$^2\Pi(1)$ state is 18 kcal/mol below[25] the $^4\Sigma^-$. In addition, the reaction

$$Li_2(^1\Sigma_g^+) + C(^3P) \rightarrow C\text{-}Li(^4\Sigma^-) + Li(^2S)$$

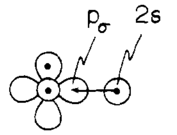
is exothermic by at least 27 kcal/mol, while the corresponding H_2 reaction

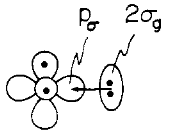
$$H_2(^1\Sigma_g^+) + C(^3P) \rightarrow C\text{-}H(^2\Pi) + H(^2S)$$

is endothermic[26] by 23 kcal/mol.

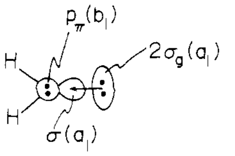
For Li_2C we have found three bound triplet states well below the first singlet. While two of these triplets, the $^3\Sigma_g^-$ and $^3A_2$ have very different geometries, they have essentially identical (at our level of accuracy) energies. We estimate that both are bound relative to $C(^3P) + Li_2(^1\Sigma_g^+)$ by at least 53 kcal/mol. If one reduces the symmetry from C_{2v} to C_s, these two triplets share the $^3A''$ symmetry and would suffer an avoided crossing. This avoided crossing will have a significant effect on the dynamics of the reaction of ground state C and Li_2.

Both the ground state of C–Li and the low-lying $^3A_2$ state of Li_2C are characterized by a donation of electrons from Li or Li_2 to an "empty" p_σ orbital on C. Schematically





completely analogous to the $N^+ + H_2$ case discussed by Dewar.[22] This observation prompts the speculation that one might fruitfully consider the recently predicted[4,6] dilithiomethane structure as carbenoids resulting from the donation of electrons from the bonding orbital on Li_2 into a formally empty σ orbital on CH_2. For example, the planar $^1A_1$ state would have the form



Our calculations on CLi_2 suggest that in this mode of bonding the Li_2 separation would be between 5 and 6 bohr and the Li_2 end of the molecule positive relative to the CH_2 end. The optimized SCF structure of Ladig and Schaefer[6] has the Li_2C angle as 101.7° and R(C–Li) = 3.485 bohr (corresponding to a Li_2 separation of 5.40 bohrs and a C–Li_2 separation of 2.20 bohrs), with a dipole moment of +4.85 D. As we rotate the Li_2 group 90° about the C_2 axis to form the "tetrahedral" isomer, we lose the stability due to the delocalization of the carbon p_π electrons into the Li p_π orbitals (a Li–Li bonding interaction), but we gain the ability to delocalize these electrons into the Li_2 σ_μ* orbital. This should result in an increased Li_2 separation and LS[6] calculated 6.49 bohrs which is an increase of 1.09 bohrs over the planar separation.

We can imagine the planar triplet being formed from the planar singlet by exciting an electron from the $2p_\pi$ on carbon to a primarily σ_g orbital (a_1 in C_{2v}) on Li_2. Qualitatively, this σ_g orbital would be the out of phase combination of the methylene σ and Li_2 $2\sigma_g$ orbitals. When this orbital is occupied, one anticipates that, relative to the planar singlet, the Li_2 separation would decrease, the C–Li_2 separation would increase, and the dipole moment be negative on the Li_2 side of the molecule. LS[6] calculate a Li_2 separation of 4.684 bohrs (a decrease of 0.721 bohr), a C–Li_2 separation of 3.131 bohrs (an increase of 0.931 bohr), and a dipole moment of −1.22 D (planar $^1A_1$ was +4.85 D). As with the planar singlet, rotating the Li_2 group in the $^3B_1$ state by 90° about the C_2 axis would destroy the delocalization of the carbon $2p_\pi$ orbital into the Li_2 π orbitals but will alow the delocalization of this $2p_\pi$ orbital into the Li_2 σ_u* orbital. Because there is only one electron in this π orbital and the Li_2 is rather distant (>3 bohrs) from the carbon, this delocalization would increase the Li_2 separation only slightly. The calculated[6] increase is 0.066 bohrs.

While the ease with which this very simple model accounts qualitatively for the structural changes in the dilithiomethane is satisfying, the speculations should, of course, be checked with detailed calculations.

Acknowledgment. J.F.H. has benefited from the stimulating environment provided by the members of the Theoretical Chemistry Group at Argonne. The willingness of B. Botch, L. Harding, and T. Dunning, Jr., to advise us on the use of the various codes has been crucial to the completion of this study.

Registry No. LiC, 81572-61-4; Li_2C, 72023-94-0.

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Electron Transfer to Complex Ligands. Radical Anions and Organomagnesium Radical Complexes of 2,2′-Bipyridines and 1,10-Phenanthrolines

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Abstract: The bidentate complex ligands 2,2′-bipyridine (**1**), 4,4′-dimethyl-2,2′-bipyridine (**2**), 1,10-phenanthroline (**3**), and 4,7-dimethyl-1,10-phenanthroline (**4**) have been reduced to radical anions by potassium metal and to organomagnesium radical complexes in a single electron transfer (SET) reaction of diphenylmagnesium. Well-resolved ESR spectra were obtained that could be analyzed on the basis of HMO calculations. In the case of the 1,10-phenanthrolines there are two low unoccupied molecular orbitals available to accommodate the additional electron; a comparison of the spin distributions demonstrates that, in contrast to earlier assumptions, it is the $5b_1$ orbital that is singly occupied. This result helps to explain the similar properties of corresponding 2,2′-bipyridine and 1,10-phenanthroline metal complexes.

2,2′-Bipyridine (bpy) and 1,10-phenanthroline (phen) have been widely used as "classical" complex ligands for metal ions and inorganic or organometallic fragments.[1-3] Apart from their good σ-donor complexing properties due to the bidentate coordination, these systems are distinguished because of their relatively low lying π^* orbitals. As a result of this particular combination of electronic properties these ligands often form highly colored coordination compounds because of a low energy charge transfer in the excited state;[2-6] they can stabilize labile inorganic or organometallic species by accepting excess negative charge;[7,8] they also form easily reducible complexes with the additional electron(s) residing often in the ligand π^* orbital,[1-3] and finally, they can function as negative molecular ions, thus stabilizing metals in formally low oxidation states.[1,6b,9,10]

Among the most simple coordination complexes of bpy and phen are the alkali metal "ion pairs"[11] that form in the reaction of the corresponding heterocycle and an alkali metal in solvating ethers. However, while 2,2′-bipyridine ion pairs were reported as early as 1958[12] and have been frequently studied since then,[13,14] the 1,10-phenanthroline negative ion has not been well documented so far. Although the electrochemical reduction of phen has been investigated,[15-18] an unequivocal ESR characterization of the reduced species is still missing: Assignments of ESR coupling constants for the phen radical anion were described as either "probable"[19] or "not unambiguous".[20] Moreover, the fact that *two*[5] molecular orbitals compete for the status of lowest unoccupied MO (LUMO) has not been critically considered before.[21]

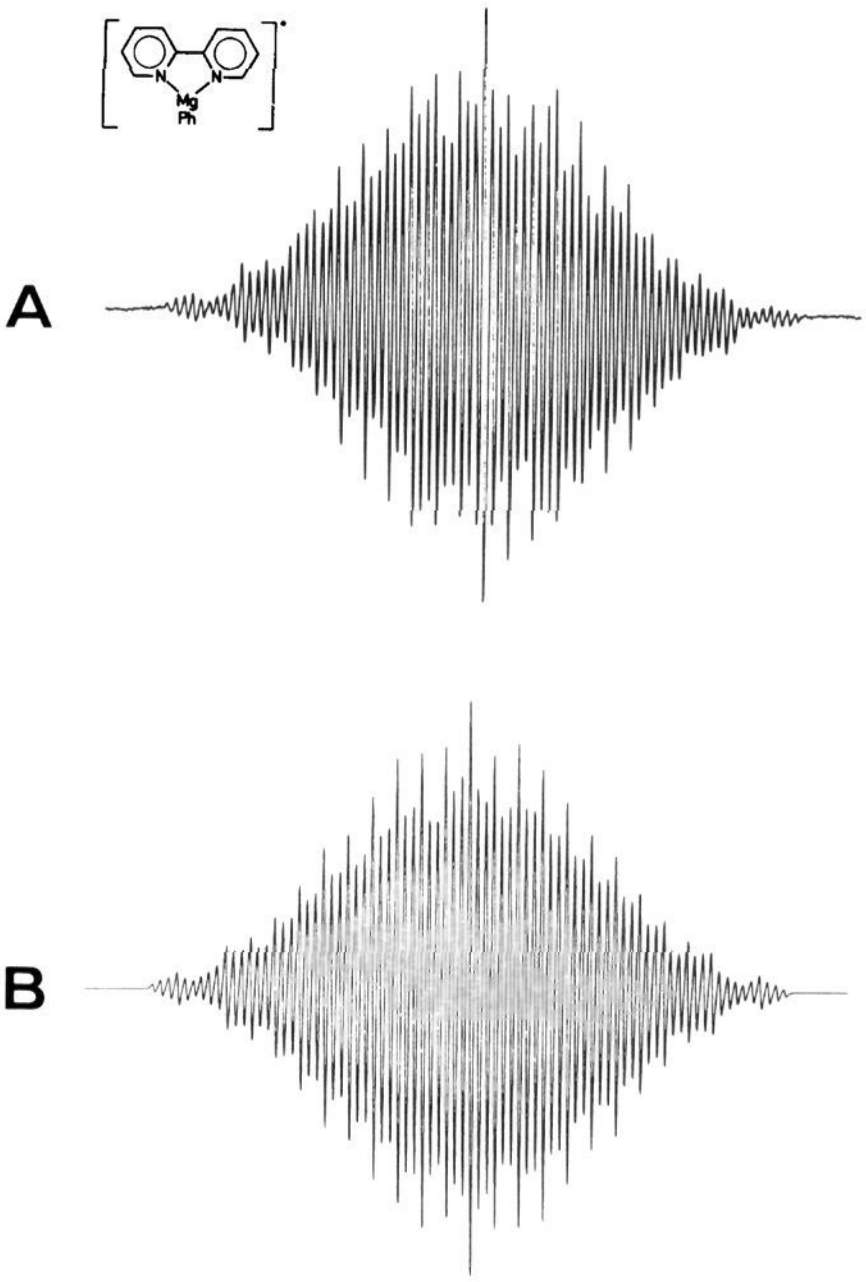

Figure 1. ESR spectrum of the radical complex formed in the reaction of 2,2′-bipyridine with diphenylmagnesium in THF (A) and its computer simulation (B). The line width is 0.010 mT.

Table I. ESR Coupling Constants a_X (mT) of 2,2′-Bipyridine Radical Complexes

radical	a_N	$a_{H(3)}$	$a_{H(4)}$	$a_{H(5)}$	$a_{H(6)}$	ref
2a	0.229	0.153	0.092[a]	0.463	0.061	this work
1a	0.261	0.122	0.106	0.464	0.057	32
2b	0.262	0.120	0.168[a]	0.429	0.049	this work
1b	0.293	0.067	0.194	0.387	0.031	14, 24

[a] Methyl proton coupling constant.

Table II. ESR Coupling Constants a_X (mT) of *1,10-Phenanthroline Radical Complexes*

radical	a_N	$a_{H(2)}$	$a_{H(3)}$	$a_{H(4)}$	$a_{H(5)}$	ref
4a	0.262	0.054	0.428	0.112[a]	0.054	this work
3a	0.280	0.041	0.360	0.280	0.041	this work
4b	0.255	*b*	0.305	0.255[a]	0.049	this work
3b	0.290	0.021	0.290	0.326	0.064	21

[a] Methyl proton coupling constant. [b] Not observed, assignment to H(2) or H(5) uncertain.

Recent investigations have demonstrated that not only alkali metals but also organometallics[22,23] such as Grignard reagents[14,21,24,25] can transfer an electron to suitable N-heterocycles, thereby forming organometallic radical complexes.[14,21-25] ESR studies have exhibited characteristic changes of the spin distribution in these radical complexes upon organometal coordination.[14,21-27] Since neither complexation by RMg^+ [21,24,25] nor the loose association with a potassium cation further complicates the

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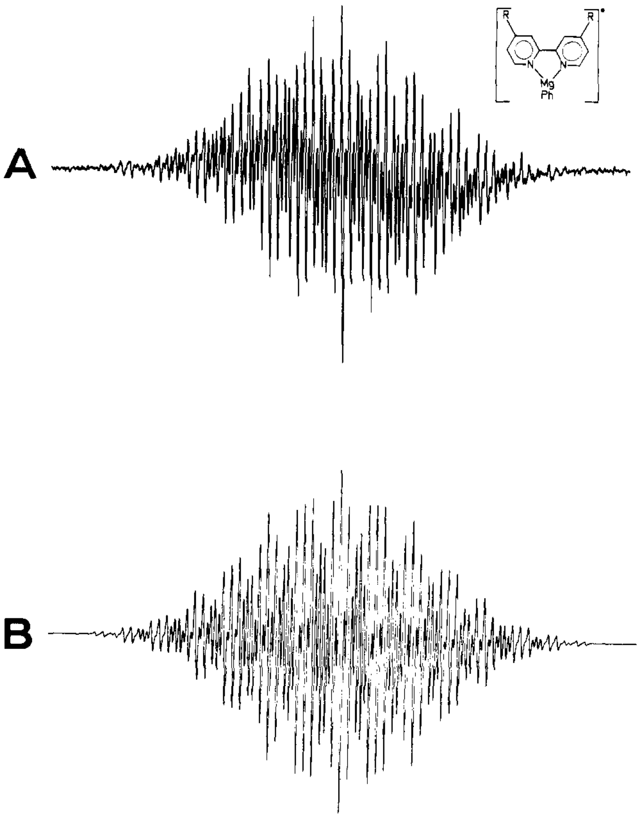
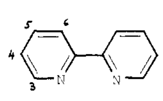


Figure 2. ESR spectrum of the radical complex formed in the reaction of 4,4′-dimethyl-2,2′-bipyridine with diphenylmagnesium in THF (A) and its computer simulation (B). The line width is 0.013 mT.

ESR hyperfine structure of the reduced complex ligands, these two reduction methods have been used to prepare paramagnetic species from 2,2′-bipyridine (**1**), 4,4′-dimethyl-2,2′-bipyridine (**2**), 1,10-phenanthroline (**3**), and 4,7-dimethyl-1,10-phenanthroline (**4**).



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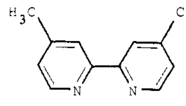

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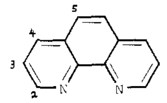

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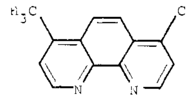

4

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$|1^{\cdot-}, K^+| = 1a$, $|2^{\cdot-}, K^+| = 2a$, $|3^{\cdot-}, K^-| = 3a$, $|4^{\cdot-}, K^+| = 4a$

$|1^{\cdot-}, RMg^+| = 1b$, $|2^{\cdot-}, RMg^-| = 2b$, $|3^{\cdot-}, RMg^+| = 3b$, $|4^{\cdot-}, RMg^+| = 4b$

R = Ph

Unambiguous determination of the ESR coupling constants helped to describe the radical ion state by the appropriate singly occupied MO, while the variation of the spin distribution upon different complexation or substitution could be rationalized with HMO correlation diagrams.[14,28]

Experimental Section

The ligands **1–4** were obtained from Alfa/Ventron and have been used without further purification.

Radical preparation has been carried out under high vacuum in sealed glass tubes by reacting a dry THF solution of the ligand with a freshly prepared potassium mirror (radicals **a**) or a solution of diphenylmagnesium ($MgPh_2$)[29] in diethyl ether (radicals **b**). For ESR measurements the radical concentration had to be reduced until satisfactory resolution (line widths of 0.01–0.02 mT) could be observed.

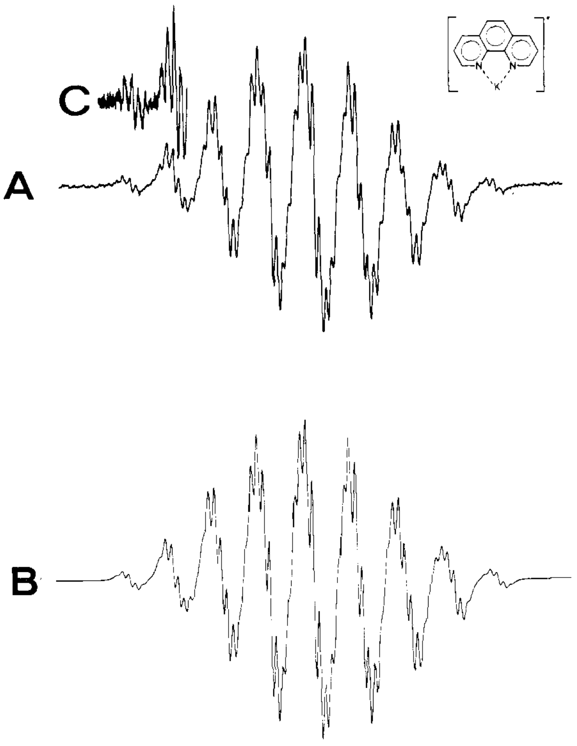

Figure 3. ESR spectrum of the radical formed in the reaction of 1,10-phenanthroline with potassium in THF (A) with its computer simulation (B). The line width is 0.034 mT. For easier analysis of the spectrum the outermost line groups have been amplified and better resolved (C).

Electron spin resonance spectra were recorded on a Varian E 9 spectrometer at a 9.5-GHz frequency, 330-mT magnetic field, and with a field modulation of 100 kHz. The perylene radical anion in DME[30] was used for calibration.

ESR spectra simulation was accomplished with the program ESPLOT.[31] The calculations were carried out on the Univac 1108 of the Hochschul-Rechenzentrum Frankfurt.

Results and Discussion

The ESR spectra obtained after reduction of the ligands **1–4** by K or $MgPh_2$ have been analyzed with the computer simulation technique (Figures 1–3). The coupling constants, whose assignment is discussed later, are summarized in Table I for 2,2′-bipyridine radicals and in Table II for 1,10-phenanthroline radicals.

Reduction of Ligands. The complex ligands **1–4** react with metallic potassium to form stable radicals. In contrast to Li^+ or Na^+ radical ion pairs,[20,32] these paramagnetic species do not exhibit a detectable alkali metal splitting;[33] the association between the ligand anions and the K^+ cation is obviously not a very close one. However, the variation of solvents from ethers to DMF has been shown to cause a significant change in the spin distribution of the bpy radical anion;[32] therefore, the potassium radical complexes might be best regarded at solvent separated ion pairs.[11]

It has also long been known that organomagnesium reagents yield colored solutions with bpy[6a] and phen,[6c] and the use of such ligands as color indicators for the quantitative determination of organomagnesium and -lithium compounds was suggested.[6c] However, the paramagnetism of these solutions was not recognized at the time, and the formation of radical intermediates in such reactions was not considered.[6a,c]

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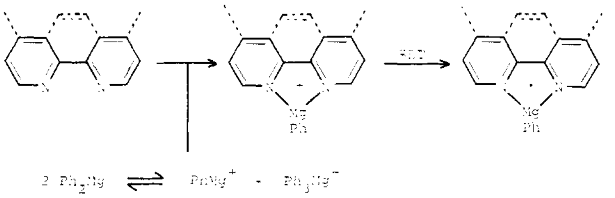
[33] ^{39}K isotope coupling constants have been observed in radical ion pairs of aromatic hydrocarbons,[34] carbonyl compounds,[35] and nitrogen-containing systems.[36]

Reduction of the ligands **1**–**4** by MgR_2 represents a single electron transfer (SET) reaction,[21,24,25,37] as has also been suggested for the Grignard reduction of aromatic ketones[38a] and hydrocarbons.[38b] Organometallics with vacant coordination sites such as diphenylmagnesium dissociate in coordinating solvents into cations (viz., $PhMg^+$) and ate-complex anions (viz., Ph_3Mg^-)[29], and initial complexation of the ligand by a RMg^+ cation seems to increase the reduction potential sufficiently[14] in order to allow a SET from the organometallic species.



(2)

Formation of organomagnesium complexes is evident from the considerable change of the spin distribution[14,24,25] (Tables I and II), and the use of different organomagnesium compounds R_2Mg and $RMgX$[39] yields only marginally different ESR spectra.[14,21,24,25] In close analogy to this interpretation, a coordination between an organometallic cation RMg^+ and (ketyl) radical anions is also suggested for the radical species found by Ashby and co-workers;[41] neither free ketyl intermediates nor radical anion–radical cation pairs can account for the reported ESR spectra[41] which are yet to be analyzed.

The ^{25}Mg isotope splitting could not be observed in any of the radical complex ESR spectra,[42] the reason being the low natural abundance (10%), the nuclear spin ($I = {}^5/_2$), and the very small isotropic hyperfine coupling constants A_{iso}[43] of this isotope. However, double coordination in pyrazine and 4,4′-bipyridine radical complexes has allowed the determination of these parameters.[24,25]

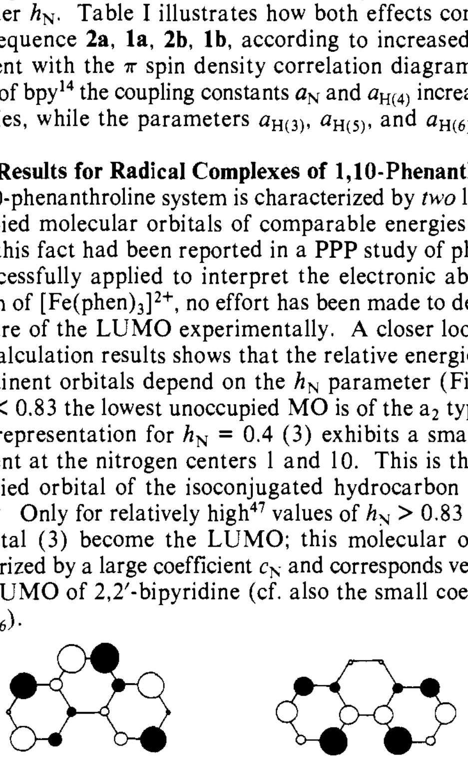
The stabilities of the radical complexes are typical for radical intermediates of Weitz redox systems;[44] complete reduction of such N-heterocycles by atom or group transfer is disfavored because of their propensity to retain at least some degree of aromatic character.[45]

ESR Results for Radical Complexes of 2,2′-Bipyridines. A HMO calculation for 2,2′-bipyridine shows that there is only one low unoccupied MO (b_1 in the cis configuration) relevant for the reduction to the radical anion (Figure 4). Reaction with potassium leads to the well-known radical species[12,13] and reduction by Ph_2Mg yields the organomagnesium radical complex.[24] On dilution, this complex displays a well-resolved ESR spectrum which can be perfectly reproduced by a computer simulation (Figure 1). The coupling constants of **1b** differ significantly from those of the radical anion **1a** (Table I); this illustrates the considerable charge transfer from the ligand anion to the organometallic fragment, according to a more covalent metal–nitrogen bond.[14]

The ESR spectra of the 4,4′-dimethyl-substituted derivatives **2a** and **2b** are quite complex because of their 945 theoretical lines; nevertheless, a small line width also allows the determination of these coupling constants (Table I). As another example of an organomagnesium radical complex the ESR spectrum of **2b** is shown in Figure 2 together with its computer simulation.

The ESR coupling constants of the radicals **2a** and **2b** are listed in Table I. Whereas the parameters $a_{^{14}N}$ and $a_{H(CH_3)}$ could be determined straightforwardly because of their unique multiplicity, the ^1H triplet couplings had to be assigned according to the established[14,32] π-electron spin density diagram for the 2,2′-bipyridine radical anion. Table I exhibits an almost continuous variation of coupling constants on going from species **2a** via **1a** and **2b** to radical **1b**. This sequence can be rationalized considering two different perturbation effects. First, the replacement of K^+ by the stronger coordinating RMg^+ ion leads to a more covalent character of the metal–nitrogen bond; in the HMO model this corresponds to an increase of the Coulomb integral parameter h_N ($\alpha_N = \alpha_C + h_N\beta$[28]) from $h_N \sim 0.3$ to $h_N \sim 0.6$.[14] Secondly, the substitution of the 4,4′-hydrogens by methyl groups causes an opposite effect: The donor substituents CH_3 weaken the ability of the ligand to function as a π acceptor; using the common organic nomenclature one can argue that the inductive effect of the methyl groups reduces the electronegativity of the nitrogen atoms, especially since the substituents are in the para position to the N atoms. Therefore, the effect of the methyl substitution on the ESR coupling constants can be simulated by a decrease of the parameter h_N. Table I illustrates how both effects combine to give a sequence **2a**, **1a**, **2b**, **1b**, according to increased h_N. In agreement with the π spin density correlation diagram for the LUMO of bpy[14] the coupling constants a_N and $a_{H(4)}$ increase along that series, while the parameters $a_{H(3)}$, $a_{H(5)}$, and $a_{H(6)}$ show a decline.

ESR Results for Radical Complexes of 1,10-Phenanthrolines. The 1,10-phenanthroline system is characterized by *two* low-lying unoccupied molecular orbitals of comparable energies.[5,21] Although this fact had been reported in a PPP study of phen[5] and was successfully applied to interpret the electronic absorption spectrum of $[Fe(phen)_3]^{2+}$, no effort has been made to determine the nature of the LUMO experimentally. A closer look at the HMO calculation results shows that the relative energies of the two pertinent orbitals depend on the h_N parameter (Figure 4). For $h_N < 0.83$ the lowest unoccupied MO is of the a_2 type ($4a_2$), and its representation for $h_N = 0.4$ (3) exhibits a small HMO coefficient at the nitrogen centers 1 and 10. This is the lowest unoccupied orbital of the isoconjugated hydrocarbon phenanthrene.[46] Only for relatively high[47] values of $h_N > 0.83$ does the $5b_1$ orbital (3) become the LUMO; this molecular orbital is characterized by a large coefficient c_N and corresponds very much to the LUMO of 2,2′-bipyridine (cf. also the small coefficients c_5 and c_6).



(3)

$4a_2$ $5b_1$

Surprisingly, the question as to which of the two orbitals is occupied on reduction of the compound has not yet been critically discussed. Numerous MO calculations have been performed for

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[37] Electron transfer has been also observed (a) in the reaction of 1,10-phenanthrolines with $Cp_2Ti(CO)_2$ (Corbin, D. R.; Willis, W. S.; Duesler, E. N.; Stucky, G. D. *J. Am. Chem. Soc.* **1980**, *102*, 5969) and (b) in the reaction of 1,4-di-*tert*-butyl-1,4-diaza-1,3-diene with Et_2Zn (Jastrzebski, J. T. B. H.; Klerks, J. M.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *210*, C49).

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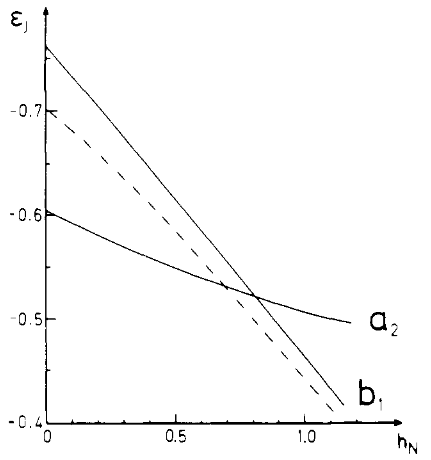

Figure 4. Correlation diagram showing the Hückel MO energies ϵ_J (β) for the two lowest unoccupied molecular orbitals of 1,10-phenanthroline (solid lines) and for the LUMO of 2,2′-bipyridine (broken line) as a function of the Coulomb integral paramter h_N.

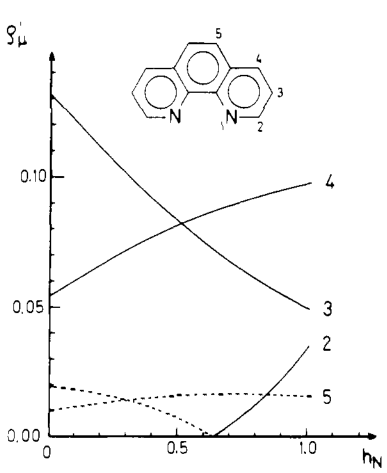

Figure 5. Correlation diagram showing the modified π spin densities $\rho_\mu' = \rho_\mu - 0.02$ as a function of the Coulomb integral parameter h_N for the $5b_1$ orbital of 1,10-phenanthroline. Broken lines denote a negative sign of the spin density ρ_μ'.

the 1,10-phenanthroline system,[5,15-18,20,48-50] and in those cases where the nature of the LUMO was stated either explicitely[5,18,20] or implicitely[17,49] it was identified as an a_2 orbital.

The dichotomy of two completely different low-lying MOs has been most strikingly illustrated in an interesting theoretical study on the radical ions of phen:[50] The results from a conventional McLachlan procedure[51] and from a more rigorous treatment (the AA method[52]) showed "a complete change in the pattern of spin densities";[50] however, the obvious reason for that "gross disparity" was not given.[50] Furthermore, in a detailed study on the sodium ion pairs of bpy and phen it was simply assumed that the first antibonding π orbitals of these systems should have different symmetry.[20]

With the unambiguous characterization of the organomagnesium radical complex **3b** of 1,10-phenanthroline[21] it became clear that these interpretations are in doubt: The almost identical values of a_N for **3b** and the bpy complex **1b** demonstrated clearly that a least in this species the $5b_1$ orbital was the singly occupied MO. It remained to be investigated, however, whether a very weakly coordinating counterion such as K^+ would lead to a reversal of the orbital sequence $5b_1/4a_2$, as had been demonstrated in the case of the LUMOs of 2,7-diazapyrene.[53]

The reduction of phen with K in THF gives a radical anion with very broad lines in its ESR spectrum. Only the very dilute solution exhibits a useful ESR hyperfine structure; the spectrum with its computer simulation is shown in Figure 3. Close examination of the outermost line groups (Figure 3C) exhibits a quintet of lines with the intensity ratio of 1:4:6:4:1, this has to be attributed to two, accidentally degenerate ^1H coupling constants of the phen radical anion. The next larger coupling constant amounts to at least 0.280 mT, and this is again the value that would be expected for the ^{14}N splitting in a phen radical anion which has a singly occupied b_1 orbital (Table II).

The assignment of the coupling constants for the phen radicals is based on the HMO spin populations which are a function of h_N. As has been successfully demonstrated in the bpy radical anion case,[14] the simple HMO spin densities $\rho^\pi = c_\mu{}^2$ can be modified with the linear correction $\rho' = \rho^\pi - 0.02$ in order to account for small, negative spin densities. Such a diagram for the $5b_1$ MO of phen is shown in Figure 5; the use of the parameters $h_N = 0.6$ for the organomagnesium complex and of $h_N = 0.3$ for the K^+ ion pair, which were found for bpy radical complexes,[14] helps to assign the ESR coupling constants for the phen derivatives (Table II). Especially noteworthy is the equivalence of the two smallest coupling constants for radical **3a** (Figure 3 and Table II); this is exactly what the diagram in Figure 5 predicts for $h_N = 0.3$. For $h_N = 0.2$, the HMO π-electron spin densities also agree very well with the values obtained from a more rigorous calculation which included quartet annihilation to the doublet ground state[50] of the phen anion radical; even the relative magnitudes of the two small coupling constants $a_{H(2)}$ and $a_{H(5)}$ are reproduced.

As in the bpy series (Table I), the incorporation of dimethyl derivatives (**4a** and **4b**) causes typical changes of the spin distribution: Upon methyl substitution the coupling constants vary according to a decrease of h_N, i.e., $a_{H(2)}$ and $a_{H(3)}$ increase while a_N and $a_{H(4)}$ are decreased. The spin density in positions 5 and 6 depends very little on h_N; consequently, the corresponding coupling constants do not display a uniform behavior (Table II).

Reduction of 1,10-phenanthroline with sodium in THF yields a radical complex with an ESR spectrum that is complicated by the additional ^{23}Na splitting ($I = {}^3/_2$). On low resolution the spectrum looks similar to the one obtained by reduction with potassium (Figure 3A); a decrease of the line width exhibits an enormously complex hyperfine structure which obviously cannot be fully analyzed with conventional ESR techniques. It seems this fact facilitated the erroneous interpretation of the ESR spectrum by Gooijer and co-workers,[20] especially since these authors assumed the singly occupied MO of phen to be of the a_2 type. However, this is obviously an invalid assumption because even in the solvent separated ion pair $K^+/phen^{-\cdot}$ it is the $5b_1$ MO that is singly occupied. In good aggrement with this assignment the temperature dependencies of the alkali metal hyperfine couplings are very much alike for the $Na^+/phen^{-\cdot}$ and the $Na^+/bpy^{-\cdot}$ ion pairs, a fact which has puzzled the authors of that study.[20] Consequently, the doubt[20] cast on the traditional explanation of the temperature dependence of the alkali metal splitting is unfounded too.

Summarizing, this investigation has clearly explained why both ligands, 2,2′-bipyridine and 1,10-phenanthroline, display such an equivalent behavior and yield complexes with similar properties: The fact that the features of interest, the lowest antibonding orbitals of both compounds, have almost identical character has been demonstrated by unambiguous ESR characterization of the corresponding radical complexes. A note of caution may be added: One-electron MO approximations may be advantageously used to describe certain experimental results such as the π-electron spin distribution; however, these methods are less reliable when the sequence of orbitals with comparable energies has to be determined.

Registry No. 1b, 80481-17-0; **2a**, 81769-75-7; **2b**, 81770-40-3; **3a**, 51778-67-7; **4a**, 81769-76-8; **4b**, 81770-39-0.

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