of anhydrous aluminum chloride, and 25 g. (0.162 mole) of *t*-butyl chloride. The reaction was run at room temperature in nitromethane solvent.³² The reaction mixture was hydrolyzed by pouring it over cracked ice. The aqueous and organic phases were separated and the nitromethane was stripped at reduced pressure. The product was then vacuum distilled; ca. 40 ml. of distillate was collected at $122-125^\circ$, followed by ca. 20 g. of product distilling at 125° . The latter fraction solidified in the receiver and was recrystallized from methanol to give white crystals of di-*t*-butylbiphenyl, m.p. $128.6-129^\circ$.

Anal. Calcd. for $\text{C}_{20}\text{H}_{26}$: C, 90.16; H, 9.84. Found: C, 89.85; H, 9.97.

A large amount of the disubstituted biphenyl separated from the fraction, b.p. $122-125^\circ$, upon the addition of cold methanol. After separating the product, the mother liquor was cooled to -20° giving a yellow pasty solid which was molecularly distilled at 40° (0.01 mm.). In this way ca. 0.5 g. of 4-*t*-butylbiphenyl, m.p. $49-51^\circ$, was obtained.

Anal. Calcd. for $\text{C}_{16}\text{H}_{18}$: C, 91.39; H, 8.61. Found: C, 91.28; H, 8.70.

The aromatic compounds prepared as described above were reduced with either sodium or sodium-potassium alloy in tetrahydrofuran at -23 or -63° (CCl_4 or CHCl_3 slush, respectively) in an apparatus which excluded air and moisture. The radical solution could be decanted directly into a prechilled, e.s.r. sample tube, which was then sealed and placed immediately in the microwave resonance cavity. While in the microwave cavity, the sample was cooled by evaporating nitrogen and passing the cold gas around the sample which was placed in a special Varian Associates dewar; the temperature was controlled by the rate of the nitrogen flow and was $-50 \pm 5^\circ$ for the low temperature work.

The e.s.r. spectra were obtained on a Varian Associates V-4500 instrument equipped with a 100-kc. field modulation unit and a Fieldial for regulation of the magnetic field strength and scanning rates. The spectra were recorded on a Varian G-10 recorder; the coupling constants were determined by measuring the distance between peak centers and applying the scan rate factor from the Fieldial. A Varian 12-in. magnet supplied the homogeneous magnetic field.

The instrument used to obtain the polarographic data has been described in detail in the literature,³³⁻³⁸ and includes a three-electrode configuration which eliminates most of the ohmic potential drop in solvents of low dielectric constant. The only uncompensated solution ohmic resistance is between the tip of the reference electrode and the dropping mercury electrode. A platinum wire served as the auxiliary electrode and silver nitrate (saturated in DMF)-silver was used as the

(32) H. Pines, private communication, suggested the use of a deactivating solvent, e.g., CS_2 or CH_3NO_2 , to prevent *meta* substitution.

(33) M. T. Kelly, D. J. Fisher, and H. C. Jones, *Anal. Chem.*, **31**, 1475 (1959); *ibid.*, **32**, 1262 (1960).

(34) D. D. DeFord, Division of Analytical Chemistry, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 1958.

(35) G. L. Booman, *Anal. Chem.*, **29**, 213 (1957); G. L. Booman and W. B. Holbrook, *ibid.*, **35**, 1793 (1963).

(36) W. M. Schwarz and I. Shain, *ibid.*, **35**, 1770 (1963).

(37) W. L. Underkoffler and I. Shain, *ibid.*, **35**, 1778 (1963).

(38) D. E. Smith, *ibid.*, **35**, 1811 (1963).

reference electrode. The source of the triangular wave potential used in the oscillographic measurements was designed by Drs. D. D. DeFord and D. E. Smith of this department. Conventional polarograms were traced on a Sargent Model SR recorder and oscillograms were displayed on a Tektronix Model 502 A oscilloscope and photographed with a Tektronix Model C-13 oscilloscope camera.

A Varian Associates A-60 instrument was used to obtain the nuclear magnetic resonance spectra of the compounds studied, and the chemical shifts were measured directly from the chart. Carbon tetrachloride was used for the solvent with 2% cyclohexane as internal reference and the concentration of each compound under investigation was 0.05 mole fraction.

Calculation of molecular quantities, *e.g.*, spin densities, bond orders, etc., was performed on an IBM 709 digital computer. The input data consisted of the elements of the H-matrix, which was then diagonalized by the Jacobi routine.

Acknowledgments. The authors especially wish to thank Dr. D. F. Shriver for the use of his computer program and Dr. D. E. Smith for the use of his polarographic equipment as well as for their many helpful discussions. The Northwestern University Computing Center generously provided computer time. This research was supported in part by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center.

The Nature of the Solution of Sodium Tetracarbonylcobaltate(-I) in Various Solvents^{1,2}

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Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana. Received February 1, 1965

The ν_{CO} of $\text{NaCo}(\text{CO})_4$ is shown to be subject to a substantial solvent shift. In pure THF, the salt shows three bands in the 5- μ region of the spectra, while only one band is observed in water and DMF solutions. Conductance data for the salt indicate that ion pairs as well as larger clusters are formed in pure THF. The shape of the Δ vs. \sqrt{C} curves for water or aqueous THF solutions is also characteristic of a solution in which ions are associated. The data are interpreted in terms of the effects of the cationic field and the interaction with the environment.

Introduction

In an extension of the studies of the infrared spectra of carbonylmetallate ions in this laboratory,⁴ it has been necessary to prepare the salt of $\text{Co}(\text{CO})_4^-$ in various solvents. It was soon observed that the carbonyl stretching frequency (ν_{CO}) of this ion in the 5- μ region of the infrared spectra is subject to a substantial solvent effect. This large shift raised the question of the factors which influence the amount of the shifts and of the nature of the solutions of carbonylmetallate ions. This paper reports the results of spectrographic and conductometric studies of the $\text{Co}(\text{CO})_4^-$ anion in solutions of various mixtures of piperidine and water, THF and water, DMF and water, and THF and DMF.

Results

Infrared Spectra. The infrared spectrum of $\text{NaCo}(\text{CO})_4$ in THF solutions was examined at 5 μ over the

concentration range from 2.0 to 0.0009 *M* with a high resolution spectrometer. The cell path length was increased with dilution to keep a similar amount of solute in the beam. The general nature of the results is shown in Figure 1. A concentrated solution of $\text{NaCo}(\text{CO})_4$ in pure THF exhibits two bands in the 5- μ region, *viz.*, at 1883 (s) and 1861 (m, sh) cm^{-1} . As the solution becomes more dilute, the dissymmetry on the high frequency side of the main band becomes very pronounced and appears to give rise to a separation into two overlapping bands (1886 and *ca.* 1890 cm^{-1}) in the most dilute solutions. At the same time, the side band at 1861 cm^{-1} seems to shift toward lower frequencies and becomes more clearly separated from the more intense absorption; it was observed at 1854 cm^{-1} in the 0.026 *M* solution.

When a small amount (8%) of water was added to a THF solution of $\text{NaCo}(\text{CO})_4$, both side bands disappeared, leaving the main band at 1886 cm^{-1} nicely symmetrical. The effect of DMF was the same but more gradual. It was not until DMF constituted about half of the solvent that the side bands disappeared completely. This is the only band observed at 5 μ in these solvents and appeared at ν_{CO} 1919 cm^{-1} in water and 1892 cm^{-1} in DMF. The band in water solution was broader than that in either DMF or THF solution.

Since marked differences in the values of ν_{CO} were observed in various solvents, the value of ν_{CO} in mixed solvents was investigated. The values of ν_{CO} in various media are presented in Table I and are plotted in Figures 2 and 3. These solvent shifts are very much larger than those characteristic of neutral metal carbonyls.⁵ In all spectra examined, only one band was observed in the 5- μ region except those of the solutions in THF and in

(1) Abstracted from the Ph.D. thesis of M. T. Yang, Purdue University, 1962.

(2) Supported by a grant from the Atomic Energy Commission.

(3) Fulbright Postdoctorate Fellow, 1959-1961.

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