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METALLAVIOLENES. AN ESR STUDY

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Summary

The preparation and ESR-spectroscopic characterization of radical complexes $[(R_nM)L(MR_n)]^{\dot{+}}$ with L = 4,4′-bipyridine is described, where MR_n = BePh, MgPh, ZnPh, $^-BEt_3$, $GaMe_2$, $InMe_2$ and $SiMe_3$. While the bis(trimethylsilyl) derivative could be obtained via one-electron oxidation of the corresponding 4,4′-(1H, 1′H)-bipyridinylidene, the other complexes were prepared by the reaction of 4,4′-bipyridine with potassium and the organometal MR_{n+1} or the halide XMR_n in THF. Use of organo-cadmium or -thallium compounds in such a procedure leads to deposition of the metals. The Grignard reagents $MgPh_2$ and BrMgPh reduce 4,4′-bipyridine in an electron transfer process to yield an unsymmetrical complex. The new organometallic 4,4′-bipyridinium ("violene") radical complexes can be incorporated into a series of related radicals which exhibits the sensitivity of the unpaired electron distribution towards metal coordination.

Introduction

4,4′-Bipyridine **1** and its *N,N′*-dialkylated derivatives **2** ("viologens") are well established among two step reversible redox systems [1]. The redox potentials of **1** and **2** lie in a convenient range for electrochemical measurements [1,2]; the intensely colored one-electron reduction intermediates, the "violenes" [1], are generally persistent, and in addition the system does not impose any steric restrictions on the groups coordinated to the nitrogen atoms. Accordingly, **1** and **2** [3] have found wide application as electron transfer mediators,

(i) between coordinated transition metals and their complexes [4,5],
(ii) between electrodes and biological substrates [6],
(iii) in membranes [7], micelles [8a], or vesicles [8b], and
(iv) on glass or semiconductor surfaces [9,10].

In those immobilized forms [7–10], the viologens **2** have been extensively used as electron carriers in photochemical systems for solar energy conversion [8–10].

Furthermore, the function of diquarternary salts **2** as herbicides ($R = CH_3$:

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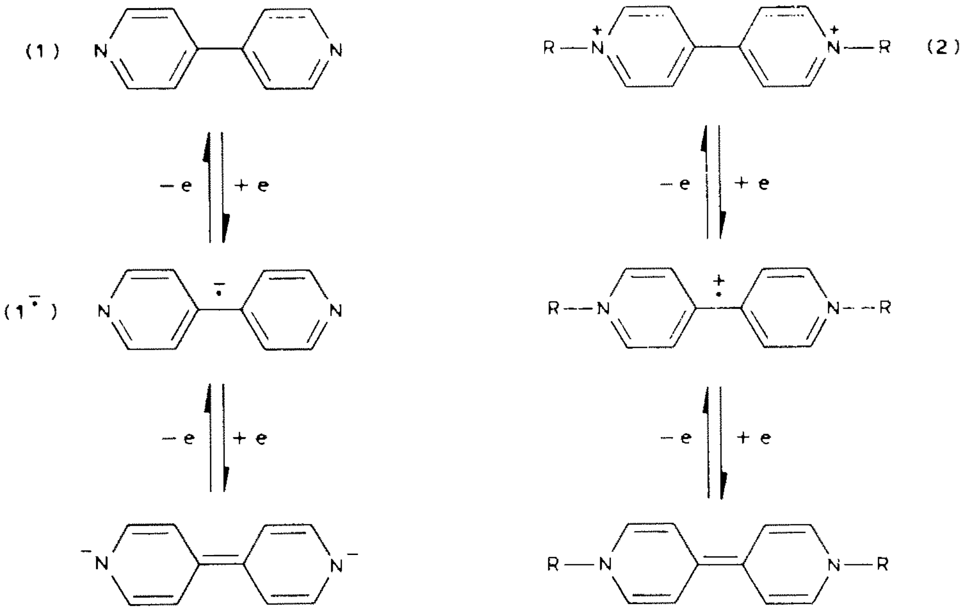
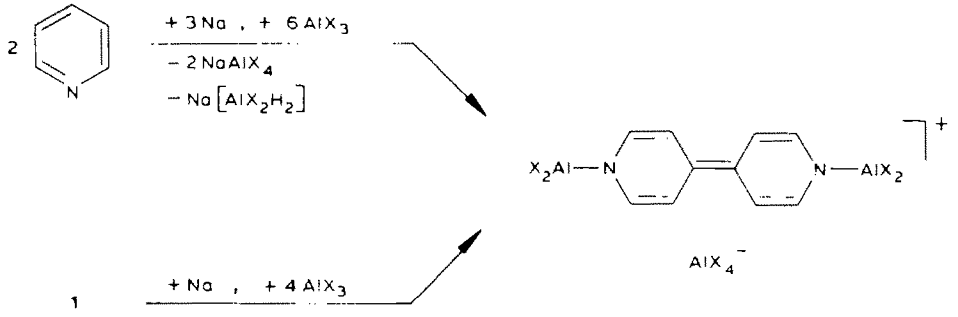


"paraquat") has also been connected with their specific photochemical and redox properties [11].

Unlike pyrazine radical anion [12], the singly reduced 4,4′-bipyridine, **1**·⁻, does not form tight ion pairs or triple ions with alkali metal cations. However, the reaction of pyridine or 4,4′-bipyridine with AlX_3 (X = Me, Et, Cl) and alkali metals was shown to yield aluminum containing 1/2 radical complexes of 4,4′-bipyridine [13].



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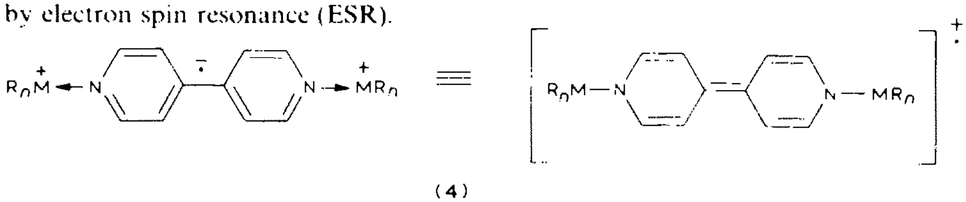
In this paper we describe more organometallic radical complexes ("metallaviolenes" **4**) of reduced **1**; these new complexes have been identified and characterized by electron spin resonance (ESR).



(4)

(MR_n = BePh, MgPh, ZnPh, BEt_2, $GaMe_2$, $InMe_2$, $SiMe_3$)

A comparison with related radicals illustrates the effect of the metal coordination on the spin distribution and may be contrasted with results obtained for corresponding 2,2′-bipyridine chelate complexes [14].

Results

Beryllium, zinc, boron, gallium, indium. Solutions of 4,4′-bipyridine and of the corresponding organometal compound ($BePh_2$, $ZnPh_2$, BEt_3 or BEt_2Cl, $GaMe_3$, $InMe_3$) in THF react with potassium to yield very persistent and intensely blue 1/2 radical complexes. Whereas the organoindium radical does not exhibit any resolved ESR hyperfine structure ($^{113,115}In$: 100%, $I = 9/2$) [15], the line rich ESR spectra of

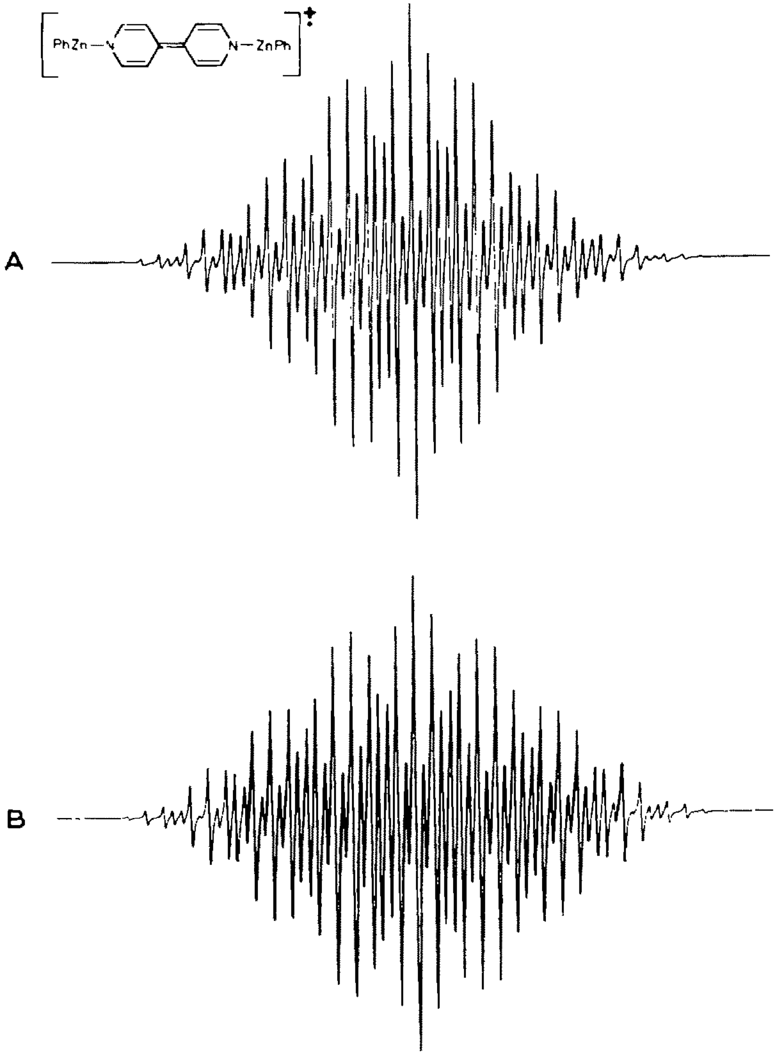


Fig. 1. (A) ESR spectrum of the radical complex **4**, MR_n = ZnPh, at 300 K in THF. (B) Computer simulation, line width 0.010 mT.

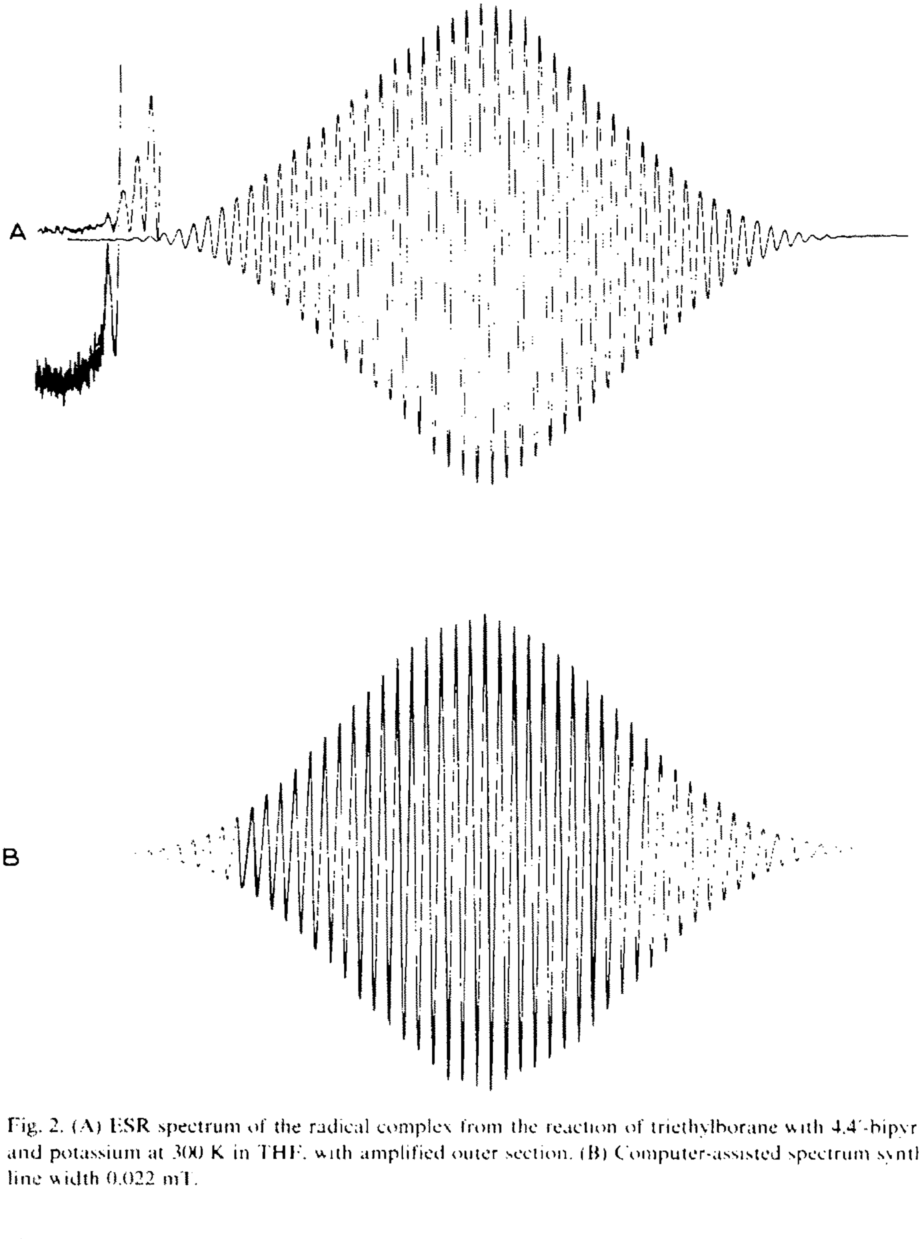


Fig. 2. (A) ESR spectrum of the radical complex from the reaction of triethylborane with 4,4'-bipyridine and potassium at 300 K in THF, with amplified outer section. (B) Computer-assisted spectrum synthesis, line width 0.022 mT.

the other complexes could be analyzed after dilution of the samples; the spectra are characterized by the relevant metal isotope hyperfine splitting.

Twofold coordination of organoberyllium cations leads to a septet splitting by ^{9}Be (100%, $I = 3/2$); in contrast, the natural abundance of ^{67}Zn (4%, $I = 5/2$) is too small to allow detection of the metal coupling [16] (Fig. 1). In case of the bis(alkylboron) or bis(dialkylgallium) radical complexes the ESR spectra consist of three subspectra from the different isotope combinations ^{10}B/^{10}B, ^{10}B/^{11}B and ^{11}B/^{11}B, or ^{69}Ga/^{69}Ga, ^{69}Ga/^{71}Ga and ^{71}Ga/^{71}Ga, respectively (^{10}B: 19%, $I = 3$; ^{11}B: 81%, $I = 3/2$; ^{69}Ga: 60%, $I = 3/2$; ^{71}Ga: 40%, $I = 3/2$).

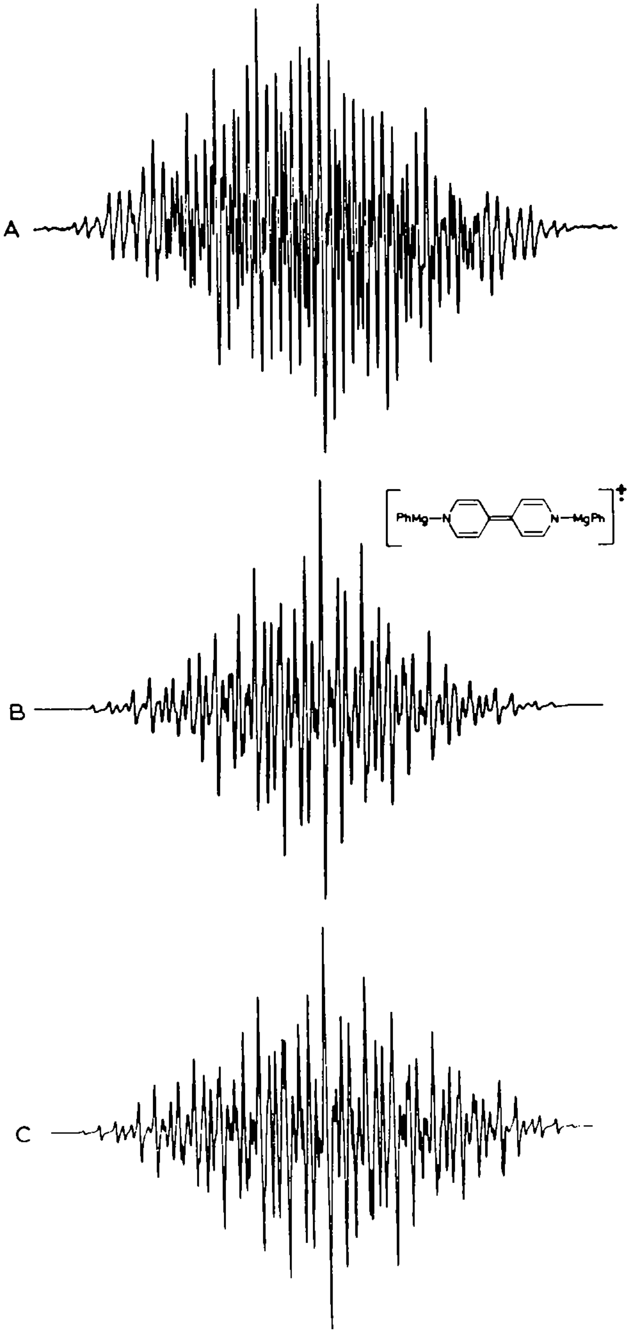


Fig. 3. (A) ESR spectrum of the radical complex formed from diphenylmagnesium and 4,4′-bipyridine at 300 K in THF. (B) ESR spectrum after reaction with potassium; (C) Computer simulation of spectrum B, line width 0.010 mT.

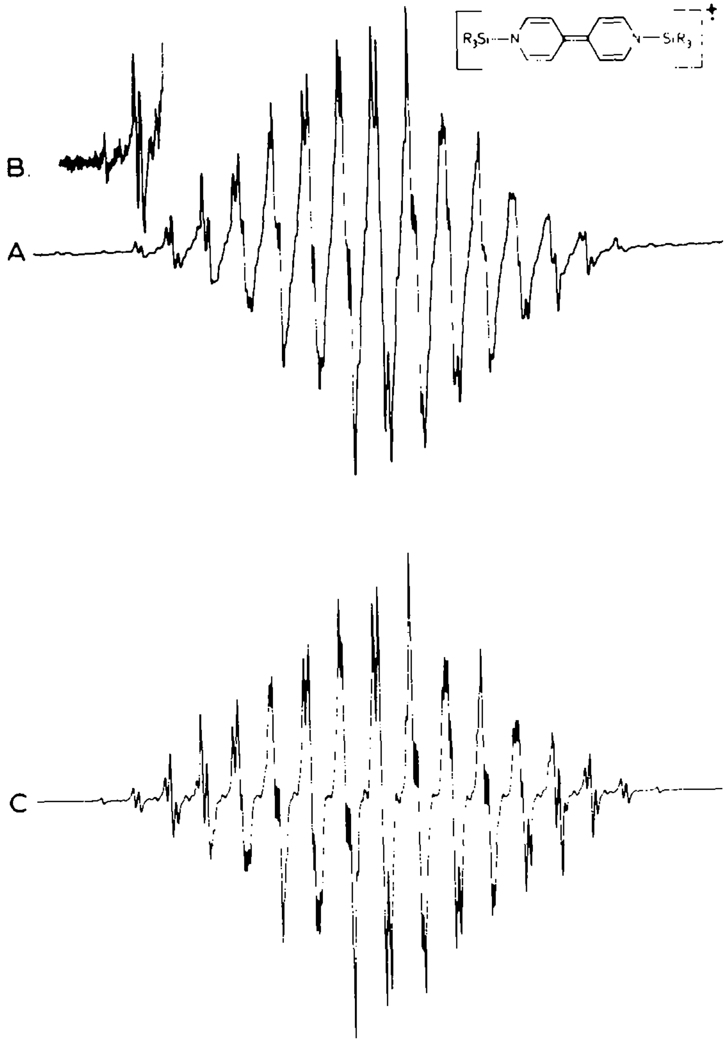


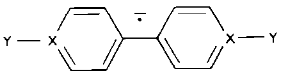
Fig. 4. (A) ESR spectrum of the radical cation of 1,1′-bis(trimethylsilyl)-4,4′ (1H, 1′H)-bipyridinylidene, generated by oxidation with $AlCl_3$ in CH_2Cl_2/Me_3SiCl at 300 K. (B) Amplified section which exhibits the ^{29}Si isotope coupling (^{29}Si: 4.7%, $I = 1/2$). (C) Computer simulation of spectrum A, line width 0.011 mT.

Depending on the ratios of the nuclear magnetic moments $\mu_{^{11}B}/\mu_{^{10}B} = 2.99$ and $\mu_{^{71}Ga}/\mu_{^{69}Ga} = 1.27$, the various isotopes exhibit different ESR coupling constants [15]. As an example, Fig. 2 shows the spectrum of the bis(organoboron) complex with its computer simulation.

Magnesium. Diphenylmagnesium or phenylmagnesium bromide reduce 4,4′-bipyridine in a single electron transfer reaction in the absence of alkali metal. The complex ESR spectrum exhibits two triplets (0.05 and 0.12 mT) as smallest hyperfine splittings and thus indicates a lower symmetry of the radical complex (Fig. 3(A)). A similar coordination behavior has been observed in the reaction of Grignard

TABLE 1

ESR PARAMETERS OF 13 ELECTRON-12 CENTER π SYSTEMS, LISTED ACCORDING TO INCREASING $a_{H(2)}$ (Coupling constants a_X in mT)



XY	$a_{H(2)}$	$a_{H(3)}$	Σa_H [b]	$a_{^{14}N}$	a_Y(Y)	g	References
CH	0.039	0.268	1.228	.	0.539 (^{1}H)	2.0026	[31]
N	0.043	0.235	1.112	0.364		2.0032	[31]
$NBEt_3$	0.068	0.204	1.088	0.408	0.136 (^{11}B)	2.0032	This work
$NMo(CO)_5$	0.071	0.201	1.088	0.432	0.088(^{95,97}Mo)	2.0039	[27]
$NW(CO)_5$	0.080	0.192	1.088	0.433	0.163(^{183}W)	2.0050	[27]
$^{+}$NMgPh	0.084	0.207	1.164	0.341	0.012(^{25}Mg)	2.0031	This work
$^{+}$NZnPh	0.084	0.205	1.156	0.372	[a] (^{67}Zn)	2.0031	This work
$^{+}NGaMe_2$	0.085	0.20	1.14	0.39	0.26(^{69}Ga) 0.33(^{71}Ga)	2.0029	This work
$^{+}NInMe_2$	ESR hyperfine structure not resolved					2.0027	This work
$^{+}$NBePh	0.086	0.205	1.164	0.350	0.029(^{9}Be)	2.0031	This work
$^{+}NAlMe_2$	0.096	0.192	1.152	0.352	0.128(^{27}Al)	2.0030	[13]
$^{+}NAlEt_2$	0.099	0.190	1.156	0.348	0.134(^{27}Al)	2.0030	[13]
$^{+}NAlH_2$	0.099	0.198	1.188	0.347	0.149(^{27}Al)	2.0031	[21]
$^{+}NAlCl_2$	0.115	0.177	1.168	0.354	0.177(^{27}Al)	2.0033	[13]
$^{+}$NMe	0.157	0.133	1.160	0.423	0.399($^{1}H_{Me}$)	[a]	[31]
$^{+}$NH	0.161 [c]	0.145 [c]	1.224	0.356	0.406(^{1}H)	[a]	[31]
$^{+}NSiMe_3$	0.165	0.141	1.224	0.319	0.135(^{29}Si)	2.0031	This work
$^{+}$S	0.236	0.058	1.176	–	–	[a]	[1,32]
$^{+}$O	0.297	0.080	1.508	–	–	[a]	[1]

[a] Not observed or reported. [b] Sum of all splittings $a_{H(2)}$ and $a_{H(3)}$. [c] Tentative assignments.

reagents with pyrazine [16,17]. Treatment of this paramagnetic solution with potassium leads to the symmetrical 1/2 complex, with the expected ESR spectrum (Fig. 3(B)).

Silicon. The reaction of 4,4′-bipyridine and trimethylchlorosilane with potassium in DMF gives fully reduced 1,1′-bis(trimethylsilyl)-4,4′(1H, 1′H)-bipyridinylidene [18]. Careful reoxidation of this electron-rich compound [2,19] with $AlCl_3/Me_3SiCl$ in methylene chloride [20] gives the blue radical intermediate; its ESR spectrum is shown in Fig. 4.

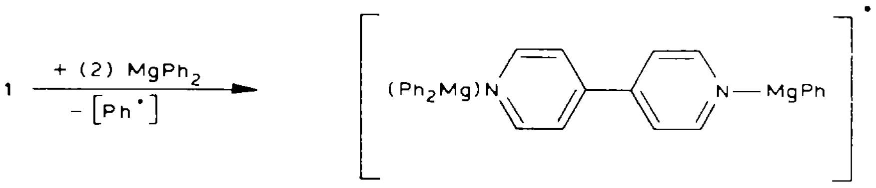
Cadmium, thallium. Mixtures of 4,4′-bipyridine and dimethyl- or diphenylcadmium in THF react with potassium to give the elemental metal; a persistent radical complex is not detected at room temperature. Similar results are obtained with trimethyl- or triphenyl-thallium.

The ESR parameters of the radical complexes **4**, the metallaviolenes, are presented in Table 1, where the data for these new species are shown alongside those for a series of related 13 electron-12 center π radicals.

Discussion

Reaction behavior

The ligand 4,4′-bipyridine has two coordination sites which, unlike those in the 2,2′-isomer, do not allow chelate formation. Another characteristic of this system is the reduction of reduced 4,4′-bipyridine to form close, i.e. ESR-detectable, coordination complexes with alkali metal cations in ethers [21]. However, stronger coordinating organometallic cations $^{+}MR_n$ do form persistent radical complexes with $\mathbf{1}^{\cdot-}$: Grignard reagents alone react with 4,4′-bipyridine via single electron transfer [22] to yield unsymmetrical complexes, possibly with coordination of organomagnesium groups at both nitrogen atoms:

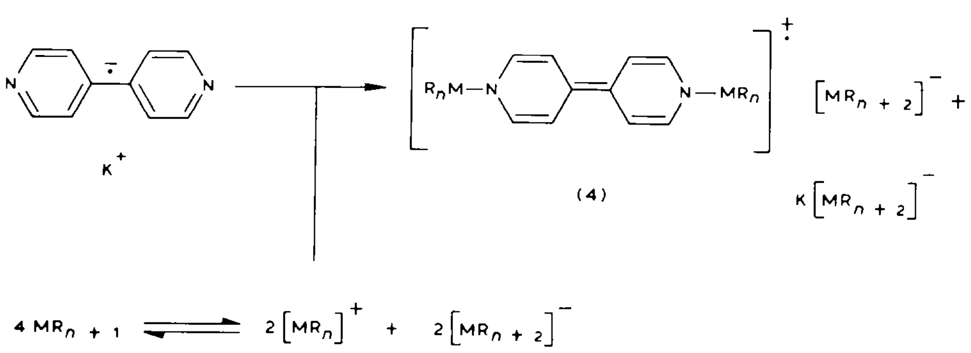


(5)

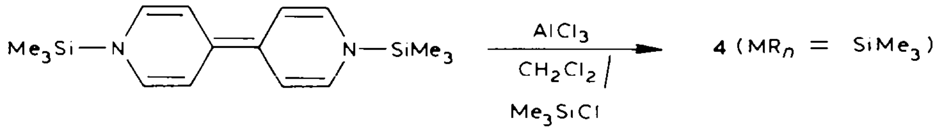
In order to obtain 1/2 radical complexes, however, **1** has to be reduced by an alkali metal such as potassium. The radical anion $\mathbf{1}^{\cdot-}$ then coordinates with organometallic cations present in the dissociation equilibrium [23] (see next formula).

The use of the halides XMR_n in case of M = B, Mg, or Al leads to identical ESR spectra. In the absence of halides, the persistence and stability of the cationic complexes is obviously assisted by the simultaneous formation of metallate anions [12b, 15, 16].

In case of the *N,N′*-bis(trimethylsilyl) system the fully reduced compound **6** had



been characterized [2, 18, 24]; thus an oxidative procedure [20] was employed to generate the radical intermediate:



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ESR parameters

The ESR spectra of the metallaviolenes are characterized by their respective metal isotope splittings a_M. The magnitude of a_M is determined by several factors; at first, a_M is connected to the typical isotropic hyperfine coupling constant A_{iso} for each isotope [25]. Furthermore, the ratio $a_M/A_{iso}(M)$ decreases within a main group of the periodic system with increasing atomic number; this has been demonstrated also for pyrazine radical complexes [15,16]. The metal coupling constants of the metallaviolenes and of corresponding pyrazine complexes exhibit a ratio of approximately 1/2 (cf. Tab. 1 and refs. 15, 16, 26, 27), however, such a general proportionality does not exist with the parameters of corresponding 2,2'-bipyridine radical complexes [14], where chelate effects play an important role. The metal coupling constants are also sensitive to changes of the organic substituent R at the metal and to temperature variations, as has been demonstrated in detail for organoaluminum radical complexes (Tab. 1 and refs. 13, 28).

The magnitude of the nitrogen coupling constant a_N in metallaviolenes **4** is largely determined by the nature of the coordinated metal. In agreement with the pattern for pyrazine radical complexes [15, 16, 26, 27], Be-, Al-, Mg-, and especially Si-coordination leads to relatively small values a_N, while Zn-, Ga-, B-, or carbonylmetal coordination causes an increase of the ^{14}N parameter relative to the values for free or diprotonated 4,4'-bipyridine radical anion. We cannot offer an explanation for this peculiar variation of a_N.

The most valuable piece of information gained from the ESR study of metallaviolenes concerns the hydrogen coupling constants, which should be proportional to the squared HMO coefficients of the singly occupied molecular orbital [29]:

$$a_H = Q \times c_{ij}^2$$

The data for the series of aluminum-containing radical complexes in Table 1 show

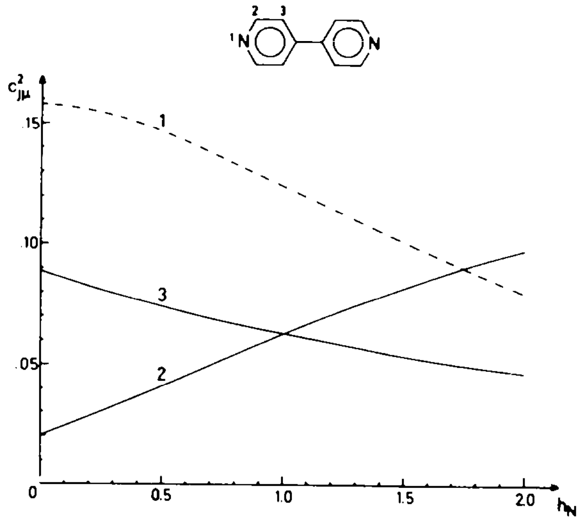


Fig. 5. Squared HMO coefficients c_i^2 (i = 1–3) as a function of the Coulomb integral h_N for reduced 4,4′-bipyridine.

that the ^{1}H coupling constants depend very little on the metal substituent unless drastic changes (R, H → Cl) are involved. The varying organometal coordination can be simulated by a variation of the N-"electronegativity" which corresponds to a change of the Coulomb integral h_N in a HMO approach [30]. Such a procedure has proved to be successful in interpreting the spin distribution in 2,2′-bipyridine radical complexes [14]. Figure 5 shows the behavior of the squared Hückel coefficients c_i^2 for the singly occupied MO (b_{1u}) of the 4,4′-bipyridine radical anion as a function of h_N ($0.0 \leqslant h_N \leqslant 2.0$).

Figure 5 displays a straightforward relation between $a_{H(2)}$ and $a_{H(3)}$, both parameters exhibit almost linear but opposite behavior as a function of h_N with a crossing at $h_N = 1.0$. In the light of this behaviour, which predicted by theory, an arrangement of the ESR data of the new radical complexes **4**, of corresponding organoaluminum [13,21] and pentacarbonylmetal complexes [27] and of related reference radicals is presented in Table 1 [1,31,32].

As expected, the coupling constants $a_{H(2)}$ and $a_{H(3)}$ draw closer on going from the isoconjugated biphenyl radical anion to derivatives of reduced 4,4′-bipyridine. The data from Table 1 involve a sequence of N-coordinated species which corresponds (with the one notable exception of BR_n) to that obtained for chelate complexes of 2,2′-bipyridine [14]. The neutral metal carbonyl fragments $M(CO)_n$ are followed by organometallic cations of magnesium, zinc, gallium, and beryllium; next are the aluminium species $^+AlX_2$, for which the substitution of alkyl groups or hydride by more electronegative chlorine atoms results in a significant shift of the ratio $a_{H(2)}/a_{H(3)}$. N-silyl and N-alkyl substitution as well as double protonation lead to almost equivalent parameters $a_{H(2)}$ and $a_{H(3)}$ for $h_N \approx 1.0$; and so the assignment in this case is ambiguous [1, 31, 33]. The sequence found for N-coordinated species reflects the increasing charge transfer between the ligand π radical anion and the organometallic cation after complexation; this corresponds to increased covalency of the metal–ligand bond.

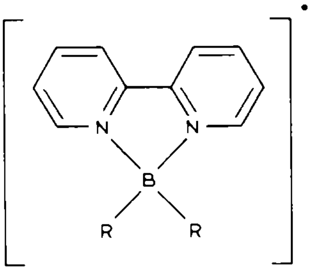
Replacement of $^{+}$NX by $^{+}$O or $^{+}$S has a further marked effect on the spin distribution; HMO calculations suggest a reversed sequence $a_{H(2)} > a_{H(3)}$ [1, 32].

The variation of the squared Hückel coefficients $c_{\mu j}^{2}$ as a function of h_N is parallelled by an increase of the Hückel energy ϵ_J of the singly occupied MO from $-0.71\ \beta$ ($h_N = 0.0$) to $-0.21\ \beta$ ($h_N = 2.0$). Accordingly, the reduction potentials have been observed to increase from -1.76 V for **1** via ~ -0.3 V for the *N*-silylated and *N*-alkylated derivatives to potentials of approximately $+0.5$ V (vs. SCE) for the bi(thio)pyrylium salts [1].

The ESR spectroscopic comparison of organometallic radical complexes of 4,4′- and 2,2′-bipyridine [14] exhibits a largely parallel sequence of *N*-coordinated metal fragments; however, the different position of the boron complexes must be noted. Whereas the chelate complex **7** displays a spin distribution comparable to that found in the R_2Al complexes [14], the boron containing violene is distinguished by relatively small coupling constants a_H (Tab. 1, cf. also the sum of the ring proton splittings).

Two explanations may be offered for this discrepancy. One explanation, assuming a coordination of boronium cations $^{+}BEt_2$ to $\mathbf{1}^{\cdot-}$, would have to take into account the ability of three-coordinate boron to take part in N–B back-bonding. This interaction would increase the number of π-centers. On the other hand, it must also be considered that the radical anion $\mathbf{1}^{\cdot-}$ might coordinate with two undissociated [23] molecules BEt_3 ro $ClBEt_2$. The comparison of coupling constants in Table 1 strongly suggests the second alternative, a future publication will elaborate on coordination equilibria involving radical anions [41].

Summarizing, the results presented for the new "metallaviolenes" have demonstrated how the gap between the redox systems of 4,4′-bipyridine **1** and of the viologens **2** can be bridged through coordination of various organometallic fragments to the nitrogen atoms of **1**. Thus, metal coordination may possibly allow modification and controll of the redox properties of this valuable and widely used electron transfer system.



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Experimental section

ESR spectra were recorded on a Varian E 9 spectrometer (frequency 9.5 GHz, magnetic field strength 330 mT, field modulation 100 kHz). Coupling constants and *g* values were determined relative to the perylene radical anion in DME [35].

ESR computer simulations were carried out at the Hochschulrechenzentrum Frankfurt using the program ESPLOT [36].

4,4′-Bipyridine (Fluka), diphenylzinc and dimethylcadmium (Alfa), triethylborane (Aldrich), and diphenylthallium chloride (Alfa) were obtained from commercial sources.

The compounds diphenylberyllium [37], diphenylmagnesium [38], diphenylcadmium [38], trimethylgallium- [34a] and trimethylindium-diethyletherate [34b], trimethyl- [39a] and triphenyl-thallium [39b] were prepared according to published procedures.

1,1′-bis(trimethylsilyl)-4,4′(1H, 1′H)-bipyridinylidene **6** was obtained via reductive silylation of 4,4′-bipyridine by the method of Hünig and Schenk [18].

Metallaviolenes **4** were generally prepared in a sealed glass apparatus under high vacuum or under argon. 1 mg of 4,4′-bipyridine **1** and an approximately five-fold excess of MR_{n-1} or of the halide XMR_n were dissolved in dry THF [40]; except in the case of magnesium (which involves formation of the 1/1 radical complex via single electron transfer) the weakly coloured solutions were diamagnetic. After short contact of these solutions with a potassium mirror the intense blue color of the 1/2 radical complexes, the metallaviolenes, developed. These solutions had then to be diluted for high-resolution ESR measurements. All the radical complexes are persistent in solution at room temperature.

The radical cation **4** with $R_n\cancel{M} = Me_3Si$ was obtained by treating a CH_2Cl_2/Me_3SiCl solution of the parent compound **6** with $AlCl_3$ [20], the chlorosilane being necessary to prevent hydrolysis.

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