the known spectrum of $FeCp_2^+$, for which a partial treatment has been given by Sohn, Hendrickson, and Gray.[16] These authors appear however to have employed a different set of basis orbitals from that used here since the diagonal energy differences and off-diagonal matrix elements listed do not correspond with the present results (which have been checked by diagonalization in the free-ion limit), and not all the one-electron excitations possible for a $^2\Delta$ ($\sigma^2\delta^3$) ground state were considered. Thus, as stated by Sohn et al. (using the D_{5d} symbolism) the $\sigma \rightarrow \delta$ and $\delta \rightarrow \pi$ excitations yield respectively the states $^2\Sigma^+$ ($\sigma\delta^4$) and $2(^2\Pi) + {}^2\Phi + {}^2H$ ($\sigma^2\pi\delta^2$), but the $\sigma + \pi$ excitation leads to $2(^2\Pi) + 2(^2\Phi)$ ($\sigma\pi\delta^3$), instead of one state of each symmetry as reported.[16] With the parameters used in Figure 1 the spectrum of the ferricenium cation may be interpreted in terms of three groups of d–d transitions (in addition to the charge-transfer band at 16,200 cm^{-1}), viz., $^2\Delta \rightarrow {}^2\Phi, {}^2\Pi, {}^2\Phi$; $^2\Delta \rightarrow {}^2\Pi, {}^2H, {}^2\Pi$; and $^2\Delta \rightarrow {}^2\Phi, {}^2\Pi$; and the bands recorded[16] at 17,700–19,100 and at 21,400 and 26,300 cm^{-1} may be tolerably well fitted on this basis yielding $Dt/B \approx 4.5$ and $B \approx 500$ cm^{-1}. (The designations ($\sigma^2\pi\delta^2$) and ($\sigma\pi\delta^3$) are omitted from the excited states because of the appreciable mixing of these closely juxtaposed levels.) With these parameters the $^2\Sigma^+$ ($\sigma\delta^4$) level is calculated to lie some 4000 cm^{-1} above the $^2\Delta$ ($\sigma^2\delta^3$) ground state, and may well not be detectable optically. However, although the NMR studies of Anderson and Rai[17] suggest the separation to be rather smaller with $^2\Sigma^+$ only 400 cm^{-1} above the lower spin–orbit component of $^2\Delta$, the $^2\Sigma^+ - {}^2\Delta$ separation is very sensitive to the value of Dt/Ds and is markedly lowered by reduction of this ratio. Also estimates[18,19] from photoelectron and susceptibility data give $E(^2\Sigma^+) - E(^2\Delta)$ as between 2300 and 3400 cm^{-1}, in much better agreement with the present calculation. It should though also be noted that a decrease of Dt/Ds corresponds to a greater $E(\sigma) - E(\delta)$ separation; consequently for the bis(arene) complexes the more effective metal–ligand interaction for the δ level results in a larger $E(\sigma) - E(\delta)$ separation, thus moving the $^2\Delta{:}^2\Sigma^+$ crossover point to lower Dt/B values and allowing $^2\Delta$ to be superseded by $^2\Sigma^+$ as the ground state for these species.[20,21]

For the d^5 bis(arene) systems there are no adequate electronic spectra available, but the ligand field model shows that for a $^2\Sigma^+$ ($\sigma\delta^4$) ground state three one-electron excitations are possible, namely, $\delta \rightarrow \sigma$, $\sigma \rightarrow \pi$, and $\delta \rightarrow \pi$. These in turn correspond to the doublet excited states $^2\Delta$ ($\sigma^2\delta^3$) and $^2\Pi$ ($\pi\delta^4$), respectively, together with the doublet states listed above for the $\sigma\pi\delta^3$ configuration.

Acknowledgment. I am greatly indebted to Dr. John Ammeter for helpful discussions and for permission to refer to his results prior to publication.

Supplementary Material Available. The Appendix, showing electrostatic repulsion matrices for d^5 configurations in $C_{\infty v}$ symmetry, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC500249-9-75.

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Tin-119 Mössbauer Quadrupole Splittings for Distorted Me_2Sn^{IV} Structures

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Partial quadrupole splittings[1] (in either the point-charge approximation[2] or the molecular orbital approximation[3,4]) have been very useful for distinguishing between *cis*- and *trans*-R_2SnL_4 isomers[5,6] and a number of six-coordinate Fe^{II} geometrical isomers[3,7] in the solid state. For many of the trans–cis Sn^{IV} and Fe^{II} pairs, the theoretically predicted 2:(−)1 trans:cis quadrupole splitting ratio is obeyed rather well. However, recent crystal structure data indicate that some Me_2SnL_4 compounds (where L_2 is a chelating ligand) and associated $Me_2SnL'_2$ compounds have structures which are intermediate between cis and trans. This rather surprising structural situation is represented by the structures of $Me_2Sn(oxin)_2$,[8] $Me_2Sn(S_2CNMe_2)_2$,[9] and $Me_2Sn(Salen)$[10] for which the C–Sn–C bond angles vary from 110 to 136 to 160°, respectively. In these three complexes (and in all the substantially distorted Me_2Sn compounds), the L–Sn–L angles differ substantially from 90° and/or the Sn–L bond lengths differ by a significant amount. Thus in $Me_2Sn(S_2CNMe_2)_2$, the Sn–S distances are 2.50, 2.51, 2.95, and 3.06 Å. The compounds appear to be unambiguously six-coordinate, however. The arrangement of the four S ligands and the Sn atom is planar with the sum of all S–Sn–S angles being close to 360°. In addition, the $J_{^{119}Sn-CH_3}$ coupling constants are normally characteristic of six-coordinate Sn. This bonding situation has been labeled by de Vries and Herber[11] as anisobidentate.

The quadrupole splittings (QS) for the aforementioned compounds $Me_2Sn(oxin)_2$, $Me_2Sn(S_2CNMe_2)_2$, and $Me_2Sn(Salen)$ are 2.02, 3.14, and 3.46 mm sec^{-1}, respectively. On the basis of these quadrupole splittings, the first structure has been labeled cis,[5] while the last two have been labeled trans[5,1,12] or distorted trans structures. From the recent structural data, it is apparent that the labeling of such compounds as cis or trans is no longer appropriate[13] for such structures. However, the additivity treatment, instead of just the 2:1 ratio,[13] is capable of rationalizing these changes in quadrupole splittings. In this paper, we present a simple model which readily accounts for the changes in QS as a function of C–Sn–C angle for 17 of 19 known Me_2Sn^{IV} structures.

Table I

		Structural data (averages)			Mössbauer data			Coupling const data	
No.	Compd[z]	∠C–Sn–C, deg	r(Sn–C), Å	Ref	CS, mm sec^{-1}	QS, mm sec^{-1}	Ref	$J_{^{119}Sn-CH_3}$, Hz	Ref
1	$Me_2SnCl_2(pyO)_2$	180	2.22	*a*	1.42	3.96	*o*	93	*y*
2	Me_2SnF_2	180	2.08	*b*	1.33	4.38	1		
3	$Me_2Sn(AcAc)_2$	180	2.14	*c*	1.16	4.02	*p*	99	*p*
4	$Me_2SnCl_2(SalenH_2)$	175–177	2.15	*d*		4.27	*q*		
5	$Me_2SnCl_2(DMSO)_2$	172	2.08	*e*	1.40	4.16	*o*	86	*y*
6	$Me_2SnCl_2Ni(Salen)$	161.0	2.13	*f*	1.50	4.06	*r*	114	*r*
7	$Me_2Sn(Salen)$	160.0	2.12	10	1.13	3.46	12	84	*x*
8	$Me_2SnCl(terpy)^+$	159	2.07	*g*	1.41	3.55	*j, s*		
9	$Me_2Sn(NCS)_2$	145.9	2.14	*h*	1.48	3.87	*t*		
10	$Me_2Sn(CN)_2$	148.7	2.11	*i*					
11	$Me_2Sn(dtc)_2$	136	2.15	9	1.57	3.14	6, 13	84	9
12	$Me_2Sn[S_2NC(CH_2)_4]_2$	130.0		13	1.59	2.85	6, 13		
13	$Me_2Sn(oxin)_2$	110.7	2.16	8	0.88	2.02	*u*	71.5	9
14	Me_2SnCl_2	123.5	2.21	*j*	1.54	3.55	*j*		
15	$Me_2Sn(NO_3)_2$	144	2.12	*k*	1.56	4.20	*v*	81.6	20
16	$Me_2SnCl_3^-$	140	2.12	*g*	1.44	3.51	*u*		
17	$Me_2SnCl(S_2NCR_2)$	128	2.19	*l*	1.28	2.98	*w*		
18	$[Me_2SnOHNO_3]_2$	139.9	2.13	*m*	1.28	3.67	This work		
19	$Me_2Sn(NCS)_2O$	140.5	2.11	*n*	1.25	3.38	This work		

[a] E. A. Blom, B. R. Penfold, and W. T. Robinson, *J. Chem. Soc. A*, 913 (1969). [b] E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5**, 995 (1966). [c] G. A. Miller and E. O. Schlemper, *ibid.*, 12, 677 (1973). [d] L. Randaccio, *J. Organomet. Chem.*, **55**, C58 (1973). [e] N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc. A*, 1257 (1970). [f] M. Calligaris, L. Randaccio, R. Barbieri, and L. Pellerito, *J. Organomet. Chem.*, 76, C56 (1974). [g] F. W. B. Einstein and B. R. Penfold, *J. Chem. Soc. A*, 3019 (1968). [h] Y. M. Chow, *Inorg. Chem.*, 9, 794 (1970). [i] J. Konnert, D. Britton, and Y. M. Chow, *Acta Crystallogr., Sect. B*, **28**, 180 (1972). [j] A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc. A*, 2862 (1970). [k] J. Hilton, E. K. Nunn, and S. C. Wallwork, *J. Chem. Soc., Dalton Trans.*, 173 (1973). [l] K. Furue, T. Kimura, N. Yasueka, N. Kosai, and M. Kakudo, *Bull. Chem. Soc. Jpn.*, **43**, 1661 (1970). [m] A. M. Domingos and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 475 (1974). [n] Y. M. Chow, *Inorg. Chem.*, **10**, 673 (1971). [o] A. G. Davies, L. Smith, and P. J. Smith, *J. Organomet. Chem.*, **23**, 135 (1970). [p] G. M. Bancroft and T. K. Sham, *Can. J. Chem.*, **52**, 1361 (1974). [q] R. Barbieri, L. Pellerito, N. Bertazzi, and G. C. Stocco, *Inorg. Chim. Acta*, **11**, 173 (1974); see ref 44. [r] L. Pellerito, R. Cefalu, A. Gianzuzza, and R. Barbieri, *J. Organomet. Chem.*, 70, 303 (1974). [s] N. W. G. Debye, E. Rosenberg, and J. J. Zuckerman, *J. Am. Chem. Soc.*, 90, 3234 (1968). [t] B. Gassenheimer and R. H. Herber, *Inorg. Chem.*, 8, 1120 (1969). [u] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 4, 65 (1970). [v] D. Potts, H. D. Sharma, A. J. Carty, and A. Walker, *Inorg. Chem.*, **13**, 1205 (1974). [w] B. W. Fitzsimmons and A. C. Sawbridge, *J. Chem. Soc., Dalton Trans.*, 1678 (1972). [x] A. Vanden Bergen, R. J. Cozens, and K. S. Murray, *J. Chem. Soc. A*, 3060 (1970). [y] V. G. Kumar Das and W. Kitching, *J. Organomet. Chem.*, 13, 523 (1968); *Aust. J. Chem.*, **21**, 2401 (1968). [z] Abbreviations: pyO, pyridine *N*-oxide; AcAc, anion of acetylacetone; $SalenH_2$, bis(salicylaldehyde)ethylenediimine; DMSO, dimethyl sulfoxide; terpy, 2,2′,2″-terpyridyl; dtc, *N,N′*-dimethylthiocarbamate; oxin, anion of 8-hydroxyquinoline.

Factors leading to such distortions are also discussed.

Results and Discussion

We use the literal interpretation of the point-charge model and assume that the quadrupole splitting is set up just by the Me_2Sn unit. This assumption will only be a reasonable one if the partial quadrupole splitting of the Me ligands, {Me}, is much larger than that of the other ligands L. Fortunately, for regular octahedral compounds containing oxygen, nitrogen, and halide ligands, the pqs values of these ligands[14] are nearly all ±0.10 mm sec^{-1}, compared to the Me value[4] of −1.03 mm sec^{-1}. Any contribution to the QS from such ligands then should be very small (±0.4 mm sec^{-1}).

The axis system given in Figure 1 is used for the Me_2Sn unit, and the EFG expressions are given by

$$V_{11} = -2\{Me\} \tag{1b}$$

$$V_{22} = 2\{Me\}(3 \sin^2 \theta - 1) \tag{1a}$$

$$V_{33} = 2\{Me\}(3 \cos^2 \theta - 1) \tag{1c}$$

V_{11} is perpendicular to the RSnR plane, while V_{22}, V_{33}, and MeSnMe are in the same plane.

For convenience in the calculation of the quadrupole splitting, we use Clark's symmetrized parameters[15] and find that

$$|QS| = 4\{Me\}[1 - 3 \sin^2 \theta \cos^2 \theta]^{1/2} \tag{2}$$

where $\{Me\} = {}^1/_2e^2Q[Me]$. Using $\{Me\} = -1.03$ mm sec^{-1}, the QS as a function of the C–Sn–C angle (180° − 2θ) can be readily calculated (Figure 2, solid line). The sign of the QS is positive from 180 to 109.5°, where it becomes negative.

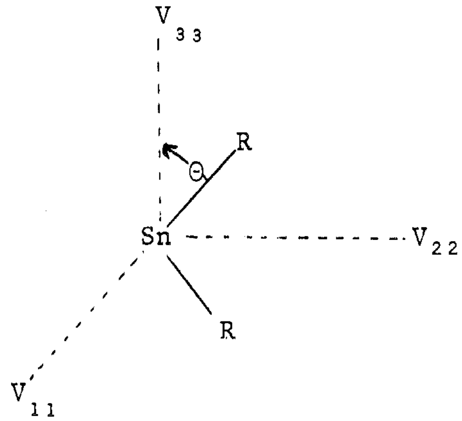

Figure 1. EFG axes for the R_2Sn unit.

Nineteen crystal structures of Me_2Sn^{IV} compounds are now available, and except for $Me_2Sn(CN)_2$, their quadrupole splittings are known (Table I). The first 13 of these structures have been classed as unambiguously six-coordinate structures, while the last four (**16–19**) have five-coordinate Sn atoms. Me_2SnCl_2 and $Me_2Sn(NO_3)_2$ have been classed as either distorted tetrahedral or octahedral structures.

In Figure 2, we plot the measured quadrupole splittings against the H_3C–Sn–CH_3 angle for these 19 compounds. The agreement between the predicted curve and the observed values is very good considering our gross assumptions: only for Me_2SnCl_2 and $Me_2Sn(NO_3)_2$ do the observed quadrupole splittings differ from those calculated by more than 0.4 mm

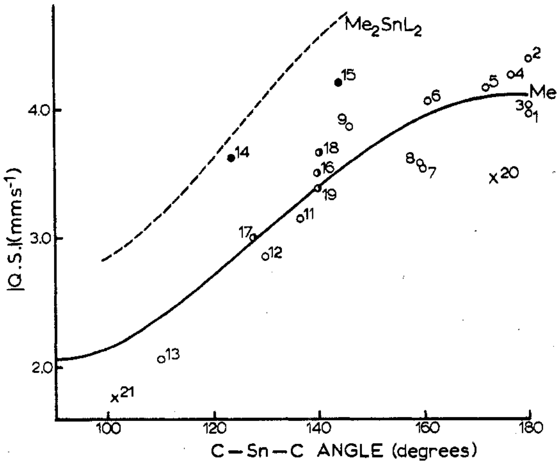

Figure 2. Plot of observed QS vs. observed C–Sn–C angle in Me$_2$Sn compounds (●, ⚬, ○) and Ph$_2$Sn compounds (×). The numbers refer to the compounds in Table I for the Me$_2$Sn compounds. See text for the Ph$_2$Sn parameters. The curves are those calculated for six-coordinate Me$_2$Sn compounds (——) and four-coordinate Me$_2$Sn compounds (- - -).

sec^{-1}. The range of QS for compounds **1–3** (3.96, 4.38, and 4.02 mm sec^{-1}) is the kind of scatter expected for a constant C–Sn–C angle due to the varying bonding natures of the ligands.

The five-coordinate compounds would be expected to lie very close to the octahedral curve in Figure 2 because the average of $\{Me\}_{ax}$ (−0.94 mm sec^{-1}) and $\{Me\}_{eq}$ (−1.13 mm sec^{-1})[16] is identical with the six-coordinate {Me} value.

It is interesting to note that the two Ph$_2$Sn^{IV} six-coordinate structures reported also appear to show the same trend. Thus, Ph$_2$SnCl(bpy)[17] (**20** in Figure 2) has a C–Sn–C angle of 173.5° and a QS of 3.45 mm sec^{-1};[1] while Ph$_2$Sn(S$_2$CNEt)$_2$ (**21** in Figure 2) has a C–Sn–C angle of 101.4° and a QS of 1.76 mm sec^{-1}.[13] Because the {Ph} value is −0.95 mm sec^{-1} [4] compared to the {Me} value of −1.03 mm sec^{-1}, the Ph$_2$Sn curve lies 0.32 mm sec^{-1} below the Me$_2$Sn curve for 180° C–Sn–C angles, and 0.16 mm sec^{-1} below for 90° C–Sn–C angles.

The good agreement between predicted and observed QS values in Figure 2 (with the exception of Me$_2$SnCl$_2$ and Me$_2$Sn(NO$_3$)$_2$) implies that the {Me} value of −1.03 mm sec^{-1} is a good *working* value. The agreement also implies that the other ligands do indeed have pqs values which are close to zero. However, {Me} values cannot really be constant. For example the large variation in the $J_{^{119}Sn-CH_3}$ values (Table I) indicates that the s character in the Sn–Me bonds decreases substantially as the C–Sn–C angle decreases.[18] There must be compensating effects which keep {Me} effectively constant. Two such compensating effects are apparent. First, as the s character of the Sn–C bond decreases (making {Me} more negative[19]), the bond length increases (making {Me} more positive). Except for compounds **1**, **3**, and **4** in Table I, there is a general increase in bond length as the C–Sn–C angle increases and the *J* value decreases but the errors in the bond lengths are too large to establish this trend firmly. Second, it seems likely that the value of {L} varies in the same direction as that of {Me} such that {R} − {L} remains nearly constant. Thus, as the s character of the Sn–Me bonds decreases with decrease in angle, the s character of the Sn–L bonds increases. These changes would result in both pqs values becoming more negative.

The only two QS values which lie substantially off the octahedral curve in Figure 2 are those for Me$_2$SnCl$_2$ and Me$_2$Sn(NO$_3$)$_2$. We suggest that these two compounds could better be classified as distorted tetrahedral structures, with Me$_2$SnCl$_2$ being slightly associated and the bidentate NO$_3$ (O–Sn–O angle of 55°) effectively occupying one structural position. For reference, we calculated the tetrahedral curve in Figure 2 using eq 1 and $\{Me\}^{tet} = -1.37$ mm sec^{-1}.[4] The two compounds lie much closer to this curve than to the octahedral curve.

For Me$_2$SnCl$_2$, a four-coordinate label is not unexpected. However, such a distinction for other compounds (such as Me$_2$Sn(NO$_3$)$_2$) is rather arbitrary at this time. It is interesting however that the $J_{^{119}Sn-CH_3}$ value of 81.6 Hz[20] is between those of Me$_2$SnCl$_2$ (70 Hz) and Me$_2$SnF$_2$ (84 Hz),[18] both of which are presumably four-coordinate in solution.

Conclusions

After careful examination of the crystal structures of the Me$_2$Sn and Ph$_2$Sn structures, it is apparent that the very distorted Me$_2$SnL$_4$ structures always have chelate L$_2$ ligands with a small bite for the relatively large Sn atom. For example, in Me$_2$Sn(AcAc)$_2$, the SnAcAc moiety gives a six-membered ring, and all bond angles are regular. In all the other non-associated structures, there are four- or five-membered rings, and the small bite of the chelate forces the two coordinating atoms into inequivalent positions.

Initially, the bonding in *trans*-Me$_2$SnL$_4$ species is thought to involve sp hybrids to the Me groups and pure p bonding to the L ligands.[21] The decrease in $J_{^{119}Sn-CH_3}$ values when the L–Sn–L angle decreases suggests that the Sn atom is forced to rehybridize. There is, however, no simple MO picture which can deal with bond angles of less than 90°.

If the effective bite of a ligand is known, it should be possible to predict qualitatively the Me–Sn–Me angle. In turn, a semiquantitative estimate of the QS can be made using Figure 2. Since the bite of a given ligand should be almost constant for Sn^{IV} in all compounds, it still seems entirely reasonable to derive a pqs value in the distorted complex using the ideal geometry electric field gradient calculations. For predictive purposes, such pqs values for highly distorted chelates will still be very useful. It will not be possible however, to use these derived pqs values for bonding estimates as has been done for regular six-coordinate structures.[14]

Registry No. Sn, 7440-31-5.

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Synthesis of Five- and Six-Membered Iron–Germanium Heterocycles: *cyclo*-1,4-Bis(tetracarbonyliron)-2,3,5,6-Tetrakis(dimethylgermanium) and *cyclo*-1,3-Bis(tetracarbonyliron)-2,4,5-Tris(dimethylgermanium)

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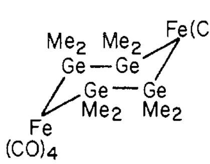
In our continuing investigation[1-4] of possible means to stabilize (pπ–pπ) bonds to silicon and germanium, we have isolated the novel heterocyclic compounds, *cyclo*-1,4-bis(tetracarbonyliron)-2,3,5,6-tetrakis(dimethylgermanium) and *cyclo*-1,3-bis(tetracarbonyliron)-2,4,5-tris(dimethylgermanium), I and II, respectively. These compounds were obtained during an attempt to synthesize a metal carbonyl-stabilized resonance extreme of a Ge═Ge double bond as shown in eq 1.



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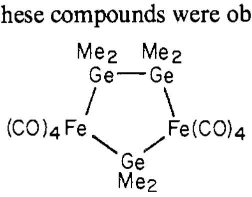
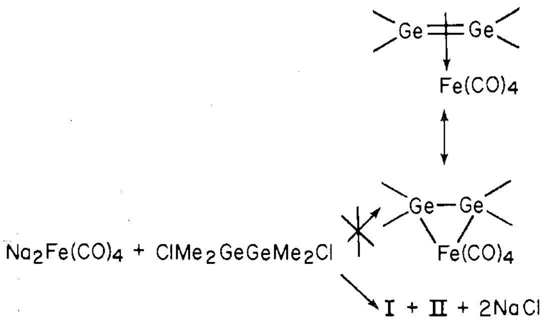


II



(1)

Experimental Section

All manipulations were carried out under dry nitrogen using standard Schlenck-ware techniques.[5] Melting points were obtained in evacuated capillaries.

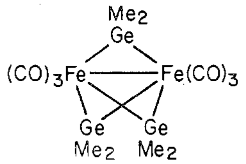
Synthesis of I and II. $Na_2Fe(CO)_4$ (1.5 g, 5.7 mmol) was slurried in 50 ml of petroleum ether (bp 30-60°) and 1,2-dichlorotetramethyldigermane (1.6 g, 5.8 mmol) was then added with the exclusion of light. (Light was also excluded as much as possible in all the following manipulations.) After stirring overnight, during which time the color had changed from red to yellow, the mixture was filtered and the filtrate concentrated to a volume of ca. 15 ml to give white crystals shown to be II. The supernatant liquid was removed with a syringe and placed in another Schlenck tube. An equal volume of methanol was added and much of the petroleum ether was removed under reduced pressure. Cooling to −78° gave white to pale yellow crystals of I.

Compound I melts at 175–176° and displays carbonyl absorptions in petroleum ether at 2048 m, 2001 s, 1992 s, and 1983 sh cm^{-1}. The NMR in C_6H_6 consists of a singlet at τ 9.18, and a parent ion at *m/e* 746 is observed in the mass spectrum. Anal. Calcd for $C_{16}H_{24}Fe_2Ge_4O_8$: C, 25.72; H, 3.22. Found: C, 25.89; H, 3.34.

Compound II melts at 302° dec and shows carbonyl absorptions at 2040 m, 2000 s, and 1985 m cm^{-1} in petroleum ether. The NMR in C_6H_6 has singlets at τ 9.23 and 8.75 in a 2:1 area ratio; *m/e* of the parent occurs at 644. Anal. Calcd for $C_{14}H_{18}Fe_2Ge_3O_8$: C, 26.10; H, 2.80. Found: C, 26.23; H, 2.93.

Results and Discussion

The interaction of $Na_2Fe(CO)_4$ with $ClMe_2GeGeMe_2Cl$ gives initially a red solution which then turns yellow. From the yellow solution, compounds I and II are obtained. When pure, these complexes are colorless, but are often obtained as pale yellow solids due to contamination by $(CO)_3Fe(\mu\text{-}GeMe_2)_3Fe(CO)_3$ (III) (see below). Compound III was previously synthesized by Brooks et al. from Me_2GeH_2 and $Fe_2(CO)_9$.[6]



III

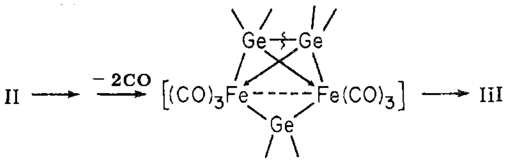
The use of more polar solvents, e.g., THF, gives poor yields of I and correspondingly higher yields of II, irrespective of the order of addition of reagents or the temperature.

The structure of I is undoubtedly analogous to the recently reported, isoelectronic complex, $[(CO)_4Cr]_2(AsMe_3)_4$ (IV),[7] which was shown by X-ray analysis to possess a cyclohexane chain conformation. As with IV, only a single NMR peak was observed down to −90°, at which point the solubility limit and viscosity broadening were reached. Thus, the interconversion of methyl groups by chair flipping must be rapid on the NMR time scale.

Compound II is assigned the five-membered ring structure on the basis of its NMR spectrum (two Me peaks in ratio of 2:1) and its IR which is similar to other $E_2Fe(CO)_4$ type structures with local C_{2v} symmetry.[8] The formation of II is somewhat surprising since a germanium–germanium bond was necessarily cleaved in its formation, and Noltes and Bulten have shown that hexamethyldigermane is insensitive to cleavage even by alkali metals.[9] II does not arise from I by a photochemical reaction since II is obtained in about 50% yield even in the absence of light.

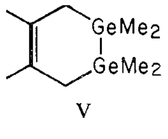
Both I and II in solution rapidly produce III when exposed to uv light. Even sunlight or fluorescent light causes a rapid yellowing of their solutions. In the transformation of I or II to III, a Ge–Ge bond is ruptured and since these bonds are not photosensitive under normal conditions, it is likely that the first step in the photolysis of I or II involves loss of carbonyl to form a coordinatively unsaturated metal.[10,11]

Rearrangements of the Ge–Ge bonds, as shown schematically for II, can then complete the 18 electron configuration on each Fe.



On going from I to III, a dimethylgermylene (Me_2Ge) group is necessarily lost and a peak at τ 9.63, observed in the photolysis reaction mixture from I, may correspond to cyclic $(Me_2Ge)_n$ (n = 5 or 6). Due to the small quantities, this substance was not isolated, however.

Several attempts were made to generate $Me_2Ge{=}GeMe_2$ by Ce(IV) or Fe(III) oxidation of I in the presence of trapping agents, e.g., 2,3-dimethylbutadiene or cyclopentadiene. Under a variety of experimental conditions, e.g., temperature, solvent, mode of addition of reagents, etc., no evidence for compounds, e.g., V, was obtained. The observed products were unreacted I and an insoluble, green residue which could not be adequately characterized, but did not contain the trapping agent.



V