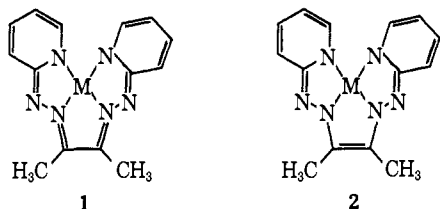


**Utility of the Electron-Transfer Series Concept.  
Deprotonated Complexes of  
Butane-2,3-dione Bis(2'-pyridylhydrazone)**

Sir:

It is well established that the title compound (BDPH) can function as a quadridentate ligand with respect to divalent metal ions, producing classical, cationic metal-(II) complexes  $[M(BDPH)]^{+2}$ ,  $M = Ni(II), Pd(II), Cu(II)$ .<sup>1,2</sup> Of considerably more interest are the deprotonation reactions<sup>2,3</sup> of these complexes which yield the intensely colored, neutral quadridentates  $[M(BDPH-2H)]^0$ , which have been formulated by Chiswell and Lions<sup>2</sup> as 1 ( $M = Ni, Pd, Cu$ ). An alternative formulation with concomitant change in the formal metal and ligand oxidation states is 2. This situation is strikingly similar<sup>4</sup> to that found with bis chelate complexes derived from ligands having an *o*-phenylene ( $[M(o-C_6H_4-NH)_2]^0$ ,<sup>5</sup>  $[M(o-C_6H_4(NH)S)_2]^0$ ,<sup>6</sup>  $[M(tdt)_2]^0$ ,<sup>7</sup>  $[M(o-C_6H_4OS)_2]^0$ <sup>8</sup>) or a *cis*-1,2-disubstituted ethylene ( $[MS_4-C_4R_4]^0$ <sup>9</sup>) structure. These complexes, as well as numer-



ous monoanions derived therefrom,<sup>5-9</sup> defy a unique description in terms of formal oxidation states of the metal and ligand<sup>10</sup> and for this reason may be considered nonclassical complexes. However, it has been demonstrated that such neutral species can be meaningfully systematized by the recognition that they represent an intermediate stage of oxidation or reduction in a series of complexes which can in principle include five members of differing total charge  $z$  ( $0, \pm 1, \pm 2$ ).<sup>5,6,8</sup>

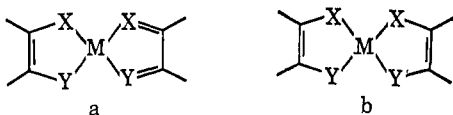
Here we present evidence<sup>11</sup> that  $[M(BDPH-2H)]^0$  ( $M = Ni, Pd$ ) is the central member of a highly probable

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(2) B. Chiswell and F. Lions, *Inorg. Chem.*, **3**, 490 (1964).

(3) Smooth deprotonation of the complex salts by stoichiometric treatment with sodium methoxide in methanol has proven to be a generally more useful method than the several published.<sup>2</sup>

(4) Formulations of the bis chelate complexes which are analogous to 1 and 2 are a and b, respectively.



(5) A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 5201 (1966).

(6) R. H. Holm, A. L. Balch, A. Davison, A. H. Maki, and T. E. Berry, *ibid.*, **89**, 2866 (1967).

(7) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965).

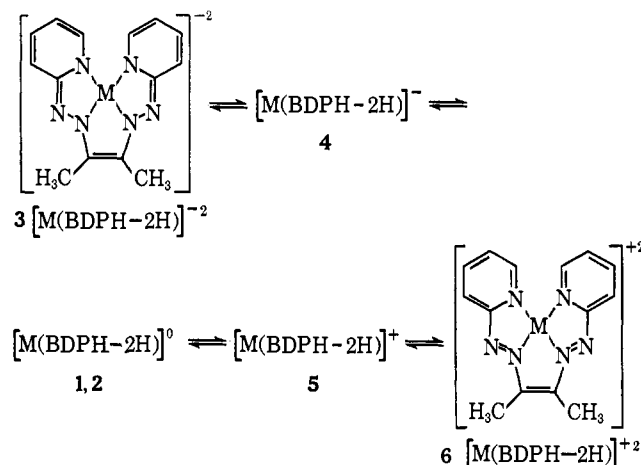
(8) A. L. Balch, F. Röhrscheid, and R. H. Holm, *ibid.*, **87**, 2301 (1965).

(9) (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963); **3**, 814 (1964); (b) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483, 3585 (1965).

(10) For the most recent discussion of this point cf. ref 6 and F. Lalor, M. F. Hawthorne, A. H. Maki, K. Darlington, A. Davison, H. B. Gray, Z. Dori, and E. I. Stiefel, *ibid.*, **89**, 2278 (1967).

(11) Electron resonance measurements were made on a Varian V-4502 spectrometer;  $g$  values were measured using the dual cavity method (cf. F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966)). Polarographic data were obtained using a three-electrode instrument, 0.05 M  $[(n-C_4H_9)_4N](BF_4)$  supporting electrolyte, rotating platinum electrode, and an sce reference electrode. Cyclic voltammetry was carried out using a hanging mercury drop or platinum microsphere electrode.

(Ni) or demonstrated (Pd) five-membered electron-transfer series 3-6 whose stable limits are defined by the terminal oxidized and reduced forms of (BDPH-2H) in combination with a stable valence state of the metal. In DMF  $[Pd(BDPH-2H)]^0$  shows two one-electron polarographic oxidations and reductions, shown to be



reversible by cyclic voltammetry, at the following half-wave potentials:  $0 \rightleftharpoons -1, -1.35$  v;  $-1 \rightleftharpoons -2, -2.0$  v;  $0 \rightleftharpoons +1, +0.33$  v;  $+1 \rightleftharpoons +2, +0.83$  v. Similar behavior is observed in acetonitrile but with a small negative shift of potentials such that the terminal reduction is obscured by breakdown of the medium. In acetonitrile  $[Ni(BDPH-2H)]^0$  exhibits two oxidations ( $+0.18, +0.58$  v) and the first reduction ( $-1.35$  v); the  $-1 \rightleftharpoons -2$  reduction is presumably masked by medium breakdown. An essential feature of the proposed electron-transfer series is the detection of the odd-electron species 4 and 5. The four radicals in question have been generated by several independent methods and the results are summarized in Table I. Chemi-

**Table I.**  $g$  Values of  $[M(BDPH-2H)]^{z-}$  Species

Species	Solvent	Method <sup>a</sup>	$\langle g \rangle^b$
$[Ni(BDPH-2H)]^+$	$CH_3CN$	cpe	2.013
	$CHCl_3$ -DMF <sup>c</sup>	cpe	2.014
	$CH_2Cl_2$	$[NiS_4C_4(CF_3)_4]$	2.012
$[Pd(BDPH-2H)]^+$	$CH_3CN, DMF$	cpe	2.011
	$CHCl_3$ -DMF	cpe	2.010
	$CH_2Cl_2$	$[NiS_4C_4(CF_3)_4]$	2.010
$[Ni(BDPH-2H)]^-$	$CHCl_3$ -DMF <sup>c</sup>	cpe	2.004
	DMF	Li-HMPA	2.004
$[Pd(BDPH-2H)]^-$	DMF	cpe	1.998
	DMF	Li-HMPA	1.998 <sup>d</sup>

<sup>a</sup> cpe, controlled potential electrolysis; Li-HMPA, stoichiometric amount of lithium dissolved in sufficient pure hexamethylphosphoramide to give a solution of 0.05 M in solvated electrons. <sup>b</sup> Solution  $g$  value,  $\pm 0.001$  unless otherwise indicated. <sup>c</sup> 1:3 v/v. <sup>d</sup>  $\pm 0.003$ .

cal generation of the monocations was effected by the use of the potent one-electron oxidizing agent  $[NiS_4C_4(CF_3)_4]^{9a}$  in the reaction  $[NiS_4C_4(CF_3)_4]^0 + [M(BDPH-2H)]^0 \rightarrow [NiS_4C_4(CF_3)_4]^- + [M(BDPH-2H)]^+$  in dry dichloromethane. Formation of the nickel monoanion was confirmed by the presence of its characteristic signal<sup>9a</sup> at  $\langle g \rangle = 2.061$ . The recent observa-

tion<sup>12,18</sup> that hexamethylphosphoramide (HMPA) dissolves alkali metals to produce solutions of solvated electrons (observed  $\langle g \rangle = 2.0022$  in pure HMPA<sup>12</sup>) has provided a facile method for generating mono-anions *via* the reaction  $[M(\text{BDPH}-2\text{H})]^0 + e^- (\text{solvated}) \rightarrow [M(\text{BDPH}-2\text{H})]^-$  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.<sup>6</sup>

It is concluded that  $[M(\text{BDPH}-2\text{H})]^0$  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  $[\text{Pd}(\text{BDPH}-2\text{H})]^0$  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<sup>5</sup> for complexes of a given metal having an  $\text{N}_4$  coordination sphere with those for complexes with  $\text{S}_4$ ,  $\text{S}_2\text{N}_2$ , and  $\text{O}_2\text{S}_2$  donor atom sets underscores the considerable increase in relative redox stability of cationic  $[M-\text{N}_4]$  complexes. For this reason complete electron-transfer series of the  $[M-\text{N}_4]^z$  type can be realized,<sup>5</sup> whereas the series for  $[M-\text{S}_4]^z$ ,  $[M-\text{S}_2\text{N}_2]^z$ , and  $[M-\text{O}_2\text{S}_2]^z$  systems is usually restricted to the  $z = 0, -1, -2$  members.<sup>6-9,14</sup>

**Acknowledgment.** This work was supported by the National Science Foundation under Grant GP-4899.

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## A Simple Hückel Molecular Orbital Treatment of the Ultraviolet Absorption Spectra of Polysilanes<sup>1</sup>

Sir:

The systematic investigation of homologous series of linear, branched, and cyclic organopolysilanes has recently been undertaken,<sup>2</sup> 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<sup>3</sup> and is capable of absorbing in the ultra-

(1) This work was supported in part by the Electronic Technology Division of the Air Force Avionics Laboratory, Wright Patterson Air Force Base, Ohio, under Contract No. AF-33(615)-67-C-1175.

(2) For a recent review, see H. Gilman, W. H. Atwell, and F. K. Cartledge, *Advan. Organometal. Chem.*, **4**, 1 (1966).

violet.<sup>4,5</sup> 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  $\text{Me}-(\text{Me}_2\text{Si})_n\text{Me}$ , 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  $-\text{Si}(\text{CH}_3)_2-$  groups. For a chain of  $n$  atoms, the  $n$  molecular orbitals will have energies which are given by eq 1.<sup>6</sup> The ultraviolet ab-

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

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

sorption is presumed to involve a transition between a  $\sigma$ -bonding orbital and the unoccupied molecular orbitals, the lowest energy of which is given by eq 1,  $j = 1$ . If  $E_\sigma$  is constant for a given homologous series, then the frequency ( $\nu_n$ ) of the transition is given by eq 2. For this equation to be valid, a plot of  $\nu_n$  against  $2 \cos(\pi/(n+1))$  should be a straight line with a slope of  $\beta_{\text{SiSi}}$ . Such a plot using literature values<sup>4c,e</sup>

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

of  $\nu_n$  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<sup>7</sup> that adjacent orbitals in chains of metals and metalloids will overlap to form delocalized molecular orbitals. The value of  $\beta_{\text{SiSi}}$  derived from this plot is 2.79 eV, and the minimum energy difference between the  $\sigma$ -bonding orbitals and the excited state is 4.21 eV (obtained from the intercept as  $n \rightarrow \infty$ ).

The absorption spectra of  $\alpha,\omega$ -diphenyl-<sup>4f</sup> and vinyl-substituted<sup>5a</sup> polysilanes have been treated in an analogous manner.<sup>8,9</sup> The data can best be accommodated using a mixture of the silicon orbitals and an unoccupied orbital ( $\pi^*$ ) 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  $-\text{Me}_2\text{Si}-$  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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(8) The ultraviolet absorption spectra of two vinyl-substituted polysilanes have been satisfactorily treated by the free electron method: D. R. Armstrong and P. G. Perkins, *Theoret. Chim. Acta*, **5**, 69 (1966).

(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. Shiryayev, *Peor. i Experm.-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  $\pi$  symmetry.