which boron atoms were subsequently placed. The R-factor then dropped to 20.4%. These additional positions indicate an excess of sites, which can be attributed to a statistical distribution of inter-icosahedral atoms; also, aluminum has not yet been positioned. The exact distribution of the inter-icosahedral atoms is a matter for three-dimensional analysis, which is in progress.

The icosahedra are centered at 4(c) with the coordinates x/a, y/b, $z/c = 0.1, 0.25, 0$; $0.9, 0.75, 0$; $0.6, 0.25, 0.50$, and $0.4, 0.75, 0.50$.

The symmetry required of the B_{12} configuration by the space group is mm2, and no conclusion can be drawn at this time as to what degree the symmetry mmm of a regular icosahedron is approximated. Within the icosahedra, preliminary bond distance calculations reveal boron–boron distances ranging from 1.77 to 1.91 Å., in agreement with bond lengths reported for elementary boron.

U. S. ARMY ELECTRONICS RESEARCH AND   GEORG WILL
DEVELOPMENT LABORATORY
FORT MONMOUTH, NEW JERSEY
RECEIVED MAY 10, 1963

High Resolution Nuclear Magnetic Resonance Spectra of Methylsilicon Compounds

Sir:

There is considerable current interest in the correlation between spin–spin coupling constants and hybridization of the atoms participating in the chemical bondings of the compounds studied. A series of important relations have been established for a number of organic[1–8] and tin–organic[9,10] compounds, using the indirect spin–spin interaction of ^{13}C and $^{117,119}Sn$ with protons as a reference. In recent papers[5,6,11] these investigations were extended to the interactions of the ^{29}Si isotope (natural abundance 4.7%, spin $^1/_2$) with protons directly bonded to silicon, but the results are not yet as readily understood in terms of hybridization.

$^1H-^{29}Si$ interactions in compounds with protons *not* directly bonded to silicon, however, are not easily detected in n.m.r. spectra of ordinary resolution because of the small coupling constants, and corresponding data are known only for a small number of organosilicon compounds.[7,11,12] As a part of our current high resolution n.m.r. studies on alkylsilicon compounds this communication now reports the $H-C-^{29}Si$ and $H-^{13}C$ coupling constants of some series of methylsilicon derivatives, which show significant dependence on the nature of the ligands attached to the central silicon atom.

The chemical shifts and coupling constants of tetramethylsilane (I) and the four trimethylsilicon halides (II–V), given in Table I, show a marked decrease in the δ values and an increase in $J(H-^{13}C)$ and J $(H-C-^{29}Si)$ in the sequence CH_3, F, Cl, Br, I. These relations are in contradiction to customary electronegativity considerations . . . . . (F > Cl > Br > I > CH_3), from which an opposite trend should be expected. (Proton shielding usually is restricted by an increasing electronegativity of the substituent introduced in a compound, and the spin–spin interactions should be greater

TABLE I

CHEMICAL SHIFTS δ AND COUPLING CONSTANTS J OF SOME TRIMETHYLSILICON DERIVATIVES

Varian A-60, 60 Mc., room temperature, TMS as an internal reference. All compounds in CCl_4 with $c = 5 \pm 1$ % [v./v.] for δ, and $c = 20 \pm 2$ % [v./v.] for J values. Standard deviations are ± 1[c.p.s.] for δ, $J(H-^{13}C)$, and $J(H-C-Sn, Pb)$, and ± 0.05 [c.p.s.] for $J(H-C-^{29}Si)$ and $J(H-C-Si-F)$.

No.	Formula		δ^e	J (H–^{13}C)	J(H–C–^{29}Si)
I	Me_4Si		0.0	118.5	6.78
II	Me_3SiF^a		-12.2	118.8	7.00
III	Me_3SiCl		-25.4	120.5	7.10
IV	Me_3SiBr		-42.5	121.0	7.23
V	Me_3SiI		-47.0	121.5	7.30
VI	$Me_3SiOSiMe_3$		-3.5	118.0	6.86
VII	$Me_3SiSSiMe_3$		-19.5	119.5	7.10
VIII	$Me_3SiSeSiMe_3$		-25.7	120.5	7.15
IX	$Me_3SiOGeMe_3$	Me_3Si	0.0	117.8	6.80
		Me_3Ge	-21.0	126.0	...
X	$Me_3SiOSnMe_3^b$	Me_3Si	+2.5	116.8	6.72
		Me_3Sn	-20.5	128.5	...
XI	$Me_3SiOPbMe_3^c$	Me_3Si	+3.5	115.5	6.69
		Me_3Pb	-73.0	136.0	...
XII	$(Me_3Si)_3N$		-10.7	118.0	6.76
XIII	$(Me_3Si)_2NGeMe_3$	Me_4Si	-7.2	118.0	6.75
		Me_3Ge	-23.5	125.4	...
XIV	$(Me_3Si)_2NSnMe_3^d$	Me_3Si	-5.0	118.0	6.60
		Me_3Sn	-18.8	130.0	...
XV		Me_3Si	0.0	117.5	6.78
		Me_2Si	-14.0	118.5	7.20
XVI		Me_3Si	0.0	118.5	6.80
		Me_2Si	-15.0	119.0	7.05
XVII	$[(Me_3SiO)_3Al]_2$	bridges	-19.0	119.0	7.00
		terminal	-4.0	116.0	6.65

^{a} $J(HCSiF) = 7.48$. ^{b} $J(H-C-^{117,119}Sn) = 54.9, 57.4$. ^{c} $J(H-C-^{207}Pb) = 69.5$. ^{d} $J(H-C-^{117,119}Sn) = 53.4, 55.8$. ^{e} In c.p.s., negative values are downfield of TMS.

in the compound having the most polarized silicon–halogen bonding, which would lead the central silicon atom to a maximum $sp^3 \rightarrow sp^2$ rehybridization.) From these considerations trimethylfluorosilane should show the lowest chemical shielding and the highest J-values. The results are readily explained, however, by the assumption of a systematic decrease of $d\pi-p\pi$-interactions between silicon and the halogens, the magnitude of which is a function of the relative atomic radii of the atoms. These π-interactions provide an increase in polarity of the Si–halogen bonding in the direction F < Cl < Br < I ("back-donation") and an increase in s-character of the silicon and even the carbon orbitals, being in close relation with each other by the Si–C-bondings, following this sequence. Similar results were obtained for hexamethyldisiloxane and its analogs (VI–VIII),[13] as presented in the table, and can be interpreted in a corresponding manner, following the sequence O, S, Se. Among other evidences the well

known decrease of the bond angles in the series Si—O—Si, Si—S—Si, Si—Se—Si is a good support for this assumption.[14]

Tris-trimethylsilylamine (XII) and the cyclic trisilylamine compounds XV and XVI[15] gave surprisingly low values for the Me_3Si- groups and illustrate the unusual

(1) M. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).
(2) M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959).
(3) J. N. Shoolery, *ibid.*, **30**, 1427 (1959).
(4) N. Muller and D. E. Pritchard, *ibid.*, **30**, 768, 1471 (1959).
(5) E. R. Malinowsky, *J. Am. Chem. Soc.*, **83**, 4479 (1961).
(6) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).
(7) H. S. Gutowsky and C. Juan, *J. Am. Chem. Soc.*, **84**, 307 (1962).
(8) G. Klose, *Ann. Physik*, **9**, 262 (1962).
(9) J. R. Holmes and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 3903 (1961).
(10) G. P. van der Kelen, *Nature*, **193**, 1069 (1962).
(11) E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2628 (1962).
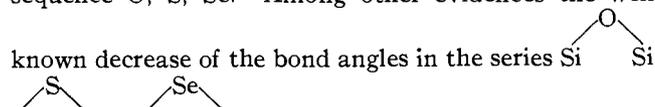(12) G. Fritz, E. A. V. Ebsworth, *et al.*, *Z. anorg. allgem. Chem.*, **321**, 10 (1963).

(13) For $Me_3SiSeSiMe_3$ see: M. Schmidt and H. Ruf, *Z. anorg. allgem. Chem.*, **32**, 270 (1963).
(14) R. J. Gillespie, *J. Am. Chem. Soc.*, **82**, 5978 (1960).
(15) W. Fink, *Angew Chem.*, **73**, 736 (1961), and *Helv. Chim. Acta*, **46**, 720 (1963); We thank Dr. Fink for providing the samples.

strong π-bonding in these molecules having planar hybridization at the nitrogen atoms.[16,17]

From an examination of some closely related hexamethyl*hetero*siloxanes (IX–XI)[18] and nonamethyl-*hetero*disilazanes (XIII, XIV),[19] we could gain further knowledge of the influence of hetero-atoms on the nature of the Si–O– and Si–N– bonds. As shown in the table, we have found, that on substitution of Si by Ge, Sn, or Pb the remaining Me_3Si– group(s) tend to show a steadily increasing chemical shielding and decreasing coupling constants, thus indicating increasing back-donation in the Si–O or Si–N bonds and increasing p-character of the Si valences. When compared with the corresponding data of $Me_3GeOGeMe_3$[20] and $Me_3SnO-SnMe_3$,[21] the δ and J values of the trimethylmetaloxy groups indicate the expected rehybridization of the hetero-atoms in the opposite direction.

XV

XVI

XVII

Finally, it is interesting to note that the bridging and terminal trimethylsiloxy groups in compound XVII[22] show significant differences in $J(H-^{13}C)$ and $J(H-C-^{29}Si)$ and thus confirm earlier suggestions for this and some analoguous "bridged" heterosiloxanes.[23]

Acknowledgment.—The author is indebted to Prof. Dr. Max Schmidt for great support.

(16) J. Goubeau and J. Jimenez-Barbera, *Z. anorg. allgem. Chem.*, **303**, 217 (1960).

(17) P. J. Wheatley, *J. Chem. Soc.*, 1721 (1962); 2562 (1963).

(18) H. Schmidbaur and M. Schmidt, *J. Am. Chem. Soc.*, **83**, 2963 (1961).

(19) O. Scherer and M. Schmidt, *Angew Chem.*, **75**, 642 (1963).

(20) M. P. Brown and D. E. Webster, *J. Phys. Chem.*, **64**, 698 (1960); I. Ruidisch, private communication.

(21) H. Schmidbaur and H. Hussek, *Angew Chem.*, **75**, 575 (1963).

(22) H. Schmidbaur and M. Schmidt, *ibid.*, **74**, 328 (1962).

(23) H. Schmidbaur and M. Schmidt, *J. Am. Chem. Soc.*, **84**, 1069 (1962); **84**, 3600 (1962).

INSTITUT FÜR ANORGANISCHE CHEMIE
UNIVERSITÄT MARBURG, GERMANY   HUBERT SCHMIDBAUR
RECEIVED MAY 27, 1963

The Mechanism of the Meerwein–Ponndorf–Verley Reaction

Sir:

The current view of the Meerwein–Ponndorf–Verley (MPV) reaction, recently summarized by Bradley,[1] is that it proceeds *via* the following steps: (1) coördination of the ketone to the alkoxide monomer; (2) hydride transfer; (3) separation from the complex of the ketone produced in step 2; (4) alcoholysis of the mixed alkoxide, liberating the free alcohol.

Step 2 is generally assumed to be rate-determining.[2]

Examination of the proton resonance spectra of solutions of acetone and both trimeric and tetrameric forms[3] of aluminum isopropoxide in toluene indicates rapid and reversible coördination of the ketone with the

(1) D. C. Bradley, "Metal Alkoxides," "Advances in Chemistry Series," Number 23, American Chemical Society, Washington, D. C., 1959, p. 10.

(2) W. N. Moulton, R. E. Van Atta and R. R. Ruch, *J. Org. Chem.*, **26**, 290 (1961).

(3) V. J. Shiner, Jr., D. Whittaker and V. P. Fernandez, *J. Am. Chem.*, *Soc.*, **85**, 2318 (1963).

Fig. 1.—Yield of products in MPV reactions of Tables I and II: □, acetone; ⊙, α-phenylethanol; solid line, products of reaction with tetramer; dotted line, products of reaction with trimer of aluminum isopropoxide.

alkoxide. The spectra show only a single sharp acetone resonance, even at $-35°$, its position depending on the temperature and on the ratio of alkoxide to acetone concentration. Acetone does not cause any significant change in the fairly complex proton resonance absorption pattern of the tetramer, indicating that coördination of the ketone does not involve a breakdown of the tetrameric structure. The spectrum of the trimer, however, is modified by the addition of acetone, but this may result from coördination of the ketone interfering with the rapid intramolecular alkoxide exchange taking place in this structure.

Using proton resonance spectroscopy, we have measured the rate of formation of acetone and α-phenylethanol from a mixture of aluminum isopropoxide and acetophenone in 50 mole % benzene and isopropyl alcohol solvent. *Aluminum isopropoxide tetramer,* Table I, *gives a considerably slower reaction than does the trimer,* Table II. The results are compared in Fig. 1.

TABLE I

REDUCTION OF ACETOPHENONE WITH ALUMINUM ISOPROPOXIDE TETRAMER[a]

Time, hr.	Ketone composition, mole %		α-Phenylethanol yield as % of theoretical yield	Molar ratio, α-phenylethanol / acetone
	Acetophenone	Acetone		
0	93.3	6.7	0	..
4	74.5	25.5	6.4	0.25
10	51.8	48.2	14.8	.31
16.5	40.1	59.9	30.8	.51
24	30.7	69.3	38.4	.55
48	24.4	75.6	39.2	.52
144	23.3	76.7	46.8	.61
192	22.7	77.3	51.7	.67

[a] Temperature 25°; initial concentrations in 50 mole % benzene and isopropyl alcohol were acetophenone 0.305 M; aluminum isopropoxide 0.424 M (calculated as monomer).

In addition, it is clear that in both reactions, *the rate of α-phenylethanol formation is considerably lower than the rate of acetone formation, and therefore that the rate-determining step in these processes is alcoholysis of the mixed alkoxide and not hydride transfer.*