Journal of Organometallic Chemistry Library 2

Organometallic Chemistry Reviews: Organosilicon Reviews

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D. SEYFERTH (editor)
NEW APPLICATIONS OF ORGANOMETALLIC REAGENTS IN ORGANIC SYNTHESIS
Proceedings of a symposium at the American Chemical Society National Meeting held in New York City, April 6 – 9th, 1976

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D. SEYFERTH (coordinating editor), A.G. DAVIES, E.O. FISCHER, J.F. NORMANT and O.A. REUTOV
ORGANOMETALLIC CHEMISTRY REVIEWS: ORGANOSILICON REVIEWS

Introductory Remarks

Volume 2 of the JOURNAL OF ORGANOMETALLIC CHEMISTRY Library brings the first collection of subject reviews. These had been published as received in the JOURNAL OF ORGANOMETALLIC CHEMISTRY, but the great press of original research contributions made it necessary to seek an alternate form of publication for future subject reviews.

The present volume contains four reviews of current topics in organosilicon chemistry. This field, which has received so much attention in academic, industrial and government research laboratories since the advent of the silicone polymers some thirty years ago, remains a very vital one. Organosilicon compounds are finding important applications in organic synthesis; new synthetic methods are being developed for organosilicon compounds; silicon-containing substituents have become important in stabilizing transition metal derivatives and lower oxidation states of main group metals; novel organosilicon intermediates containing multiple linkages of silicon atoms to carbon, nitrogen, oxygen and sulfur are being generated. The reviews in this volume cover some of these exciting new topics and serve to describe in depth interesting topics which the JOURNAL OF ORGANOMETALLIC CHEMISTRY Annual Surveys of organosilicon chemistry can only point out to the interested chemist.

Professor Dietmar Seyferth

CONTENTS

CARBON TO SILICON DOUBLE BONDS: AN ANALYSIS OF THEIR INSTABILITY AND A PROPOSAL FOR THEIR PREPARATION

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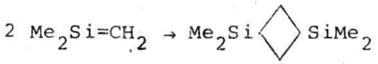
(Received November 13th, 1975)

That "multiple bonds of strength equal to or greater than a corresponding number of single bonds occur only with the first row elements" [1] is close enough to the truth to have attracted considerable attention over the years [2-10] The rule applies strictly to group IVB, and towards the right-hand side of the periodic table there are exceptions such as CS_2.

At ordinary temperatures the silicon analogues of the alkenes, acetylenes and carbonyls are unknown. However, species such as $Me_2Si{=}CH_2$ [11] and Me_2Si are transient intermediates in certain reactions [12] and at very low temperature they exist long enough for the measurement of the IR spectrum [13]. The instability of the silicon analogues is not the result of unimolecular decomposition but is due to bimolecular reactions such as [14]



At 1500° silicon monoxide is stable as the isolated SiO molecule but polymerisation sets in at lower temperatures [15].

In stable compounds, whilst carbon takes coordination numbers of 4 or less and very rarely 5, silicon takes 4, 5 or 6 but never less than 4. The reluctance of silicon to lower its coordination number below 4 exceeds that of carbon to increase

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its number above 4, for example in tetrakis(trimethylsilylmethylcopper(I)), see Fig. 1, where 5-coordinate carbon is attached to 4-coordinate silicon. On the other hand, the readiness of silicon to expand its coordination sphere is greater than that of carbon, so that racemization of optically active R'R"R"' SiX is fast in polar solvents compared with the carbon derivatives. Presumably such racemizations proceed through a 5-membered (or greater) intermediate following nucleophilic attack [16]. Racemization is even more facile among the derivatives of tin, germanium and lead.

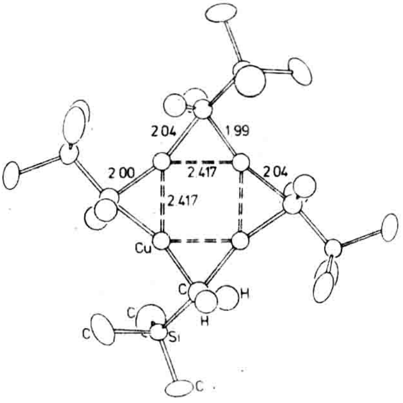
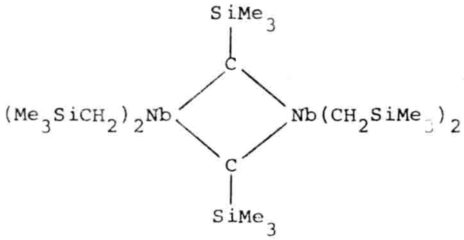


Fig. 1. Tetrakis(trimethylsilylmethylcopper(I)) in which 5-coordinate carbon is attached to 4-coordinate silicon [78].

The observation that metal complexes of the type $L_nM\text{-}CH_2CH_2R$ are unstable towards the elimination of $CH_2\text{=}CHR$ has led to the prediction of stability and preparation of stable complexes of the type $L_nM\text{-}CH_2SiMe_3$ on the basis of the instability of $Me_2Si\text{=}CH_2$ [17-21]. However this must be an example of the rule that fortune favours the brave for there is no obvious reason why $Me_2Si\text{=}CH_2$ cannot play the part of a transient intermediate here too. An unsaturated intermediate of similar type might well be involved in the otherwise puzzling formation of



observed in some reactions [17]. Presumably there is a high energy barrier and knowledge of the energy of formation would be useful.

Fig. 2 is a histogram of bond lengths from the X-ray examination of about 50 different compounds containing both carbon

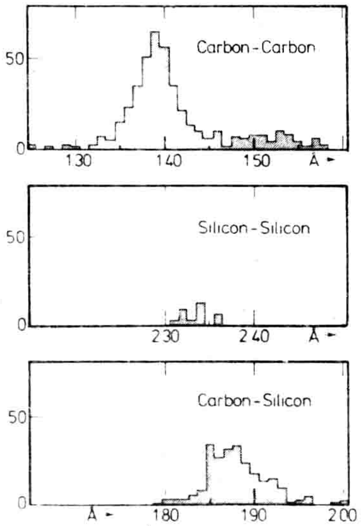


Fig. 2. Histogram of carbon-carbon, silicon-silicon and carbon-silicon bond lengths in about fifty organosilicon compounds [35-77].

and silicon. The carbon-carbon distances exhibit the double Gaussian distribution expected from the presence of both C-C and C=C bonds but single peaks only are found for Si-C and Si-Si.

Theories

Associated with the term "multiple bond" are the following concepts

(i) unsaturated chemical properties,
(ii) a low coordination number,
(iii) a short bond length,
(iv) in the language of valence bond theory, a π (or Δ etc.) bond order exceeding zero.

Of these (i) is inapplicable to CO_2 for example and is not a generally useful notion. It is clear on the basis of (ii) that P_2 is more multiply bonded than P_4 but (ii) does not help in the series SO_4^{2-}, RSO_3^- $SO_2(NH_2)_2$ [7] where there are large changes in the S-O bond length attributable to differences in the π-bond order. There is a large amount of evidence supporting the contention that there is a relationship between (iii) and (iv) and from the theoretical point of view (iv) is the obvious criterion of bond multiplicity.

Observing the large drop in bond energy on passing along the first row from C-C to N-N, Pitzer [1] emphasized the importance of inner-shell repulsions. Mulliken concluded that inner-shell/inner-shell repulsions were negligible [5] and that inner-shell/outer-shell repulsions, although not negligible, were no larger for the second row than for the first. Mulliken emphasized the importance of the overlap integral, S, calculated at the experimental bond distance and reached the conclusion that it is the strength of the second row single bonds that is anomalous (being very high) rather than the low strength of the first row single bonds. In this d-orbitals were implicated.

Concerning d-orbital participation there have been many conflicting opinions, some of which are listed in a recent review [2]. Although it is easy enough to show by group theory or otherwise whether d-orbitals can engage in bonding in any particular case it is often difficult to discover how significant the effect is. For the electronically excited states of molecules there is a much greater likelihood of significant d-orbital participation; in some cases therefore optical and UV spectroscopy implies a larger participation than does photoelectron spectroscopy. For example from theoretical calculations of the photoelectron spectrum of P_4 it was concluded that 3d-orbitals play no significant role in the ground state wave function [22]. The predictive power of the d-orbital concept is uncertain since on the basis of "efficiency of filling d-orbitals" it was predicted that SiO and $Me_2Si=CH_2$ are stable [23].

Where d-orbitals undoubtedly play their part is in the complexes of the transition metals. Thus in the photoelectron spectrum of nickel tetracarbonyl [24] there are two peaks 0.9 eV apart attributable to the ionization of the T_2 and E molecular orbitals of largely Ni(3d) character. In the corresponding trifluorophosphine complex the splitting of these peaks is about 1.0 eV [25]. In these cases the d-orbitals are part of the valence shell, the valence orbital ionization energies [26] being 10 eV (Ni(3d)) and 7.6 eV (Ni(4s)).

In the tetrahalides of group IVB where the nearest empty d-orbitals lie 7 eV or so away from the valence shell, their participation must be very much less than in the transition metal complexes. In these compounds the halogen p-orbitals span the irreducible representations A_1 , E , T_1 and T_2 (two of these) and these are the symmetries of the upper ionization states of the molecules [27]. All the orbitals are fully occupied and the average of the ionization energies, corrected for the degeneracies of the states, for the C , Si , Ge and

Sn fluorides, chlorides and bromides respectively are 18.2 , 13.6 , and 12.6 eV compared with the valence orbital ionization energies 18.7 (F(2p)) , 13.8 (Cl(3p)) and 12.5 (Br(3p)). Hence the energies of the valence shell molecular orbitals are highly suggestive of nearly pure p-character [28].

According to Mulliken [4], the incorporation of Cl(3d) character into the π molecular orbitals of Cl_2 strengthens the bonding in comparison with F_2. This can occur by the interaction of both π_g and π_u orbitals of 3p and 3d derivation. Again the energy gap between 3p and 3d is large and examination of Price's potential curves derived from the photoelectron spectra fails to indicate differences between the F_2 and the Cl_2 orbitals although Mulliken's predictions in other respects are confirmed.

In summary it appears impossible to conclude that d-orbital participation causes the *general* reluctance of the upper row elements to form multiple bonds although it is a factor to be taken into consideration in some instances.

An important factor that appears to have been overlooked is the Coulombic repulsion between nuclei. Neither the overlap integral nor any purely electronic parameter is a complete index of bond strength. In terms of the force acting on a nucleus in a molecule the Hellmann-Feynman theorem [29,30] states that classical electrostatic calculations are appropriate both for nuclear/nuclear and nuclear/electron interactions. The difficulties in making the calculations are twofold: firstly there is uncertainty about the effective charge on the nucleus after it has been screened by the electrons, and secondly there is a lack of insufficiently accurate electronic functions to enable the electron/electron repulsions to be computed. However Pauling has shown that "back-of-the-envelope" calculations of nuclear repulsion enable heats of isomerisation to be calculated [31] and as a matter of fact his method agrees quite well in the value it gives for the isomerisation

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with that derived from photoelectron spectroscopy [32]. A general and easily applied method is required in order to give semi-quantitative guidance as to the relative importance of nuclear repulsion in the first and subsequent rows of the periodic table. Following Pauling [31] the screening effects of the electrons can be accounted for by subtracting the charge on the non-valence electronic shells from the atomic number in order to give the charge on the nuclear "kernel". Calling this charge Z* the nuclear repulsion is given by $Z_1^*Z_2^*/(10R)$ where R is the internuclear separation distance. Since the kernel charges of nuclei in the same group of the periodic table are the same as calculated by this method, attention is directed towards the internuclear distances in order to find differences. According to Slater [33] a good theoretical value for the bonding radius excluding nuclear repulsion is n^{*2}/Z in units of Bohr radii, where n* is the effective principal quantum number and Z is the effective nuclear charge calculated for the valence shell by Slater's rules. Values of this radius are given in Table 1 where it is evident that the distances in the first row are between 0.5 and 0.7 of those in the second row.

Thus for P_2 the nuclear repulsion energy calculated bv the

Table 1.

Element	n^{*2}/Z Å	Element	n^{*2}/Z Å
Li	1.63	Na	2.17
Be	1.09	Mg	1.67
B	0.82	Al	1.36
C	0.65	Si	1.15
N	0.54	P	0.99
O	0.47	S	0.88
F	0.41	Cl	0.78

method of Pauling is 54% as large as for N_2. It has been found that both P_4 and N_4 are more stable, on the basis of electronic energy alone, than $2P_2$ and $2N_2$ respectively but the inclusion of nuclear repulsion results in N_4 being less stable than N_2 [34].

Calculated by Pauling's method with the above radii the difference in nuclear repulsion energy between N_2 and P_2 amounts to about 15 eV. Between C_2 and Si_2 the difference amounts to some 7.7 eV. In N_4 and P_4 there are three times as many nuclear interactions as in $2N_2$ and $2P_2$ but on the other hand the electronic energy is roughly one and a half times as great for the tetramers. According to Hückel theory the electronic energy (ignoring the s electrons) is $11\frac{1}{4}\pi+6\frac{3}{4}\sigma$ for N_4 compared with $8\pi+4\sigma$ for $2N_2$ where π and σ are the resonance integrals for π and σ overlap.

High nuclear repulsion energy predisposes towards multiple bond formation (i.e. low coordination number) and low nuclear repulsion energy predisposes towards polymerisation.

Towards the left of the periodic table the nuclear repulsion, as calculated by this method, diminishes. The difference between Li_2 and Na_2 for example is only 0.1 eV, which explains the fact that in the alkali metals there is little to choose in stability between clusters of the formulae Na_2 Na_3, Na_4, etc.

Stable silicon analogues of the alkenes.

Since there appears to be no intrinsic instability for the silicon analogues of the alkenes but merely a thermodynamically based propensity towards polymerisation the clue to the synthesis of these compounds presumably lies in the prevention of polymerisation. The attachment of very bulky ligands, B, to the multiple bond, as in $B_2C{=}SiB_2$, would secure this. Oddly, among the bulkiest ligands are silicon derivatives of the type $CH(SiMe_3)_2$ [21].

Bulky ligands of this and related types form a large range of complexes of low coordination number. Thus reaction of $(Me_3Si)_2CHLi$ with an intermediate of the type $F_2Si{=}SiF_2$ should produce an ethylene analogue. Such compounds and others like B_2SiO should be stable.

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