Nature of the Bonding between Silicon and the Cobalt Tetracarbonyl Group in Silylcobalt Tetracarbonyls.
II. Mass Spectral Evidence

F. E. Saalfeld,[1a] M. V. McDowell,[1a] and A. G. MacDiarmid[1b]

Contribution from the Naval Research Laboratory, Washington, D. C. 20390,
and John Harrison Laboratory of Chemistry and the Laboratory for Research
on the Structure of Matter, University of Pennsylvania,
Philadelphia, Pennsylvania 19104. *Received July 8, 1969*

Abstract: In a previous paper X-ray data and molecular orbital calculations were presented which support the argument that some (d → d)π double-bond character might exist between the silicon and cobalt atoms and/or also that an intramolecular interaction between the axial silicon atom and equatorial carbonyl groups may be present in these trigonal-bipyrimidal silylcobalt tetracarbonyls. This paper presents mass spectral data for Cl$_3$SiCo(CO)$_4$ and (CH$_3$)$_3$SiCo(CO)$_4$ which can be interpreted in support of these interactions. It is pointed out that previously published mass spectral data concerning various cobalt carbonyl derivatives also support the existence of an intramolecular interaction between the axial substituent and the equatorial ligands. The fragmentation of these molecules, which have the general formula RCoL$_4$ (R = H, Cl$_3$Si, (CH$_3$)$_3$Si, F$_3$Si, (CH$_3$)F$_2$Si; L = CO and/or PF$_3$), indicates that ions of the formula RCoL$_x^+$ are more abundant than the CoL$_{x-1}^+$ ions for x = 4 or 3. This type of fragmentation can be interpreted as support for the existence of an intramolecular interaction between the R substituent and the equatorial ligands. The value of the R–CoL$_4$ dissociation energies calculated from the appearance potential measurements indicates that this bond is relatively strong in the silyl compounds. This observation is consistent with the presence of partial (d → d)π double-bond character in the Si–Co bond and/or intramolecular interaction between the R and the equatorial groups.

Several recent publications[2–15] have discussed the nature of the R–Co (R = H, Cl$_3$Si, (CH$_3$)$_3$Si, F$_3$Si, (CH$_3$)F$_2$Si) bond in some cobalt carbonyl derivatives. Infrared studies[3,4a] of the carbonyl stretching frequency in these molecules have led to the postulation of partial (d → d)π double-bond character in the silicon–cobalt bond. Moreover, an examination[2] of the X-ray and other physical data[5–12] available for the silyl cobalt tetracarbonyl derivatives suggested that, in addition to double-bond character of the Si–Co bond, an intramolecular interaction between the R substituent and the equatorial carbonyl groups might also exist. This interaction may be responsible, at least in part, for many of the experimental observations previously attributed solely to the (d → d)π bonding. An interaction between the axial hydrogen atom and the equatorial carbonyl groups in HCo(CO)$_4$ has been suggested previously from infrared data[16] and molecular orbital calculations.[17–21] Since HCo(CO)$_4$ is the parent compound of the species RCoL$_4$ (R = (CH$_3$)$_3$Si, Cl$_3$Si, F$_3$Si, and (CH$_3$)F$_2$Si; L = CO and/or PF$_3$), it is of interest to consider the possibility of similar effects in all of these compounds.

This report covers the results of a mass spectral investigation of two more silyl cobalt carbonyl derivatives which support (but do not prove) the existence of such an intermolecular interaction. Moreover, mass spectral data published previously[13–15] also support the existence of intramolecular interactions in HCo(CO)$_x$(PF$_3$)$_{4-x}$,[13] F$_3$SiCo(CO)$_4$,[15] and (CH$_3$)F$_2$SiCo(CO)$_4$.[14] Finally, the relatively large R–CoL$_4$ bond dissociation energies observed in the silyl cobalt carbonyls can be explained by the existence of partial (d → d)π double-bond character in the silicon–cobalt bond and/or an intramolecular interaction between the axial R substituent and the equatorial groups.

Experimental Section

Details of the preparation, separation, and handling of these compounds have been described in the literature.[3,5–12] All of the mass spectral data reported except the metastable transitions were obtained on a modified[22] Bendix time-of-flight (TOF) instrument using techniques described previously.[13] The bond energies reported here should be viewed as upper limits of the true energy because of the errors inherent in the appearance potential measurements.[13]

Results

Monoisotopic mass spectral fragmentation patterns obtained at 70 V for Cl$_3$SiCo(CO)$_4$ and (CH$_3$)$_3$Si-

---

(1) (a) Naval Research Laboratory; (b) University of Pennsylvania.

(2) A. D. Berry, E. R. Corey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).

(3) Y. L. Baay and A. G. MacDiarmid, *Inorg. Chem.*, **8**, 986 (1969).

(4) (a) A. P. Hagen and A. G. MacDiarmid, *ibid.*, **6**, 686 (1967); (b) *ibid.*, **6**, 1941 (1967).

(5) O. Kahn and M. Bigorgne, *J. Organometal. Chem.*, **10**, 137 (1967).

(6) J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *J. Chem. Soc., A*, 1199 (1968).

(7) E. W. Abel, J. Dalton, I. Paul, J. G. Smith, and F. G. A. Stone, *ibid.*, 1203 (1968).

(8) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

(9) D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 891 (1967).

(10) W. A. G. Graham, *ibid.*, **7**, 315 (1968).

(11) D. J. Patmore and W. A. G. Graham, *ibid.*, **7**, 771 (1968).

(12) T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *ibid.*, **8**, 763 (1969).

(13) F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **90**, 3684 (1968).

(14) F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *Inorg. Chem.*, **7**, 1465 (1968).

(15) F. E. Saalfeld, M. V. McDowell, A. P. Hagen, and A. G. MacDiarmid, *ibid.*, **7**, 1665 (1968).

(16) W. F. Edgell, C. Magee, and G. Gallup, *J. Amer. Chem. Soc.*, **78**, 4185 (1956).

(17) W. F. Edgell and G. Gallup, *ibid.*, **78**, 4188 (1956).

(18) F. A. Cotton, *ibid.*, **80**, 4425 (1958).

(19) L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, **3**, 22 (1964).

(20) D. A. Brown and N. J. Fitzpatrick, *J. Chem. Soc., A*, 1793 (1967).

(21) B. B. Wayland, private communication, 1969.

(22) F. E. Saalfeld and M. V. McDowell, *Inorg. Chem.*, **6**, 96 (1967).

Table I. Monoisotopic Fragmentation Pattern of $Cl_3SiCo(CO)_4$

Ion	% total ion current ($I_i/\Sigma I_i$)	Ion	% total ion current ($I_i/\Sigma I_i$)
$Cl_3SiCo(CO)_4^+$	0.9	$Co(CO)_2^+$	0.5
$Cl_3SiCo(CO)_3^+$	3.4	$ClCo^+$	2.0
$Cl_3SiCo(CO)_2^+$	6.6	$Co(CO)^+$	8.7
$Cl_3SiCo(CO)^+$	15.1	$SiCl^+$	21.0
Cl_3SiCo^+	10.1	Co^+	14.1
Cl_2SiCo^+	3.1	Cl^+	0.9
$ClCo(CO)_2^+$	0.2	CO^+	13.3

Table II. Monoisotopic Fragmentation Pattern of $(CH_3)_3SiCo(CO)_4$

Ion	% total ion current ($I_i/\Sigma I_i$)	Ion	% total ion current ($I_i/\Sigma I_i$)
$(CH_3)_3SiCo(CO)_4^+$	0.9	$Co(CO)_2$	10.2
$(CH_3)_3SiCo(CO)_3^+$	2.6	$Co(CO)^+$	13.2
$(CH_3)_3SiCo(CO)_2^+$	2.2	$(CH_3)_3Si^+$	17.9
$(CH_3)_3SiCo(CO)^+$	4.3	Co^+	25.4
$(CH_3)_3SiCo^+$	6.0	CO^+	12.6
		CH_3^+	0.7

Table III. Energetic Results for $Cl_3SiCo(CO)_4$[a]

Ion	Neutral product	Appearance potential, eV	$\Delta H_f°$ (ion), kcal/mol
$Cl_3SiCo(CO)_4^+$	...	9.0 ± 0.1[b]	−140
$Cl_3SiCo(CO)_3^+$	CO	9.4 ± 0.1	−104
$Cl_3SiCo(CO)_2^+$	2CO	10.6 ± 0.2	−51
$Cl_3SiCo(CO)^+$	3CO	11.8 ± 0.2	3
Cl_3SiCo^+	4CO	13.3 ± 0.3	64
$Co(CO)_2^+$	$SiCl_3 + 2CO$	14.3 ± 0.3	122
Co^+	$SiCl_3 + 4CO$	19.2 ± 0.3	287[c]

[a] $\Delta H_f°(Cl_3SiCo(CO)_4) = -347 \pm 10$ kcal/mol, calculated from the last two processes cited in this table and the known[23] $\Delta H_f°(Co^+) = 287$ kcal/mol. [b] Standard deviation of the mean. Average of seven independent measurements determined by Warren's method of extrapolated differences: J. W. Warren, *Nature*, **165**, 810 (1950). Calibrating gases: Ar (IP = 15.8 V), Kr (IP = 14.0 V), and Xe (IP = 12.1 V). [c] Reference 23.

$Co(CO)_4$ are shown in Tables I and II. These patterns have been corrected for residual background in the mass spectrometer and for any impurities in the samples. Ions whose abundance was less than 0.05% of the total ion current have been neglected. Any ambiguities as to the chemical composition of the ion have been resolved by the use of high-resolution mass measurement. It is interesting to note that the elements of $SiCl_2$ are eliminated in two of the decompositions of the ions produced by electron impact of $Cl_3SiCo(CO)_4$. Since it is impossible to detect ions formed by metastable decompositions in our TOF mass spectrometer, a mass spectrum of $Cl_3SiCo(CO)_4$ was obtained on an Atlas CH4 mass spectrometer. The spectrum obtained at the minimum ion source temperature of the CH4 (<150°) agreed well with that obtained on the TOF spectrometer and, in addition, several peaks representing metastable transitions were observed. These included a peak whose maximum intensity was at *m/e* 90.8 for the transition $Cl_3SiCo(CO)_2^+ \rightarrow ClCo(CO)_2^+$ (calcd 90.73) and another peak at *m/e* 46.1 for $Cl_3SiCo^+ \rightarrow ClCo^+$ (calcd 46.02), thus strengthening the argument for the postulated loss of the $SiCl_2$ radical. Actually, these metastable transition peaks are many overlapping peaks due to the naturally occurring isotopes of the atoms. The isotopes, principally those of chlorine, cause the metastable peaks to be very broad (3–4 amu), and the calculated metastable *m/e* above is for the most abundant transition. It should be pointed out that data indicating the loss of the radical SiF_2 were noted in the mass spectral studies of $(CH_3)F_2SiCo(CO)_4$[14] and $F_3SiCo(CO)_4$.[15]

The appearance potentials and the heats of formation of selected positive ions of $Cl_3SiCo(CO)_4$ together with the postulated neutral species are cited in Table III. Unfortunately, the sample of $(CH_3)_3SiCo(CO)_4$ was contaminated with $((CH_3)_3Si)_2O$, a decomposition product, and therefore no appearance potential measurements were made on this compound. The heat of formation of $Cl_3SiCo(CO)_4$ was obtained by first calculating $\Delta H_f°(Co(CO)_2^+)$ from the data presented in the last two lines of Table III using the known[23] $\Delta H_f°(Co^+)$ and then using this value to find $\Delta H_f°(Cl_3SiCo(CO)_4) = -347 \pm 10$ kcal/mol from the data. The ionization efficiency curves of the $Co(CO)_2^+$ and Co^+ ions did not have extensive tailing, and an analysis[24,25] of the peak shapes of the $Co(CO)_2^+$ and Co^+ ions near their threshold potential did not indicate the presence of excess kinetic energy in these ions. Nonetheless, the thermochemical values calculated from these appearance potentials should be regarded with the usual reservations associated with appearance potential calculations, *i.e.*, $\Delta H_f°$(ions) is an upper limit and $\Delta H_f°$(compounds) is a lower limit.

The compound $Cl_3SiCo(CO)_4$ undergoes consecutive unimolecular eliminations of CO similar to the fragmentation mechanisms of other transition metal carbonyl compounds.[13–15] It is noted that the ionization potential (IP) of $Cl_3SiCo(CO)_4$ (9.0 V) is equal to that of $(CH_3)F_2SiCo(CO)_4$[14] (9.0 V) and is lower than that of $F_3SiCo(CO)_4$[15] (9.7 V), as expected. The low value for the ionization potentials suggests that the electron removed in the ionization is associated mainly with a nonbonding molecular orbital. Moreover, if there is any $(d \rightarrow d)\pi$ bonding between the metal and the silyl group, one should expect the IP of the molecule to be increased compared to a similar molecule where no $(d \rightarrow d)\pi$ exists. This is indeed the case as the IP of each molecule above is greater than the IP of $HCo(CO)_4$ (8.7 eV)[13] where no $(d \rightarrow d)\pi$ bonding can occur.

Discussion

All of the molecules discussed here have the trigonal-bipyrimidal structure with the equatorial carbonyl groups displaced in an umbrella-type fashion about the axial R substituent.[2] The mass spectral fragmentation patterns support the concept of an interaction between the equatorial ligands and the axial substituent when interpreted in the manner described below. We are aware of the danger of placing too great an emphasis on the relative abundance of the ions observed at 70 V since these patterns are greatly influenced by the large amount of energy in the system and may also be controlled by kinetic effects. However, in view of the number of cobalt carbonyl spectra which can be in-

---

(23) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 1952.

(24) J. L. Franklin, P. M. Heirl, and D. Whan, *J. Chem. Phys.*, 47, 3148 (1967).

(25) P. M. Heirl and J. L. Franklin, *ibid.*, 47, 3154 (1967).

Table IV. R–L$_{\text{equi}}$ Intramolecular Interaction[a]

	HCo(CO)$_4$[b]	HCo(CO)$_3$-(PF$_3$)[b]	HCo(CO)$_2$-(PF$_3$)$_2$[b]	HCo(CO)-(PF$_3$)$_3$[b]	HCo(PF$_3$)$_4$[b]	F$_3$SiCo-(CO)$_4$[c]	Cl$_3$SiCo-(CO)$_4$	(CH$_3$)SiF$_2$-Co(CO)$_4$[d]	(CH$_3$)$_3$Si-Co(CO)$_4$
CoL$_4^+$/RCoL$_3^+$	0	0	0	0	0	0	0	0	0
CoL$_3^+$/RCoL$_2^+$	0.59	0.36	0.22	0.18	0.17	0	0	0	0
CoL$_2^+$/RCoL$^+$	9.75	2.73	2.55	1.24	1.01	4.30	0.76	0.83	4.64
CoL$^+$/RCo$^+$	20.0	14.19	14.28	12.32	10.4	1.51	0.86	0.65	2.20

[a] CoL$_x$/RCoL$_{x-1}$ ratio; the smaller the ratio, the larger the R–L$_{\text{equi}}$ interaction and/or the stronger the R–Co bond energy. [b] Reference 13. [c] Reference 14. [d] Reference 15.

terpreted by this approach and the physical evidence presented previously,[2] we believe the following argument to be appropriate.

According to the quasi-equilibrium theory of mass spectra,[26] the molecule is first ionized and then fragmentation commences. In the first fragmentation process either an R–CoL$_4^+$ bond or an RCol$_3^+$–L bond may be broken. As can be clearly seen in Table IV, which shows the ratio of the CoL$_x^+$/RCoL$_{x-1}^+$ ion currents, only the RCoL$_3^+$–L bond is cleaved. We postulate that the ligand *trans* to the axial R substituent is lost in this fragmentation; sterically, at least, this fragmentation would permit the "equatorial" ligands to relax from the umbrella-like relationship about the R substituent and weaken the R–L equatorial intramolecular interaction. Further, the metastable transition for this process was of the normal gaussian shape, indicating simple bond cleavage. In the second fragmentation process some loss of the R substituent might be expected, provided the R–CoL$_3^+$ bond energy is weak. This is the situation for the relatively weak H–CoL$_3^+$ bond.[13] In the silyl compounds where the R–CoL$_3^+$ bond is stronger,[14,15] loss of R does not occur; indeed, even in the hydride series, the loss of hydrogen is less abundant than loss of the ligand. The loss of a second ligand molecule should greatly reduce the interaction between the ligands and the R substituent. Therefore, the third fragmentation should favor the loss of R unless the R–CoL$_2^+$ bond is extremely strong. This is the case; loss of R is favored in all of the molecules reported in Table IV except (CH$_3$)F$_2$SiCo(CO)$_4$ and Cl$_3$SiCo(CO)$_4$. In these two cases the appearance potential data indicated that the R–Co bond energy in the R–CoL$_2^+$ ion is very large[16] which suggests the presence of some (d $\rightarrow$ d)π double-bond character in this linkage. The preferred loss of R is even more evident in the last fragmentation of the molecule, again with the exception of (CH$_3$)F$_2$SiCo(CO)$_4$ and Cl$_3$SiCo(CO)$_4$. For the HCo(CO)$_x$(PF$_3$)$_{4-x}$ molecules,[13] we note that the CoL$_x^+$/HCoL$_{x-1}^+$ ratio decreases with increasing PF$_3$ substitution. This suggests either the H–L "equatorial" interaction increases and/or the H–CoL$_x^+$ bond energy increases with increasing PF$_3$ substitution. Moreover, the metastable transitions representing the loss of the second and third ligand molecules are flat-top peaks, indicating a decomposition involving more than the rupture of a single bond. The Cl$_3$Si–Co(CO)$_4$ bond dissociation energy (DE) may be calculated by using the hypothetical reaction

$$\text{RCoL}_4 \longrightarrow \text{R} + \text{CoL}_4 \qquad (1)$$

and the equation

$$\text{DE(R–CoL}_4) + 2.4\ \text{kcal/mol} = \Delta H_{\text{reaction}} = \Delta H_f°(\text{R}) + \Delta H_f°(\text{CoL}_4) - \Delta H_f°(\text{RCoL}_4) \qquad (2)$$

(where the 2.4 kcal/mol is the estimated $\Delta C_p \approx 4RT$) provided ancillary data are available for the quantities ΔH_f°(R) and ΔH_f°(CoL$_4$). Fortunately, when L = CO sufficient data are in the literature for such an evaluation; they are (in kcal/mol): ΔH_f°(Co(CO)$_4$) = −132[27] and ΔH_f°(SiCl$_3$) = −87.[28] Using these values and ΔH_f°(Cl$_3$SiCo(CO)$_4$), DE(Cl$_3$Si–Co(CO)$_4$) is found to be 128 kcal/mol, a surprisingly large value. In view of this large dissociation energy, which is shown in Table V together with the dissociation of several other silyl cobalt tetracarbonyl derivatives, a few comments as to possible sources of error are appropriate. As is known,[13] the heat of formation of a molecule, determined by the appearance potential methods, should be taken as a lower limit to the true value. Such an error would make the DE too large; however, an absolute error of more than 15 kcal/mol is unlikely. It is difficult to assess either the magnitude or the direction of the error in ΔH_f°(R) in eq 2 because of insufficient data. The heat of formation of Co(CO)$_4$ deserves comment; the value of −132 kcal/mol was derived by Winters and Kiser in their study of Co$_2$(CO)$_8$[27] and rests on their estimation of ΔH_f°(CO$_2$(CO)$_8$) (−340 kcal/mol) and their appearance potential measurement of Co$^+$. Their estimation of ΔH_f°(Co(CO)$_8$) was obtained by interpolations and extrapolations from thermochemical data reported for similar compounds: Ni(CO)$_4$, Fe(CO)$_5$, Cr(CO)$_6$, Mo(CO)$_6$, W(CO)$_6$, and Mn$_2$(CO)$_{10}$. Since none of the details of this extrapolation are delineated in their paper[27] and attempts to duplicate the calculation yield values ranging from −320 to −360 kcal/mol,

Table V. R–Co(CO)$_4$ Bond Dissociation Energies (DE)

Compound	Dissociation energy of RSi–Co(CO)$_4$ (kcal/mol) if ΔH_f°(Co-(CO)$_4$) = −132 kcal/mol	ΔH_f°(Co-(CO)$_4$) = −163 kcal/mol
Cl$_3$Si–Co(CO)$_4$	126 ± 25[a]	95 ± 25[a]
F$_3$Si–Co(CO)$_4$	105[b]	74
(CH$_3$)SiF$_2$–Co(CO)$_4$	127[c]	96

[a] The error reported represents the error in the measured appearance potential plus an estimate of the error in the ΔH_f°(Co(CO)$_4$). [b] Reference 14. [c] Reference 13.

---

(26) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).

(27) R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, **69**, 1618 (1965).

(28) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," St. Martin's Press, New York, N. Y., 1966.

the estimation of the $\Delta H_f°(Co(CO)_8)$ might be a source of considerable error. Bidinosti and McIntyre have reported[29] that the Co–Co bond energy (76 kcal/mol) cited by Winters and Kiser[27] for $Co_2(CO)_8$ is too large. These authors[29] find the Co–Co dissociation energy to be 11.5 kcal/mol. Thus, the reaction

$$Co_2(CO)_8 \longrightarrow 2Co(CO)_4$$

has a heat of reaction of 14 kcal/mol. If this heat of reaction is used together with Winters and Kiser's estimate of $\Delta H_f°(Co_2(CO)_8)$, a value of -163 kcal/mol is found for $\Delta H_f°(Co(CO)_4)$. At present, it is impossible to decide which of the values for $\Delta H_f°(Co(CO)_4)$ is correct; therefore, two values for the dissociation energies of several silylcobalt tetracarbonyls are shown in Table V. As can be seen, the dissociation energies are large for both values of $\Delta H_f°(Co(CO)_4)$; however, the energies based on the $\Delta H_f°(Co(CO)_4) = -164$ kcal/mol appear to be more reasonable. It should be noted that while the absolute values of the DE are questionable owing to the large errors, the differences between the DE's reported are thought significant to ±15 kcal/mol.

In conclusion, the mass spectral results reported here and previously[13–15] are not inconsistent with the postulation that partial $(d \rightarrow d)\pi$ double-bond character exists in the R–Co linkage. Furthermore, they are consistent with an intramolecular interaction that exists between the R substituent and the equatorial groups. It should be stressed than an experimental determination of $\Delta H_f°(Co_2(CO)_8)$ is needed before any confidence can be given to the absolute values of DE reported here.

Acknowledgment. The authors thank Dr. John M. Ruth of the Pesticide Chemical Research Branch, U. S. Department of Agriculture for the high-resolution mass measurements. We also wish to acknowledge the help of Alan D. Berry and James F. Bald, Jr., of the Department of Chemistry, University of Pennsylvania, for supplying the compounds reported here.

---

(29) D. R. Bidinosti and N. S. McIntyre, *Chem. Commun.*, 555 (1966).

Electron Spin Resonance Studies of Substituent Effects.[1] III. Electron Withdrawal by Group IV and Group VI Elements

E. Thomas Strom[2] and Jack R. Norton

Contribution from the Mobil Research and Development Corporation, Field Research Laboratory, Dallas, Texas 75221. *Received October 31, 1969*

Abstract: Electron withdrawal by group IV and group VI elements was studied by incorporating the elements in substituents and determining the effect of these substituents on methyl hyperfine splitting in 1-phenyl-1,2-propanesemidiones. The following order of electron withdrawal is found: p-OCH$_3$ < m,p-di-OCH$_3$ < p-OPh < p-C(CH$_3$)$_3$ < p-H < p-SCH$_3$ ≈ p-SeCH$_3$ ≈ m-OCH$_3$ < p-Ge(CH$_3$)$_3$ < p-Si(CH$_3$)$_3$ < p-SPh ≈ p-SePh < p-SOCH$_3$. It is argued that splitting constants in all aromatic radical systems will follow an additivity relationship on substitution, similar to that found in nmr, and the splittings in the m-OCH$_3$ derivative are partially assigned by this procedure. Contrary to the predictions of σ constants, the p-Si(CH$_3$)$_3$ and p-Ge(CH$_3$)$_3$ substituents are moderately good electron-withdrawing groups. The p-Si(CH$_3$)$_3$ substituent in this system withdraws spin about as well as p-Cl. The p-OCH$_3$ group is a better electron donor than the p-OPh group in these radicals, reversing the order predicted by σ constants. There is little esr evidence for $d\pi$–$p\pi$ bonding within the p-SOCH$_3$, p-SCH$_3$, and p-SeCH$_3$ substituents. The p-SPh and p-SePh groups, however, are powerful electron withdrawers, better than the *meta* halogens. The σ^- constants derived from esr data are 0.40 ± 0.03 and 0.42 ± 0.02, respectively, as compared to the 0.29 value for p-SPh obtained from phenol ionization. This result is best explained by invoking $d\pi$–$p\pi$ bonding within the p-SPh and p-SePh substituents. The rehybridization at the divalent atom apparently is a consequence of the conjugative effect of the phenyl group. Molecular orbital calculations were performed on the derivatives which gave results consistent with the above conclusions.

The question of participation of 3d orbitals in bonding involving elements in the third row of the periodic table is of continuing interest. In recent years attempts have been made to attack this problem by electron spin resonance (esr) spectroscopy.[3] There is strong esr evidence that the d orbitals of silicon can contribute to free-radical stabilization. Compared to analogous carbon radicals, silicon appears more capable of delocalizing spin.[4–6] More recent work has shown the remarkable fact that decamethylcyclopentasilane forms a stable anion radical.[7] Studies of 1,4-disilacyclohexadiene anion radical[8] and other silyl-substituted

---

(1) (a) Part II: E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, 32, 3853 (1967); (b) presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) Author to whom inquiries should be addressed.

(3) For recent reviews of esr investigations on radicals containing group IV elements and sulfur, see (a) G. Urry in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, pp 275–300; (b) M. M. Urberg and E. T. Kaiser, *ibid.*, pp 301–320.

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

(5) (a) J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, 59, 53 (1963); (b) S. P. Solodovnikov and E. A. Chernyshev, *J. Struct. Chem.* (USSR), 3, 642 (1963).

(6) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Amer. Chem. Soc.*, **85**, 822 (1963).

(7) E. Carberry, R. West, and G. E. Glass, *ibid.*, **91**, 5446 (1969).

(8) E. G. Janzen, J. B. Pickett, and W. H. Atwell, *ibid.*, **90**, 2719 (1968).