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ELECTRON SPIN RESONANCE STUDIES OF RADICAL ANIONS OF GROUP IV DIBENZO[b,f]METALLEPINS

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SUMMARY

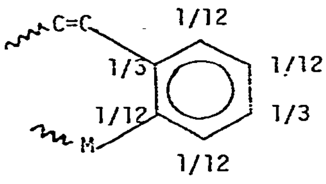
Stable radical anions are produced from 5,5-dimethyl-5H-dibenzo[b,f]-silepin, 5-methyl-5-phenyl-5H-dibenzo[b,f]silepin, 5,5-diphenyl-5H-dibenzo[b,f]silepin or 5,5-diphenyl-5H-dibenzo[b,f]germepin on contact with sodium/potassium alloy in dry, degassed ether solutions at room temperature. The esr spectra of the radical anions show little sensitivity to the metal atom or metal atom substituent. Except for dimethylsilepin, which exhibits a temperature dependent spectrum, esr spectra of the dibenzometallepins have hyperfine line positions that superimpose on each other and that are temperature independent from -100° to +70°. The unpaired electron distribution in the anions is determined by the cis-stilbene-like portion of the metallepin molecule. Under similar conditions the radical anion of 9,9-dimethyl-9H-tribenzo[b,d,f]silepin is produced. Its esr spectrum may be interpreted in terms of an appropriately substituted o-terphenyl. Hückel molecular orbital calculations provide satisfactory rationalizations of all the observed esr spectra.

INTRODUCTION

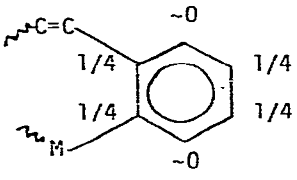
The recent synthesis and characterization of group IV dibenzo[b,f]-metallepins provides a family of model compounds for the study of the influence of group IV metals on electron density distributions in aromatic compounds.[1,2] The known stability of radical anions of related compounds (e.g., tolan,[3] cis- and trans-stilbene,[3] 1,2:5,6-dibenzocyclooctatetraene,[4] and 1,2-diphenylcyclobutene [5]) as well as those of directly analogous compounds (e.g., dibenzo[b,f]thiepin[6] and 5H-dibenzo[a,d]cycloheptene[7]) suggested that the present investigations would be feasible.

Recently we reported esr studies of group IV organometal-substituted benzenes that utilized a perturbation model to describe the influence of alkyl (electron-releasing) and organometal (electron-withdrawing) substituents on the benzene MO's.[8] In competitions between alkyl and organosilyl or organogermyl substituents, the organometals determine the form of the MO occupied by the extra electron of the radical anions. The metallepin systems studied in the present work represent competition between an organometal substituent and an alkenyl substituent that is likely to be strongly electron-withdrawing. The results of the esr studies of radical anions of compounds related to the experimental compounds of this study support the strong influence that would be expected for alkenyl-substituents conjugated with the benzene nucleus.[3] Measurement of the esr spectra of this family of radical anions permits determination of the form of the empty MO's actually lying lowest in energy and hence gives an indication of the competitive electron-withdrawing strength of the organometal vs. alkenyl and phenyl substituents.

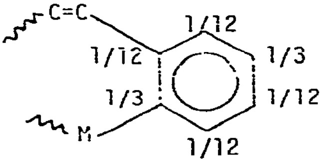
The form of the molecular orbitals of the metallepins, at least for limiting cases, can be predicted using considerations developed earlier.[8,9] Three possible situations with regard to relative electron-withdrawing power may be summarized: (1) alkenyl substituent >> organometal substituent; (2) alkenyl substituent = organometal substituent; and (3) alkenyl substituent << organometal substituent. The corresponding spin density distributions would be:



Case 1: C=C>>M



Case 2: C=C = M



Case 3: C=C<<M

For the metallepins studied in this work, the above estimates must be divided by two because of delocalization of the unpaired electron over two ring systems connected by the ethylenic bridge. Although Case 1 appears superficially identical to Case 3 (because of the equal numbers of large and small spin density positions),they may be distinguished because Case 1 would also have large interactions with the ethylenic protons, an interaction that presumably would be absent or considerably diminished in Case 3 because of the low spin density at the carbon atom adjacent to the ethylenic substituent. Further, these estimates will be reduced correspondingly as spin density is delocalized into the antibonding *pi* MO of the ethylenic bridge. An alternative view considers the unpaired electron to be delocalized from the ethylenic double bond into the pi systems of the substituent phenyl groups. Of course the MO calculations reported below consider the pi electron system of the entire molecule.

RESULTS AND DISCUSSION

ESR results. In general silepins and germepins are reduced readily under the experimental conditions employed. Clean, relatively well-resolved esr spectra are observed and confirm the expected similarity between the lowest empty MO of silyl- and germyl-metallepins and that of the related dibenzocycloheptene.[7] In Table 1 are reported the hyperfine coupling constants derived from the esr spectra of the dibenzometallepins studied in this work. Data for dibenzocycloheptene are presented for comparison.

The esr spectra of the radical anions of diphenyldibenzosilepin (Fig. 1),

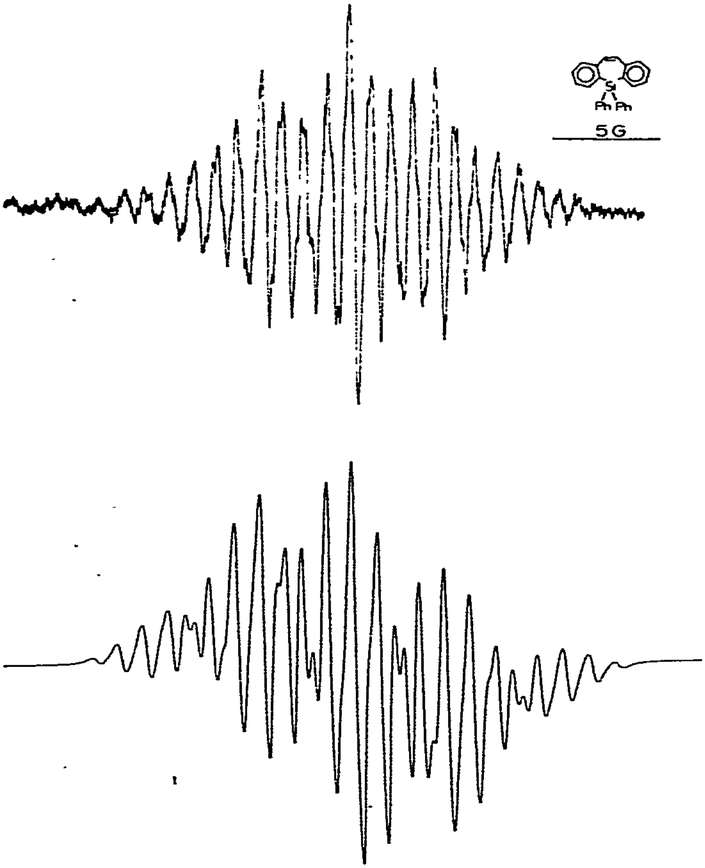


Fig. 1. (Above) ESR spectrum of diphenyldibenzo[b,f]silepin radical anion; (Below) Computer simulation of same esr spectrum using coupling constants from Table 1.

methylphenyldibenzosilepin (Fig. 2), and diphenyldibenzosilepin (Fig. 3) are superimposable with regard to line positions. Small variations in these wide hyperfine lines (linewidths ca. 0.5 gauss) among the radicals cause the observed differences in line intensities. The esr spectra of the dibenzo-

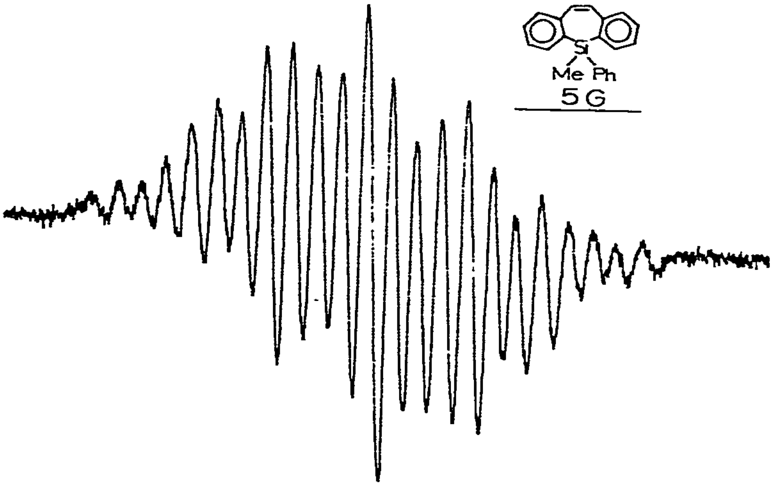


Fig. 2. ESR spectrum of methylphenyldibenzo[b,f]silepin radical anion.

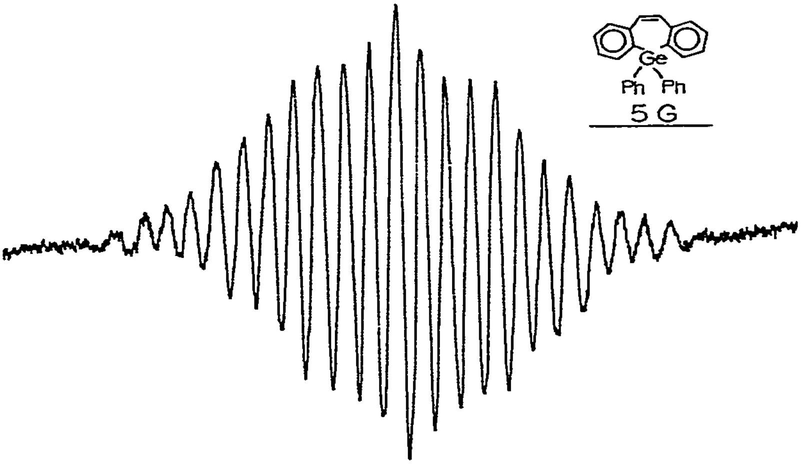


Fig. 3. ESR spectrum of diphenyldibenzo[b,f]germepin radical anion.

metallepins (except that of dimethyldibenzosilepin) are temperature independent in either linewidth or resolution in the temperature range -100° to +70°. The spectra appear to arise from hyperfine splitting by protons at either two or four positions of large spin density plus smaller splittings. A computer-simulated spectrum based on the large hyperfine splitting evident in Fig.1 does not reproduce the experimental spectrum exactly. The simulated spectrum is quite sensitive to small variations in the choice of coupling constants owing to complex interferences among line intensity contributions in the central portion of the spectrum. Also shown in Fig.1 is the best simulated spectrum, and the assignments for this spectrum simulation are reported separately in Table 1.

The esr spectrum of tribenzosilepin radical anion (Fig. 4) is extremely narrow in spectra width (11.96 gauss) and has the same broad lines (0.69 gauss) as do the metallepin radicals discussed above. If allowance is made for the

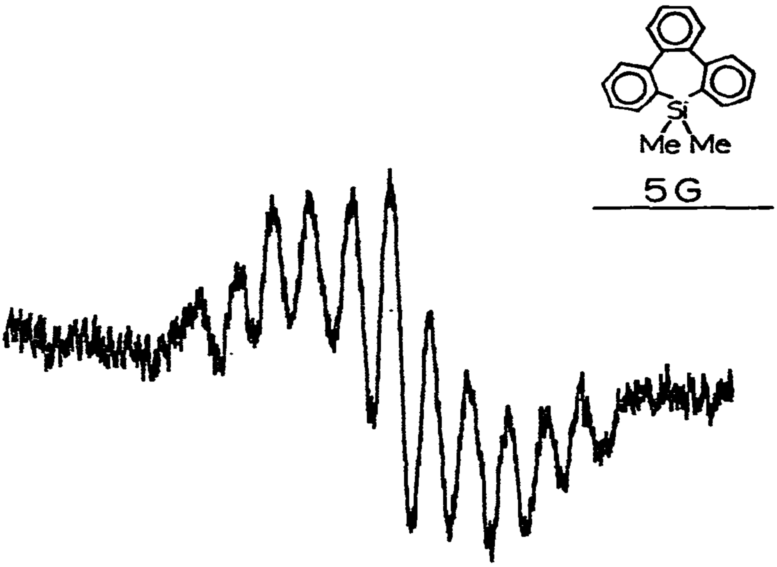
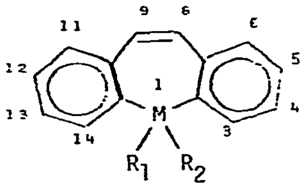


Fig. 4. ESR spectrum of tribenzosilepin radical anion.

TABLE 1

ESR Results for Anion Radicals of Dibenzometallepins[a,b]



M	R_1	R_2	Line Width	Spectrum Width	a_3	a_4	a_5	a_6	a_8
Si[c]	Ph	Ph	0.44	22.6	1.06	4.12	1.06	2.00	4.12
Si[c]	Ph	Me	0.50	22.6	1.02	4.14	1.02	2.04	4.14
Ge[c]	Ph	Ph	0.41	22.6	1.02	4.14	1.02	2.00	4.14
Computer Simulation (See Fig 1)			0.44		1.17	3.10	1.17	2.40	4.20
Si	Me	Me	<0.15	24.7	0.59	3.94	0.59	2.98	4.50
Computer Simulation (See Fig 5)			0.10		0.59	3.94	0.59	2.98	4.50
C[d]	H	H	....	....	0.51	4.19	1.03	2.30	4.20

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[a] Coupling constants are reported in gauss and are, in principle, accurate to ±0.05 gauss. Widths are reported in gauss.

[b] Hyperfine coupling constants are assigned by analogy to results reported in References 3, 5, and 7, and on the basis of molecular orbital calculations reported in Table 4.

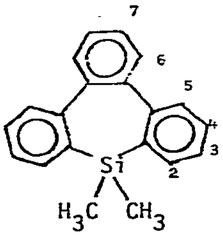
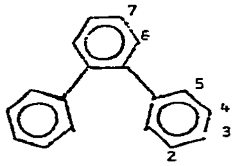
[c] The reported coupling constants are measured from the esr spectra. However, the large linewidths and severe overlapping of hyperfine lines make these values suspect. Note that the measured values are all within one or two linewidths of the spectrum values fitted by computer simulation Thus the measured values may be in error by as much as ±0.5 to ±1.0 gauss.

[d] Hyperfine coupling constants are quoted from Reference 7.

disappearance of small hyperfine splittings in the large linewidth, the spectrum can be rationalized as arising from hyperfine splitting by three pairs of almost-equivalent protons. This rationalization has been verified by computer simulation of the spectrum. The experimental coupling constants are reported in Table 2 where they are compared with predictions based on Hückel MO calculations for the radical anions of o-terphenyl.

TABLE 2

ESR Results for Dimethyltribenzosilepin Radical Anion[a,b]
Compared with Calculated Results for o-Terphenyl Radical Anion[c]

	a_3	a_4	a_5	a_6	a_7
	2.64	~0	2.03	~0	2.21
	2.58	0.24	1.71	0.33	2.18

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[a] Assignments of hyperfine coupling constants to positions are based on Hückel MO calculations for dimethyltribenzosilepin using $h_{Si} = -2.7$ and $k_{CSi} = 0.7$.

[b] Linewidth of esr lines is ca. 0.69 gauss; spectrum width, ca. 11.96 gauss (see Fig 4). All hyperfine coupling constants are reported in gauss.

[c] Hyperfine coupling constants for o-terphenyl radical anion are estimated using McConnell's equation with Q = -28 gauss and spin densities from C. A. Coulson and A. Streitwieser, Jr., Dictionary of π-Electron Calculations, W. H. Freeman and Company, San Francisco, 1965, p. 95.

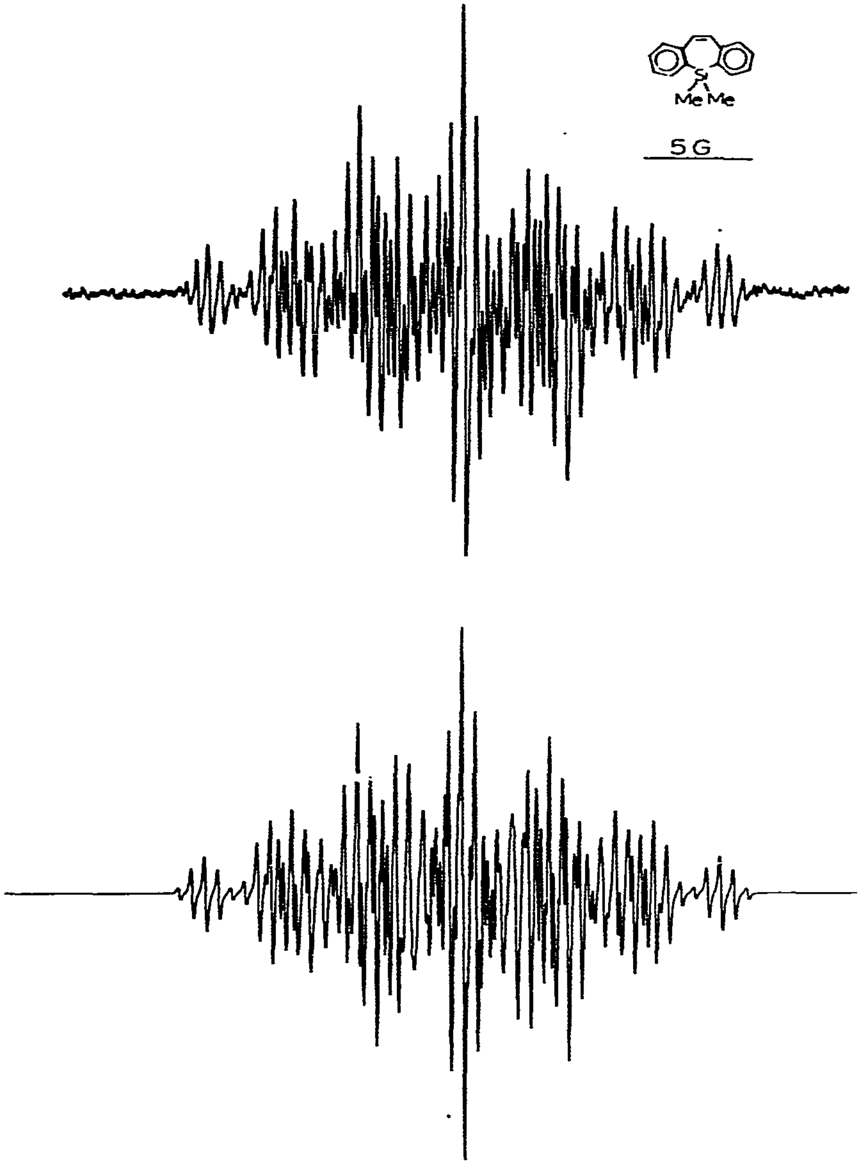


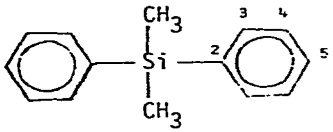
Fig. 5.(Above) ESR spectrum of dimethyldibenzo[b,f]silepin radical anion. (Below) Computer simulation of same esr spectrum using coupling constants from Table 1.

In contrast with the metallepins discussed above, dimethyldibenzosilepin radical anion has a strongly temperature-dependent esr spectrum with narrow hyperfine lines (linewidths ca. 0.15 gauss). The anion is stable over a wide range of temperatures, but well-resolved spectra are observed only at or below ca. -50°. Figure 5 presents the spectrum observed at -94° as well as a computer-simulated spectrum generated from the hyperfine coupling assignments reported in Table 1. The simulation is extremely sensitive to small variations in the two largest hyperfine coupling constants. A simulated spectrum with negligible linewidth (ca. 0.01 gauss) indicates that this sensitivity arises from the interference of many hyperfine components in the central region of the spectrum. No hyperfine splitting from hyperfine interaction of the unpaired electron with the silyl-methyl protons is observed.

Molecular Orbital Calculations. Simple Hückel molecular orbital calculations treat the dibenzometallepin molecule as being planar and incorporate the metal atom as a pseudoheteroatom in the pi electron system. In previous studies of trimethylsilyl-substituted benzene anions, the $-SiMe_3$ group was assigned a coulomb parameter $h_{Si} = -2.0$ and resonance parameter $k_{CSi} = 0.7$ to correlate electron spin densities that were determined by esr measurements.[8] For the present systems, a value of $h_{Si} = -2.70$ was chosen for $-SiMe_2-$ by fitting the spin density distributions reported for dimethyldiphenylsilane radical anion.[10] Table 3 reports the reasonable agreement between calculated and experimental spin densities achieved using this value. Table 4 reports molecular orbital calculations for dimethyldibenzosilepin using the coulomb parameter derived from $Ph_2SiMe_2^{\overline{\cdot}}$. Systematic variation of the coulomb parameter for $-SiMe_2-$ in the dimethyldibenzosilepin Hückel calculation confirmed that the value of -2.70 produced optimal agreement between calculated and experimental values of the spin densities. The resonance parameter for the ethylenic double bond was chosen as $\beta_{C=C} = 1.2\beta_0$ where β_0 is the resonance parameter appropriate to a

TABLE 3

Test of Heteroatom Parameters for -SiMe$_2$-



Position:	3	4	5	3/5	4/5
HFCC[a]	1.44	0.34	4.15	0.347	0.082
ρ_{expt}[b]	0.051	0.012	0.148		
ρ_{calc}[c]	0.051	0.030	0.148	0.345	0.203

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[a] Experimental hyperfine coupling constants (HFCC) in gauss as reported by Reference 10.

[b] Calculated from experimental HFCC of reference 10 using McConnell's equation with Q = -28.

[c] Calculated by Hückel molecular orbital theory for Ph$_2$SiMe$_2^{\cdot -}$ using h_{Si} = -2.7 and k_{CSi} = 0.7.

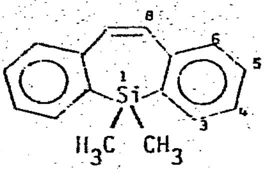
[d] Although the agreement of calculated and experimental spin densities for position 4 is only moderate, the density at position 4 is small. MO calculations on related molecules are characterized by relatively poor agreement for positions *meta*- to a silicon substituent (*cf.* Reference 8).

conjugated double bond (*e.g.*, in benzene). This value for $\beta_{C=C}$ was chosen by interpolation from a graph of β as a function of carbon-carbon bond length.[11]

The symmetry of dibenzometallepins results in Hückel calculations that predict a node through the metal atom. This is the origin of the insensitivity of esr spectra of metallepins to variations in either the metal atom or metal-atom substituents. Molecular orbital calculations based on the semi-empirical, self-consistent field method of McLachlan,[12] when used with appropriate pseudoheteroatom parameters for the organometal moiety,[8,13]

TABLE 4

Results of Molecular Orbital Calculations for Dimethyldibenzosilepin



Position:	3	4	5	6	8	3/8	4/8	5/8	6/8
HFCC[a]	0.59	3.94	0.59	2.98	4.50	0.130	0.876	0.130	0.658
ρ_{expt}[b]	0.021	0.141	0.021	0.106	0.161				
ρ_{calc}[c]	0.024	0.111	0.002	0.092	0.159	0.148	0.698	0.013	0.575

[a] Experimental hyperfine coupling constants (HFCC) in gauss from Table 1.

[b] Calculated from experimental HFCC using McConnell's equation with Q = -28. This value of Q has been established as most appropriate for extended pi systems (see References 8 and 13).

[c] Calculated by Hückel molecular orbital theory using $h_{Si} = -2.7$ and $k_{CSi} = 0.7$.

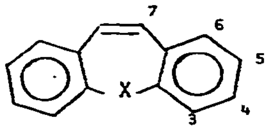
place only small spin densities at the metal atom or on its substituents. The predicted spin densities are too small to produce observable hyperfine splittings but might contribute to the linewidth of the observed esr lines.

The dihedral angle between the "benzo" rings of methylphenyldibenzosilepin has been determined to be 131°,[14] and one might expect that this nonplanarity would have a significant influence on the unpaired electron distribution. Nonplanar systems are treated in the Hückel formalism by incorporating a cosine dependence in the "β" values for bonds connecting the individually-planar systems.[15] Systematic variation of β for the appropriate bonds in dimethyldibenzosilepin produced small variations in the predicted spin densities but did not produce any improvement in agreement with experimental values.

Comparison with related compounds. The similarity of the spectra observed for the family of dibenzometallepin anions of this study suggests that the metal atom has little, if any, influence on the molecular orbital occupied by the unpaired electron. Because the observed delocalization of the unpaired electron is complete throughout the molecule and is independent of temperature, it is not possible to detect any influence of the metal atom on electron transfer between the aromatic rings in dibenzometallepin radical anions.[10] Detailed comparison of hyperfine

TABLE 5

ESR Results for Dibenzometallepins and Related Compounds



X	a_3	a_4	a_5	a_6	a_7	Ref.
-C=C-	0.20	1.80	1.80	0.20	2.80	4
>C=O	3.50	0.81	3.04	0.34	0.34	7
>S=O	0.71	3.52	0.14	0.95	3.52	a
>S	1.41	3.79	0.00	1.41	3.79	6
>CH_2	0.55	4.20	1.10	2.20	4.20	7
>$SiMe_2$	0.59	3.94	0.59	2.98	4.50	b
>$SiPh_2$	1.17	3.10	1.17	2.40	4.50	c

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[a] Hyperfine coupling constants quoted from A. Trifunac and E. T. Kaiser, J. Phys. Chem., 74 (1970) 2236.

[b] This work

[c] This work, computer simulation values.

coupling constants from analogous compounds from the literature (see Table 5) indicates that the dibenzometallepin anions closely resemble those of dibenzo[b,f]thiepin and 5H-dibenzo[a,d]cycloheptene and bear little resemblance to those of strongly-electron-withdrawing substituents, e.g., -C=C-, >C=O, and >S=O.

CONCLUSION

Dibenzometallepins of silicon and germanium are reduced readily to form stable radical anions that have the unpaired electron distribution determined by the *cis*-stilbene-like portion of the molecule. The esr spectra show little sensitivity to variation of the metal atom or metal-atom substituents or, with the exception of dimethyldibenzometallepin, to variations in temperature. Hückel MO calculations that satisfactorily rationalize the esr spectra indicate that the metal atom lies in a node of the MO occupied by the unpaired electron. Dibenzometallepins have esr spectra that are similar to those of the related dibenzothiepin and dibenzocycloheptene radical anions.

EXPERIMENTAL

Materials. Dibenzo[b,f]metallepins were synthesized, purified, and characterized as previously reported.[1,2] The compound 5-methyl-5-phenyl-5H-dibenzo[b,f]silepin was synthesized and characterized by methods analogous to those previously reported.[1,2] Dibenzo[b,f]dimethylsilepin was purified by preparative gas chromatography using a Hewlett-Packard 5711 gas chromatograph equipped with a nine foot column packed with 20% QF-1 on 60/80 mesh Chromosorb P.

Electron spin resonance spectra. Esr spectra were determined on a component-assembled spectrometer that consisted of a six-inch magnet (Alpha Scientific Laboratories, Inc.) equipped with Fieldial (Varian Associates), a microwave bridge constructed around a four-port circulator and Schottky diode detector (Microwave Associates), X-band microwave cavity (Varian Associates) and a Gunn diode microwave source (Fairchild, Inc.). Modulation and detection to produce first derivative esr spectra were accomplished with a 100 kHz modulator (Varian V4560) and a 100 kHz phase-sensitive amplifier (EMC, Inc.). A custom-constructed, low-noise preamplifier was used to boost the detector crystal signal before phase detection. The microwave frequency was stabilized by locking the Gunn diode oscillator to the microwave cavity (Teltronics, Inc.). The spectrometer system thus assembled had resolution of ca. 100 milligauss and a sensitivity of ca. 10^{12} spins/gauss at microwave power levels of ca. 1 milliwatt in the microwave cavity. Low temperature spectra were measured using a dewar cold-finger inserted into the microwave cavity with a current of cold nitrogen gas passing over the esr sample tube. Temperatures were controlled by varying the rate of boil-off of liquid nitrogen to vary the flow rate of gaseous nitrogen and were monitored by a copper-constantan thermocouple referenced to an ice-water bath. For ease of temperature monitoring, the thermocouple voltage was amplified, scaled by operational amplifiers, and displayed on a digital voltmeter (Heath Co.) as the appropriate temperature in millivolts. Temperatures thus controlled and measured are believed accurate to ±5°C.

Radical anions of metallepins were generated by reduction with sodium-potassium alloy in ether solvents at the temperature of toluene slush. Details of the reduction procedures have been published previously.[8,16-18] Samples were approximately millimolar in the appropriate substrate.

ACKNOWLEDGEMENTS

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REFERENCES

1 J. Y. Corey, M. Dueber, and B. Bichlmeir, J. Organometal. Chem., 26 (1971) 167.

2 J. Y. Corey, M. Dueber, and M. Malaidza, J. Organometal. Chem., 36 (1972) 49.

3 C. S. Johnson, Jr. and R. Chang, J. Chem. Phys., 43 (1965) 3183.

4 A. Carrington, H. C. Longuet-Higgins, and P. F. Todd, Mol. Phys. (1964) 45.

5 I. B. Goldberg, Org. Mag. Res., 5 (1973) 29.

6 M. M. Urberg and E. T. Kaiser, J. Amer. Chem. Soc., 89 (1967) 5391.

7 B. J. Tabner and J. R. Zdysiewicz, J. Chem. Soc. Perkin II, (1973) 811.

8 H. J. Sipe, Jr. and R. West, J. Organometal. Chem., 70 (1974) 353, 367.

9 J. A. Bedford, J. R. Bolton, A. Carrington, and A. H. Prince, Trans. Faraday Soc., 59 (1962) 53.

10 Y.-P. Wan, D. H. O'Brien, and F. J. Smentowski, J. Amer. Chem. Soc., 94 (1972) 7680; E. S. Kean, K. Fisher, and R. West, J. Amer. Chem. Soc., 94 (1972) 3246.

11 A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists, John Wiley & Sons, Inc., New York, 1961, p.105.

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

13 M. D. Curtis and A. L. Allred, J. Amer. Chem. Soc., 87 (1965) 2554.

14 E. R. Corey, private communication.

15 J. Y. Corey and E. R. Corey, Tetrahedron Lett., 46 (1972) 4669.

16 G. R. Husk and R. West, J. Amer. Chem. Soc., 87 (1965) 3993.

17 D. E. Paul, D. Lipkin, and S. A. Weissman, J. Amer. Chem. Soc., 78(1956)116

18 P. R. Jones and R. West, J. Amer. Chem. Soc., 90 (1968) 6978.