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ELECTRON DELOCALIZATION IN 9-OXIDOPHENALENONE COMPLEXES OF BORON AND BERYLLIUM

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Abstract—The preparation and characterization of a series of 9-oxidophenalenone (9-opo) complexes of beryllium and boron is reported. The structure of (9-opo)$_2$Be has been established by X-ray crystallographic analysis. The complexes have been studied with electrochemical techniques and electron spin resonance spectroscopy and evidence is presented for an unusual mode of electron delocalization (spiroconjugation) in the reduced species obtained from the bis(9-opo) complexes.

Although long neglected, the chemistry of beryllium and particularly boron complexes has experienced a resurgence in recent years under the new heading of organononmetallic chemistry.[1-9] Nevertheless there has not been a great deal done to physically characterize these compounds and structural, electrochemical and spectral data are lacking.

In this paper we report the preparation and characterization of a series of 9-oxidophenalenone (9-opo) complexes of beryllium (**1**) and boron (**2**–**5**). The structure of the former compound has been established by X-ray crystallographic analysis. The complexes have been studied with electrochemical techniques and electron spin resonance (ESR) spectroscopy and evidence is presented for an unusual mode of electron delocalization in the reduced species obtained from the bis(9-opo) complexes.

There have been a number of previous reports[10-17] on complexes involving the phenalenyl unit (most of which involve coordination to a transition metal) and compounds **1**[12] and **4**[10] have been briefly mentioned in the literature, but again physical characterization is lacking.

RESULTS

Preparation and chemical properties of complexes

The complexes were prepared by interaction of 9-hydroxyphenalenone (**7**)[18] with beryllium chloride (**1**) or the appropriate boron halide (**2**–**4**). In some cases the crude yield was improved by the presence of a tertiary amine but the mixture became very dark during the course of the reaction and the quality of the products was considerably degraded.

All of the complexes proved to be crystalline, high-melting compounds. The dimethylboron derivative (**5**) was reasonably soluble in a variety of solvents, but was found to be extremely moisture sensitive although it could be stored indefinitely in an argon atmosphere. The other complexes ranged from difficultly soluble ($\mathbf{2}^+$, X^-, **3**, **4**) to very insoluble (**1**) and required extremely polar solvents in order to achieve any dissolution whatsoever. The investigation of the solution chemistry was hampered by these solubility problems which probably result from the charge separation inherent in these structures. This latter point follows from the low-field chemical shifts found for the aromatic protons in complexes **1**–**4**.

In contrast to **1**, $\mathbf{2}^+$, X^- and **4** which gave rise to yellow or orange crystals, **5** was obtained as bright red needles and **3** crystallized as black plates. Unfortunately the sensitivity of these latter compounds to hydrolysis has precluded solution electronic spectroscopy. It is tempting to suggest that the long wavelength transition in these compounds originates from an intramolecular charge transfer transition to the 9-oxidophenalenone unit from the other part of the molecule as the electrochemistry (*vide infra*) shows that the coordinated 9-opo system is a good electron acceptor. The appearance of the catecholate compound **3** (black plates) contrasts with the color (yellow needles) observed for an analogous tropolone derivative (3-methyltropolonato)B(catecholate).[5]

Electrochemistry of (9-opo)$_2$B$^+$($\mathbf{2}^+$), PF$_6^-$

Cyclic voltammetry of $\mathbf{2}^+$, PF$_6^-$ showed the presence of two reduction waves at −0.27 and −0.56 V. Coulometry indicated that about 1 F mol^{-1} is consumed in each reduction step. ESR spectroscopy showed the appearance of **2** at potentials below about −0.3 V. Chemical reductions employing zinc, magnesium, tin chloride or mercury/tetrabutylammonium bromide produced the same radical. The Hg/Bu$_4$N$^+$Br$^-$ reductant is especially useful because its potential is insufficient to generate a secondary radical and optimum concentrations of **2** are easily achieved. This reductant coupled with the exceptional stability of the radical enabled us to detect the major spectral components of the outermost 3H multiplet, but not the weakest lines.

Prolonged (2 h) reduction with Hg/Bu$_4$N$^+$Br$^-$ resulted in a diamagnetic solution. During the course of the reduction the intensity of the ESR spectrum rose to a maximum and fell to zero; addition of $\mathbf{2}^+$, PF$_6^-$ at this point revived the ESR of **2**.

Electron spin resonance spectroscopy of (9-opo)$_2$B(**2**)

Figure 1 illustrates the central portion of the ESR spectrum of **2** as a function of temperature. These spectra saturate in a normal fashion with increasing microwave power, no additional resonances were apparent at maximum power, and no half-field resonances were detected. The room temperature spectra were unchanged in the presence of lithium or potassium ions.

The room temperature spectrum is nearly (but

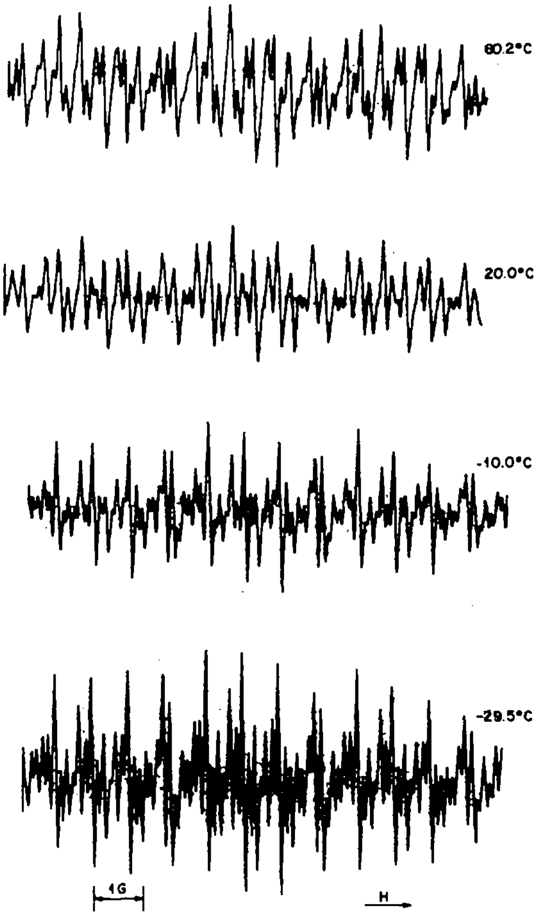
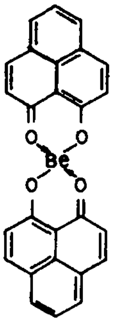


Fig. 1. Electron spin resonance spectra of 2 in DMF as a function of temperature.

incompletely), computer simulated employing splittings of (for example) 8H = 2.984, 6H = 0.711, $1\,^{11}$B (I = 3/2, 80%) = 0.426, $1\,^{10}$B (I = 3, 20%) = 0.143, two sets of 12 equivalent ^{13}C (I = 1/2, 1.1%) = 3.990 and 4.554, and linewidths of 70 mG. Incompleteness stems from the fact that the size of the ^{13}C splittings are unproven. Their selection is based on previous MO calculations[19] and on those splittings (of 10 possibilities) most complementary to the simulation. Note that one of the ^{13}C splittings implies an accidental degeneracy (not ruled out by the MO calculations nor by the known ^{13}C splittings of phenalenyl[19]) of $6\,^{13}$C and $6\,^{13}$C. In spite of all these nuclei and the many simulation subtleties, the selected splittings render a few of the weaker lines either 10–20% too weak or 10–20% too strong. This can perhaps be attributed to either faulty selection of ^{13}C splittings and/or to the frequently observed linewidth variations in ^{13}C resonances.[20] Although their presence is apparent, computer simulation shows that lines from ^{10}B are not resolved until linewidths are reduced to 60 mG (and then only barely). The temperature dependence probably results from the increase in the boron splitting of about 100 mG as the temperature is lowered.

Electron spin resonance spectroscopy of species obtained by further reduction of 2

Electrolysis at potentials more negative than about −1.2 V generates either of two radicals depending most probably on solvent basicity. These are the 9-oxidophenalenone dianion radical (8^{2-}) and the corresponding protonated (9-hydroxyphenalenone, 7) anion radical. We have confirmed the identities of these two radicals by the reduction of 9-hydroxyphenalenone in DMSO and acetonitrile, respectively. To further clarify the results, additional mono(9-opo) boron complexes were reduced and their ESR spectra



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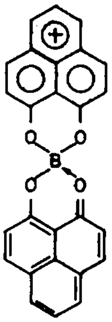

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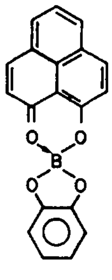

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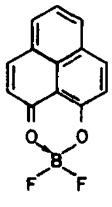

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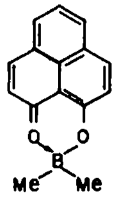

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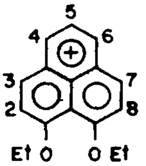

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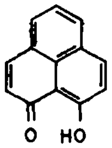

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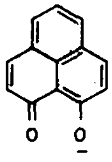

8⁻

obtained; the ESR parameters for these radicals are summarized in Table 1.

The identification of a radical we initially assigned to $\mathbf{2}^{2-}$ remains elusive. Primarily this is a consequence of the inconclusive electrochemistry at potentials below −0.6 V. *In situ* electrochemical generation appears straightforward, but the pervasive stability of **2** makes identification impossible except following extended (days) electrolysis. In comparison, Zn reduction proceeded through **2**, diamagnetic $\mathbf{2}^-$ (presumably), and to $\mathbf{2}^{2-}$ in a few hours. ESR parameters for $\mathbf{2}^{2-}$ (?) are 2H = 5.929, 2H = 5.697, 1H = 1.638, 2H = 1.168, $1\,^{11}B = 0.471$, and $1\,^{10}B = 0.158$ G at $g = 2.00279$. Note that only one phenalenyl moiety is evident, and that the splittings (except for the boron which is nearly unchanged) are approximately twice as large as those of **2**. Some of the ^{11}B lines are resolved and the ratio of the intensities of the $^{10}B : {}^{11}B$ spectra are close to the theoretical value of 1 : 0.133. No ^{13}C splittings are apparent and the computed simulation is excellent.

Electrochemistry of $(9\text{-opo})_2Be$ (**1**)

Cyclic voltammetry of **1** was complicated by solubility problems, although it was apparent that there were two reductions at about the same potentials (−0.3, −0.6 V) as those found for $\mathbf{2}^+, PF_6^-$. Chemical reduction with metals ($Hg/Bu_4N^+Br^-$) gave a green coloration near the metal surface which diffused into the body of the solution but did not persist, and *in situ* Zn reduction yielded no ESR. Chemical reaction of **1** with a trace of tetrabutylammonium hydroxide (25% in MeOH) occasionally gave useful albeit transient ESR spectra of $\mathbf{1}^-$. The sole reliable technique proved to be electrochemical reduction over mercury in DMSO, DMF, PC or HMPA in the cavity of the ESR spectrometer.

Table 1. Electron spin resonance data

Species reduced	Solvent g-value	Hyperfine splitting constants	
		Nucleus	G
1	PC/HMPA	4H	(2.860)
	(2 : 1)	4H	(2.561)
	2.00284	4H	(0.095)
		2H	(0.823)
		1Be	0.199
$\mathbf{2}^+, PF_6^-$	DMSO	8H	2.984
	2.00262	6H	0.711
		$1B^{11}$	0.426
		$1B^{10}$	0.143
		$12C^{13}$	(4.554)
		$12C^{13}$	(3.990)
3	DMSO	2H	5.910
		2H	5.705
		2H	1.167
		1H	1.667
		$1B^{11}$	0.500
4	CH_3CN	2H	5.827
	2.00280	2H	5.627
		2H	1.152
		1H	1.625
		$1B^{11}$	0.487
		2F	0.938
$\mathbf{6}^+, BF_4^-$	CH_3CN/CH_2Cl_2	4H	0.65
		2H	6.16
	2.0026	2H	6.00
		2H	1.53
		1H	1.76
7	CH_3CN	2H	5.903
		2H	5.162
		2H	0.505
		1H	1.620
		1H	0.921
8	DMSO	2H	5.795
	2.00285	2H	5.186
		2H	0.647
		1H	1.596

Electron spin resonance spectroscopy of $(9\text{-opo})_2Be^-$ ($\mathbf{1}^-$)

We were unable to uniquely determine the hyperfine splittings. The most we could glean from the spectra with certainty is that: (i) the sum of the two largest splittings (4H and 4H) is 5.4 G, and that they differ by 0.1–0.5 G, (ii) the g-value is 2.00284 (DMF), and (iii) the Be atom splitting is ~0.2 G. Representative values of the hyperfine splittings of $\mathbf{1}^-$ are given in Table 1. In DMF, peak-to-peak linewidths are 35 mG, whereas in HMPA with peak-to-peak linewidths of 100 mG, alternating linewidth effects are apparent. In the major nine groupings the central group is sharp while alternate group intensities are drastically depressed.

Electron spin resonance of species obtained by further reduction of $\mathbf{1}^-$

As with $\mathbf{2}^+, PF_6^-$, reduction of **1** at potentials more negative than about −1.2 V gave rise to the spectrum of one of the 9-opo derived radicals.

During chemical reductions with tetrabutylammonium hydroxide, an ESR spectrum with a beryllium atom splitting was observed. The spectrum obtained in PC/HMPA (2:1) yielded: 2H = 5.797, 2H = 4.884, 1H = 1.594, 2H = 0.244, 1Be = 0.244 and a g-value of 2.00315. Initially we had hoped this would prove to be $\mathbf{1}^{3-}$, but supporting evidence has been unattainable.

DISCUSSION

X-ray crystal structure of $(9\text{-opo})_2Be$(**1**)

The crystallographic findings are summarized in Figs 2 and 3 and Tables 2 and 3. The bond lengths are compared with those of 9-hydroxyphenalenone[21] (**7**) in Fig. 4. The beryllium atom lies on a C_2 axis so that the two 9-oxidophenalenone units are related by symmetry; the bond lengths of both molecules shown in Fig. 4 were obtained by averaging over C_{2v} symmetry. Although **7** is found to be of (effective) C_{2v} symmetry in the crystallographic experiment, the molecule has been shown to be localized (as is the case with 9-butoxyphenalenone[22]), and the hydrogen in **7** is known to move in a symmetric double-well potential.[23–28] Clearly the bond lengths found for **1** are very similar to those observed for the averaged structure of 9-hydroxyphenalenone[21] (**7**).

The only previous crystal structure determination of a bis-β-ketoenolate complex of beryllium was contained in a low precision study[29] of bis (acetylacetonato)beryllium (**9**) published 25 years ago and although there have been many publications on

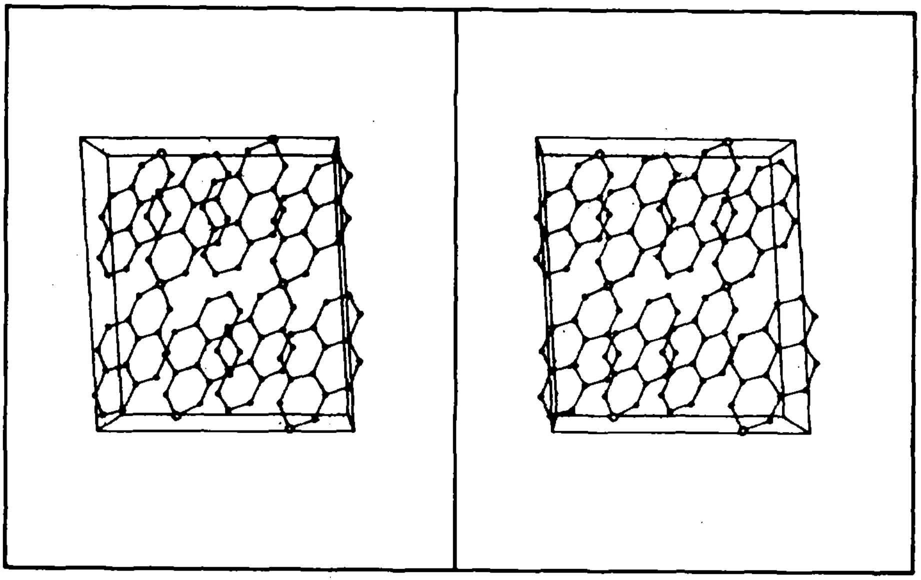

Fig. 2. Stereoview of the $(9\text{-opo})_2Be(1)$ unit cell as viewed down the *y*-axis

the crystal and molecular structure of other β-keto-enolate complexes,[30] very few have been concerned with condensed ring systems and none have involved the 9-oxidophenalenone unit.

The bond lengths found for **1** and **9**[29] within the 6-membered chelate rings exhibit significant differences: Be—O, 1.615, 1.70 Å; C—O, 1.288, 1.24; C—C, 1.428, 1.33 (respectively). The coordination around the beryllium atom is pseudo-tetrahedral in both cases with internal O—Be—O angles of 107° (**1**) and 104° (**9**).[29] The two (9-opo)Be halves of the molecule (**1**) are very close to planarity with atomic deviations of less than 0.1 Å from the best molecular planes which in turn are near perpendicular (88.2°) to one another. Nevertheless the molecule is slightly bent at the oxygen atoms—the Be, O_1, O_2 plane makes an angle of 5.2° with respect to the 9-opo best molecular plane.

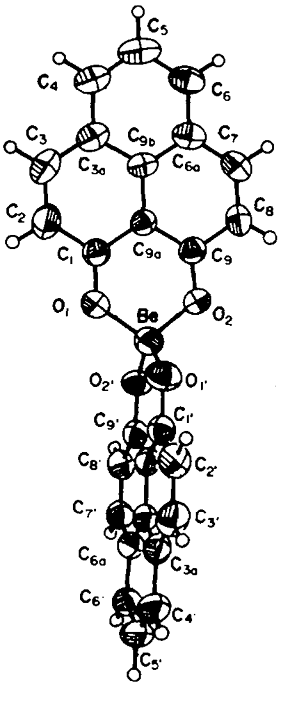

Fig. 3. Perspective ORTEP diagram of $(9\text{-opo})_2Be(1)$ with non-hydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atom spheres are of arbitrary dimensions. Primed (′) atoms are related to non-primed atoms by the crystallographic C_2 axis at 0, *y*, 1/4.

The structure found for **1** contrasts strongly with the localized geometry observed in 9-butoxy-

Table 2. Bond lengths involving non-hydrogen atoms in crystalline $(9\text{-opo})_2Be(1)$[a]

Type[b]	Length (Å)
$Be—O_1$	1.621(2)
$Be—O_2$	1.610(2)
$O_1—C_1$	1.287(2)
$O_2—C_9$	1.290(2)
$C_1—C_2$	1.427(3)
$C_1—C_{9a}$	1.421(2)
$C_2—C_3$	1.345(3)
$C_3—C_{3a}$	1.422(3)
$C_{3a}—C_{9b}$	1.422(2)
$C_{3a}—C_4$	1.397(2)
$C_4—C_5$	1.375(3)
$C_5—C_6$	1.384(3)
$C_6—C_{6a}$	1.400(2)
$C_{6a}—C_{9b}$	1.408(2)
$C_{6a}—C_7$	1.423(2)
$C_7—C_8$	1.349(2)
$C_8—C_9$	1.430(2)
$C_9—C_{9a}$	1.426(2)
$C_{9a}—C_{9b}$	1.424(2)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] Atoms are labeled in agreement with Fig. 3.

Table 3. Bond angles involving non-hydrogen atoms in crystalline (9-opo)$_2$Be (1)[a]

Type[b]	Angle (deg.)
O_1BeO_2	107.0(1)
$O_1BeO_{1'}$[c]	110.2(2)
$O_2BeO_{1'}$[c]	110.4(1)
$O_2BeO_{2'}$[c]	112.0(2)
BeO_1C_1	123.7(1)
BeO_2C_9	123.6(1)
$O_1C_1C_2$	118.9(2)
$O_1C_1C_9$	122.5(2)
$O_2C_9C_8$	119.0(1)
$O_2C_9C_{9a}$	122.5(1)
$C_1C_2C_3$	121 4(2)
$C_1C_{9a}C_9$	120.5(1)
$C_1C_{9a}C_{9b}$	119.9(1)
$C_2C_1C_9$	118.6(1)
$C_2C_3C_{3a}$	121.8(2)
$C_3C_{3a}C_4$	122.5(2)
$C_3C_{3a}C_{9b}$	118.6(2)
$C_{3a}C_4C_5$	121.2(2)
$C_{3a}C_{9b}C_{6a}$	119.7(1)
$C_{3a}C_{9b}C_{9a}$	119.7(1)
$C_4C_{3a}C_{9b}$	118.9(2)
$C_4C_5C_6$	120.0(2)
$C_5C_6C_{6a}$	121.1(2)
$C_6C_{6a}C_7$	122.9(2)
$C_6C_{6a}C_{9b}$	119.0(2)
$C_{6a}C_7C_8$	122.5(2)
$C_{6a}C_{9b}C_{9a}$	120.6(1)
$C_7C_{6a}C_{9b}$	118.0(1)
$C_7C_8C_9$	120.8(2)
$C_8C_9C_{9a}$	118.4(1)
$C_9C_{9a}C_{9b}$	119.6(1)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] Atoms are labeled in agreement with Fig. 3.

[c] Primed (′) atoms are related to non-primed atoms by the crystallographic C_2 axis at 0, y, $\frac{1}{4}$.

phenalenone[21] and it seems clear that the phenalenyl units in 1 are highly delocalized in support of the polar, charge-separated structure depicted in Fig. 5.

Electrochemistry and electron spin resonance spectroscopy

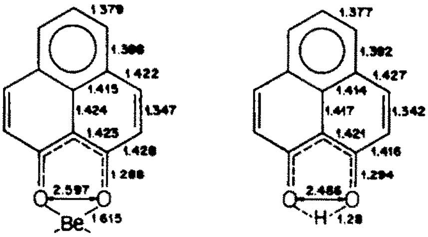

Fig. 4. Comparison of the crystallographically determined bond lengths of (9-opo)$_2$Be(1) and 9-hydroxyphenalenone (7).[21]

Although the electrochemical and spectroscopic studies do not allow a complete picture of the reductive chemistry of 1 and 2^+ a number of conclusions emerge. The first reduction product of 1 and 2^+ is formed at potentials more negative than about −0.3 V. This species is paramagnetic and the spin density is delocalized over both of the 9-opo units (at least on the ESR time scale). This latter conclusion follows from the magnitude of the hyperfine splitting constants which are about half of those found for the products obtained by reduction of the mono(9-opo) complexes 3, 4 and 6^+, BF_4^- (Table 1) where the electron is presumably confined to a single 9-oxidophenalenone unit.

The first reduction potential of 6^+, BF_4^- occurs at −0.29 V (contrary to the literature value[31] which is apparently referenced to the SHE) in acetonitrile (SCE), very close to the value found for the bis(9-opo) complexes 1 and 2^+, PF_6^-. It seems apparent that the polar nature of these compounds (cf. Fig. 5), originally suggested by the solubility data, ^{1}H-NMR spectra and the molecular structure of 1, is also supported by their ease of reduction.

The second reduction of 1 and 2^+ occurs at potentials about 0.3 V more negative than the first and gives rise to diamagnetic products. Beyond this point interpretation of the electrochemistry and ESR spectroscopy becomes more uncertain. It seems clear, however, that the two 9-opo units in 1 and 2^+ do not act independently insofar as their reductive chemistry is concerned. In the completely independent extreme, 1 and 2^+ would be expected to exhibit a single two-electron reduction to paramagnetic products with an unpaired spin localized on each of the 9-opo units as shown in Fig. 5. It is clear that this picture is inadequate, and that some mechanism is operative which electronically couples the two 9-opo units of 1 and 2^+ on reduction.

The hfs constants obtained for 4 (Table 1) suggest that there is some transmission of electron density via the orbitals of the central atoms, although this may

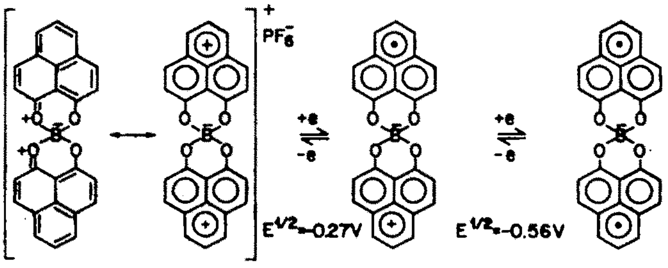

Fig. 5. Reduction chemistry of (9-opo)$_2$B$^+$ (2^+), PF_6^-.

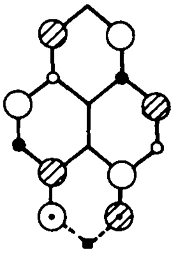

Fig. 6. The lowest unoccupied molecular orbital (LUMO) of the 9-oxidophenalenone (9-opo) unit.

occur via the hyperconjugative mechanism[32] in the case of the fluorine and thus would be expected to be ineffectual in the long range distribution of electron spin density. The observation that the spin density in **3** is confined to the 9-opo unit and does not leak into the catecholate moiety also supports this interpretation. Nevertheless in this latter case the electron affinities of the two bis-oxido units are very different and it is not possible to completely eliminate the through-bond coupling of the two 9-opo units in **1** and $\mathbf{2}^+$ as the mechanism for transmission of electron spin density.

An attractive rationalization for the delocalized nature of the first two reduction products of **1** and $\mathbf{2}^+$, PF_6^- is to invoke a spiroconjugative interaction[33,34] among the oxygen functionalities. The lowest unoccupied molecular orbital (LUMO) for 9-opo derives from the non-binding MO of the parent phenalenyl system.[35] The LUMO for 9-opo as calculated by Hückel MO theory is shown in Fig. 6 and it may be seen to possess the requisite antisymmetry with respect to the perpendicular mirror plane. The orientation and overlap of the pair of LUMOs (Figs 7 and 8) makes them ideal candidates for spiroconjugative delocalization of the unpaired spin density.[36–39]

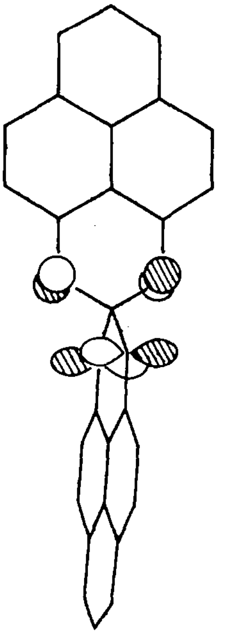

Fig. 7. Perspective view of the spiroconjugative overlap between the 9-opo LUMOs in **1** and $\mathbf{2}^+$ ([·] = Be, B).

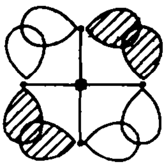

Fig. 8. Projection along the long axis of the spiroconjugative overlap at the oxygen atoms between the 9-opo LUMOs in **1** and $\mathbf{2}^+$ ([·] = Be, B).

As noted previously, it is not possible to provide a rigorous interpretation of the electrochemistry of **1** and $\mathbf{2}^+$ beyond their first two reduction products. Nevertheless evidence was adduced for an additional species in both cases on chemical reduction. If these do indeed correspond to triply reduced **1** and $\mathbf{2}^+$ it remains to explain why the unpaired spin density is localized on a single 9-opo unit (in contrast to the behavior of the first and second reduction products). One possibility is that the third electron reduces the energy gain of spiroconjugation to the point where localization occurs.

Most previous examples of spiroconjugation have involved overlap among carbon atoms which are linked to a spiro carbon atom,[33,34,36–40] but the present results suggest that, in the absence of other mechanisms of delocalization the phenomenon may be more widespread than previously realized—particularly in the case of coordination complexes.

There has not been a great deal of work reported on the ESR spectroscopy of boron complexes,[41] very little on beryllium compounds and none involving these elements in spiroconjugation. Nevertheless, while the variable temperature ESR spectroscopy of **2** (Fig. 1) is unusual, it is not without precedent.[42–44]

EXPERIMENTAL

$(9\text{-opo})_2Be$ (**1**). 9-Hydroxyphenalenone[18] (0.98 g, 0.005 mol) in THF (25 ml) was treated with beryllium chloride (0.16 g, 0.002 mol) and stirred overnight. The orange solid was separated by filtration (0.74 g, 40% yield). Recrystallization from propylene carbonate gave orange needles: m.p. >300°. (Found: C, 78.07; H, 3.67; Be, 2.11. Calc for $C_{26}H_{14}O_4Be$: C, 78.19; H, 3.53; Be, 2.25%.) IR (CsI) 3040 (vw), 1625 (s), 1573 (m), 1502 (m), 1425 (m), 1380 (vw), 1270 (s), 1237 (m, sh), 1183 (m), 1138 (s, sh), 989 (vs), 965 (w), 902 (vw), 840 (br), 755 (w), 711 (s), 689 (m), 638 (s), 570 (vw), 530 (m), 475 (m), 439 (w). UV [λ_{max} (propylene carbonate)] 243 nm (ε 53,800), 260 (sh, 19,900), 330 (sh, 11,300), 347 (20,900), 365 (52,200), 400 (6600), 415 (sh, 8400), 425 (13,900), 439 (11,500), 450 (20,900). ^{1}H-NMR (CD_3CN, Me_4Si) δ 7.10–8.65 (m).

$(9\text{-opo})_2B^+(\mathbf{2}^+)$, Cl^-. 9-Hydroxyphenalenone (2.94 g, 0.015 mol) in 1,2-dichloroethane (100 ml) was treated with boron trichloride (5 ml, 0.005 mol) at 0°. The mixture was then stirred and refluxed for about 30 min. The yellow solid was isolated by filtration (1.95 g, 89% yield), m.p. 230–232°.

$(9\text{-opo})_2B^+(\mathbf{2}^+)$, PF_6^-. Compound $\mathbf{2}^+$, Cl^- (1.09 g, 0.0025 mol) was dissolved in acetic acid and combined with a soln of sodium hexafluorophosphate (0.84 g, 0.005 mol) in acetic acid. The yellow ppt was separated by filtration (1.35 g, 99% yield). Recrystallization from acetonitrile/acetic acid gave chunky yellow crystals, m.p. 240°. IR (CsI) 3050 (br), 1620 (m), 1600 (m), 1565 (m), 1500 (m), 1470 (m), 1435 (m), 1420 (m), 1355 (m), 1340 (m), 1305 (s), 1240 (s), 1220 (m), 1189 (w), 1145 (m), 1125 (w), 1025 (br), 960 (w), 850 (br), 770 (vw), 745 (vw), 715 (vw), 698 (s), 590 (vw), 555 (vs), 498 (m), 470 (w), 425 (vw), 412 (vw). UV [λ_{max} (acetonitrile)] 235 nm (ε 56,200), 253 (12,900), 350 (sh, 13,700), 391 (81,100), 428 (sh, 1500), 441 (sh, 14,880), 455 (16,100). ^{1}H-NMR (CD_3CN, Me_4Si) δ 7.55–9.00 (m).

$(9\text{-opo})_2B^+(2^+)$, $FeCl_4^-$. Compound 2^+, Cl^- (4.11 g, 0.0094 mol) was dissolved in acetic acid (20 ml) and combined with a soln of ferric chloride (4.11 g, 0.025 mol) in acetic acid. The yellow–green solid was isolated by filtration. (Found: C, 51.95; H, 2.43; B, 1.92; Fe, 9.24; Cl, 23.55. Calc for $C_{26}H_{14}O_4BFeCl_4$: C, 52.15; H, 2.34; B, 1.80; Fe, 9.38; Cl, 23.68%.)

(9-opo)B(catecholate) (3). 9-Hydroxyphenalenone (1.55 g, 0.008 mol) was added to a soln of *o*-phenylene bromoboronate[45] (2 ml, 0.005 mol) in toluene and the mixture refluxed for about 15 h. A brown solid was obtained by filtration (2.13 g, 85%), m.p. > 300°. Recrystallization from propylene carbonate gave shiny black plates. (Found: C, 72.66; H, 3.38; B, 3.60. Calc for $C_{19}H_{11}O_4B$: C, 72.66; H, 3.53; B, 3.44%.) IR (CsI) 3025 (vw), 1625 (m), 1580 (m), 1475 (m), 1440 (w), 1420 (m), 1350 (m), 1230 (m), 1189 (w), 1145 (w), 1029 (br), 990 (vw), 952 (m), 910 (w), 845 (s), 825 (w), 810 (w), 785 (vw), 759 (vs), 750 (vs), 715 (w), 695 (m), 500 (m), 455 (w). ^{1}H-NMR (DMSO-d_6, Me_4Si) δ 7.00 (br d, 4H), 7.50–8.85 (m, 7H).

$(9\text{-opo})BF_2$(4). A soln of 9-hydroxyphenalenone (0.20 g, 0.001 mol) in 1,2-dichloroethane was treated with boron trifluoride etherate (12 ml, 0.001 mol) and stirred for 2 h. The yellow solid was isolated by filtration (yield 0.17 g, 61%), m.p. > 300°. (Found: C, 63.76; H, 2.97; F, 15.51. Calc for $C_{13}H_7O_2BF_2$: C, 63.99; H, 2.89; F, 15.57%.) IR (CsI) 3100 (w), 3070 (w), 2879 (vw), 2765 (vw), 2660 (vw), 1980 (br), 1630 (vs), 1580 (vs), 1505 (vs), 1485 (m), 1447 (s), 1428 (m), 1358 (vs), 1320 (vs), 1242 (vs), 1228 (m), 1195 (m), 1140 (br), 983 (m), 851 (vs), 830 (w), 825 (vw), 805 (w), 765 (s), 745 (s), 700 (s), 565 (w), 498 (m), 470 (w), 280 (w). UV [λ_{max} (acetonitrile)] 231 (ε 18,600), 253 (4700), 335 (sh, 5000), 369 (20,900), 396 (sh, 2900), 410 (sh, 3500), 421 (5000), 435 (sh, 5300), 446 (7100). ^{1}H-NMR (DMSO-d_6, Me_4Si) δ 7.60–9.10 (m).

$(9\text{-opo})BMe_2$(5). Dimethylboron bromide (0.605 g, 0.005 mol), was slowly added to an acetonitrile soln of tetrabutylammonium 9-oxidophenalenone[22] (17 ml, 0.005 mol) at −20° and the mixture allowed to warm to room temp overnight. The red solid was isolated by filtration (0.69 g, 58% yield). Recrystallization from cyclohexane gave bright red needles, m.p. 234–238°. The compound was stored under an inert atmosphere. (Found: C, 76.49; H, 5.51; B, 4.41. Calc for $C_{15}H_{13}O_2B$: C, 76.34; H, 5.50; B, 4.58%.) IR (CsI) 2930 (w), 1630 (w), 1580 (w), 1505 (w), 1480 (vw), 1440 (m), 1420 (m), 1350 (m), 1335 (w), 1290 (w), 1238 (m), 1182 (w), 1138 (vw), 1125 (vw), 1075 (vw), 1025 (br), 989 (vw), 975 (vw), 840 (s), 800 (s), 755 (m), 725 (vw), 690 (s), 640 (vw), 600 (vw), 580 (vw), 538 (m), 520 (m), 460 (w), 420 (vw). UV [λ_{max} (acetonitrile)] 235 nm (ε 27,800), 265 (7200), 335 (sh, 7400), 352 (16,600), 370 (15,800), 414 (6100), 437 (7400), 464 (3500). ^{1}H-NMR ($CDCl_3$, Me_4Si) 0.17 (s), 7.00–8.10 (m).

Electron spin resonance spectroscopy. The ESR apparatus consisted of a modified X-band Varian spectrometer employing 100 kHz field modulation.[46] Hyperfine splitting (hfs) constants are given in gauss (G).

Electrochemistry. Spectroquality dimethylsulfoxide (DMSO), dimethylformamide (DMF), hexamethylphosphoramide (HMPA) and propylene carbonate (PC) were dried over molecular sieves. Except where noted, DMSO was employed as solvent, and Pt gauze as working electrode. Potentials are referenced to the SCE. Either tetrabutylammonium tetrafluoroborate or tetrapropylammonium perchlorate were used as the supporting electrolyte. Lithium or potassium were introduced as the percholate which had been dried at 80° under vacuum.

X-ray crystallography. Performed by C. S. Day, Crystallytics Co., P.O. Box 82286, Lincoln, Nebraska 68501. Orange needles of $Be(O_2C_{13}H_7)_2$ suitable for X-ray crystallographic study were grown by slowly cooling a boiling propylene carbonate soln of 1. The crystal selected for examination had dimensions 0.12 × 0.18 × 0.95 mm (rectangular parallelipiped). Mol wt 399.4, monoclinic $C_{2/c}$, $a = 14.172(4)$ Å, $b = 10.953(4)$ Å, $c = 12.331(4)$ Å, $\beta = 93.40(2)°$, $V = 1911(1)$ Å^3, ρ(calc) = 1.39 g cm^{-3}, $Z = 4$. Scan technique: θ–2θ. Direct methods were employed to solve the structure. Number of independent data: 1147. Number of parameters refined: 142. Hydrogen atoms were inserted at calculated position. $R = 0.032$, $R_w = 0.042$.

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