tion[12,13] that hexamethylphosphoramide (HMPA) dissolves alkali metals to produce solutions of solvated electrons (observed $\langle g \rangle = 2.0022$ in pure HMPA[12]) has provided a facile method for generating monoanions *via* the reaction $[\mathrm{M(BDPH{-}2H)}]^0 + e^-(\text{solvated}) \rightarrow [\mathrm{M(BDPH{-}2H)}]^-$ in HMPA or DMF solutions. The satisfactory agreement among the *g* values of the various species generated both chemically and electrochemically, together with the polarographic results, serves to demonstrate the existence of the species **4** and **5** for both nickel and palladium. Their solution *g* values are suggestive of, but do not necessarily require, a description of these complexes as essentially cation-stabilized free radicals.[6]

It is concluded that $[\mathrm{M(BDPH{-}2H)}]^0$ complexes are best understood as nonclassical species which are in fact the central members of five-membered electron-transfer series, the completeness of which for $[\mathrm{Pd(BDPH{-}2H)}]^z$ we regard to be demonstrated. These results support the general utility of the electron-transfer series concept for complexes having the common requisite electronic property of combining several distinct stages of ligand oxidation with a stable oxidation state of the coordinated metal such that the terminal members, and hence the potential scope, of the series are defined. Finally, a comparison of half-wave potentials reported here and elsewhere[5] for complexes of a given metal having an N_4 coordination sphere with those for complexes with S_4, S_2N_2, and O_2S_2 donor atom sets underscores the considerable increase in relative redox stability of cationic $[\mathrm{M{-}N_4}]$ complexes. For this reason complete electron-transfer series of the $[\mathrm{M{-}N_4}]^z$ type can be realized,[5] whereas the series for $[\mathrm{M{-}S_4}]^z$, $[\mathrm{M{-}S_2N_2}]^z$, and $[\mathrm{M{-}O_2S_2}]^z$ systems is usually restricted to the $z = 0, -1, -2$ members.[6-9,14]

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A Simple Hückel Molecular Orbital Treatment of the Ultraviolet Absorption Spectra of Polysilanes[1]

Sir:

The systematic investigation of homologous series of linear, branched, and cyclic organopolysilanes has recently been undertaken,[2] for the most part in the laboratories of Gilman and Kumada. One of the more interesting aspects of these studies has been the realization that the silicon–silicon bond has conjugating properties[3] and is capable of absorbing in the ultraviolet.[4,5] The purpose of this communication is to demonstrate that the absorption maxima of methyl-, phenyl-, and vinylpolysilanes may be correlated with remarkable success by zero-order HMO theory.

Considering first the permethylated series $\mathrm{Me(Me_2Si)_nMe}$, we have made the reasonable assumption that the excited state of the transition can be constructed as a linear combination of unoccupied orbitals which are localized on individual $-\mathrm{Si(CH_3)_2}-$ groups. For a chain of *n* atoms, the *n* molecular orbitals will have energies which are given by eq 1.[6] The ultraviolet absorption is presumed to involve a transition between a σ-bonding orbital and the unoccupied molecular orbitals, the lowest energy of which is given by eq 1, $j = 1$. If E_σ is constant for a given homologous series, then the frequency (ν_n) of the transition is given by eq 2. For this equation to be valid, a plot of ν_n against $2\cos(\pi/(n+1))$ should be a straight line with a slope of β_{SiSi}. Such a plot using literature values[4c,e] of ν_n is shown in Figure 1. Apart from the not unexpected divergence when $n = 2$, the excellent linear correlation for $n = 3$–6, 8, 10 is evidence both for the validity of this treatment and for the hypothesis[7] that adjacent orbitals in chains of metals and metalloids will overlap to form delocalized molecular orbitals. The value of β_{SiSi} derived from this plot is 2.79 ev, and the minimum energy difference between the σ-bonding orbitals and the excited state is 4.21 ev (obtained from the intercept as $n \rightarrow \infty$).

$$E_j = \alpha_{\mathrm{Si}} + (\beta_{\mathrm{SiSi}})2\cos\frac{j\pi}{n+1} \qquad (1)$$

$$j = 1, 2, 3 \ldots\ldots\ldots n$$

$$h\nu_n = (\alpha_{\mathrm{Si}} - E_\sigma) + (\beta_{\mathrm{SiSi}})2\cos\frac{\pi}{n+1} \qquad (2)$$

The absorption spectra of α,ω-diphenyl-[4f] and vinyl-substituted[5a] polysilanes have been treated in an analogous manner.[8,9] The data can best be accommodated using a mixture of the silicon orbitals and an unoccupied orbital (π^*) of the phenyl or vinyl group as the excited

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[6] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y, 1961, p 46. This equation depends only on the existence of an unoccupied orbital transforming under the local symmetry properties of the $-\mathrm{Me_2Si}-$ group. While it is tempting to label these localized orbitals as silicon 3d orbitals, this is not essential to the treatment.

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[9] An alternative treatment of the permethylated series, using the Sandorfy C method, has been suggested: P. P. Shorygin, V. A. Petukhov, O. M. Nefedov, S. P. Kolesnikov, and V. I. Shiryaev, *Peor. i Experim.-Khim., Akad. Nauk. Ukr. SSR*, **2**, 190 (1966). This approach, which assumes a $\sigma \rightarrow \sigma^*$ transition, does not appear to be satisfactory for the phenylated series because of the apparent involvement of orbitals of π symmetry.

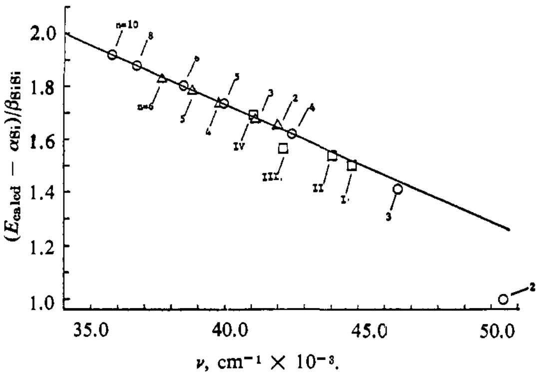

Figure 1. Plot of $(E_{calcd} - \alpha_{Si})/\beta_{SiSi}$ *vs.* ν ($cm^{-1} \times 10^{-3}$) for the series (A) $Me(Me_2Si)_nMe$, -○-○-○-, with n = 2–6, 8, 10; (B) $(C_6H_5\text{-}(Me_2Si)_nC_6H_5$, -△-△-△-, with n = 2–6; (C) vinylpentamethyldisilane (I), 1,2-divinyltetramethyldisilane (II), 1-vinylheptamethyltrisilane (III), and 1,4-divinyloctamethyltetrasilane (IV), -□-□-□-.

state. Using various values for the energy of the π^* orbital relative to that of the silicon d orbital, expressed in the form $\alpha_{\pi^*} = \alpha_{Si} + \mu\beta_{SiSi}$, and the resonance integral between the π^* and $-Me_2Si-$ orbitals, $\beta_{Si\pi^*} = \lambda\beta_{SiSi}$, the energy of the orbital for a given compound (i) was obtained as

$$E_i = \alpha_{Si} + f_i(\lambda,\mu)\beta_{SiSi}$$

The reported[4f,5a] absorption maxima (ν_i) were plotted against the function $f_i(\lambda,\mu)$. The values of λ and μ which gave the best linear correlation (see Figure 1) are presented in Table I. Since the data for methyl-, phenyl-, and vinyl-substituted polysilanes can be fitted to the same straight line, it is implied that the lower state of the transition for each series has the same and constant energy, *i.e.*, that of the Si_σ framework.

Table I

Series	λ	μ	β_{π^*Si}, ev	$(\alpha_{\pi^*} - \alpha_{Si})$, ev	$(\alpha_{\pi^*} - E_\sigma)$, ev
$-(SiMe_2)_n-$	1	0	−2.79	0	9.79
$C_6H_5(SiMe_2)_nC_6H_5$	0.245	1.55	−0.68	−4.32	5.47
$CH_2{=}CH(SiMe_2)_n-$	0.224	1.44	−0.62	−4.02	5.77

The success of this simple treatment allows us to predict certain of the properties of polysilanes. For example, the absorption maxima of other permethylated polysilanes may be deduced: $Me(Me_2Si)_nMe$ (n, λ_{max} (mμ)) 7, 267.4; 9, 275.8; 11, 280.9; 12, 282.9; ∞, 294.

The energy of this transition also corresponds to the activation energy of electron transport along a one-dimensional chain of silicon atoms and may be used to predict the semiconductor properties of such molecules.

It is reasonable to anticipate that the simple HMO treatment may be extended to catenates of other elements which possess empty (or partially filled) d orbitals of accessible energy. However, it should be mentioned that the ultraviolet absorption maxima of branched[4d] and cyclic[4c,10] polysilanes cannot readily be correlated by the above treatment.

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Volatile Silicon Complexes of Etioporphyrin I[1]

Sir:

The presence of several homologous series of porphyrins has been demonstrated in some oil shale rocks, shale oils, and petroleums.[2] However, the application of microanalytical techniques (*i.e.*, mass spectrometry and gas chromatography[3]) to structure determination of individual porphyrin components has been limited due to their low volatility.

We wish to report the synthesis of several novel Si^{IV}–etioporphyrin I derivatives and the effects that their various additional silicon ligands have on porphyrin volatility as measured by gas chromatography at normal pressure.

The treatment of etioporphyrin I (50 mg) with silicon tetrachloride or hexachlorodisiloxane (0.5 ml)[4] and anhydrous pyridine (3.0 ml) in a sealed glass tube at 185° for 6 hr, followed by the hydrolysis of the residue in dilute (1 N) aqueous, ethanolic hydrochloric acid (10 ml), gave, after purification on alumina ($CHCl_3$ solvent), a 60% yield of product A. The absorption spectrum was metalloporphyrin-like with a Soret band at $\lambda_{max}^{CHCl_3}$ 405 mμ (ε 314,000) and two longer wavelength bands at $\lambda_{max}^{CHCl_3}$ 535 (ε 11,700) and 572 mμ (ε 13,800). The mass spectrum of A showed a strong molecular ion at m/e 538, followed by a more intense peak at m/e 521 corresponding to the loss of an OH ligand. Thus the structure dihydroxy-$Si^{(IV)}$-etioporphyrin I was indicated.

Silylation of A with bis(trimethylsilyl)acetamide (BSA) in pyridine gave a product B, subliming at 145° (0.05 mm).[5] Mass spectral analysis of the sublimate showed predominant ions at m/e 682 and 593. The fragment m/e 593 was the most intense peak, corresponding to loss of one ligand of 89 mass units ($OSi(CH_3)_3$). Thus B was assigned the structure bis(trimethylsiloxy)-$Si^{(IV)}$-etioporphyrin I.

(1) Work supported, in part, by the National Aeronautics and Space Administration (Grant NsG 101-61) and, in part, by the U. S. Atomic Energy Commission.

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