Preliminary communication

ELECTRON TRANSFER TO 1,10-PHENANTHROLINE BY GRIGNARD
REAGENTS. THE SPIN DISTRIBUTION IN ORGANOMAGNESIUM
RADICAL COMPLEXES

WOLFGANG KAIM

*Institut für Anorganische Chemie der Universität, Niederurseler Hang,
D-6000 Frankfurt 50 (West-Germany)*

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Summary

1,10-Phenanthroline (phen) reacts with Grignard reagents RMgBr or R_2Mg
to yield organomagnesium radical complexes [phen(MgR)]$^{\cdot}$. The spin distribu-
tion derived from well-resolved ESR spectra permits a distinction to be made
between the two possible singly occupied molecular orbitals a_2 and b_1.

The classical complex ligands 2,2'-bipyridine (bipy) and 1,10-phen-
anthroline (phen) can function as negative molecular ions, thus stabilizing
metals in formally low oxidation states [1]. While the anion radical of bipy
has been extensively studied in the form of its various ion pairs [2], the ESR
characterization of the phen negative ion has not been well documented [3];
an assignment based on the correlation to the isoconjugated phenanthrene radi-
cal anion [4] led to unsatisfactory results [5]. This is the more surprising
since a standard Hückel MO calculation predicts a crossing of the two lowest
unoccupied molecular orbitals [6] of phen within the normal range of the
Coulomb integral parameter h_N for the two nitrogen centers (Fig. 1). This di-
chotomy is also reflected in more rigorous calculations of π electron spin den-
sities for the phen anion radical [7]. Other molecular orbital treatments of the
1,10-phenanthroline molecule have given the a_2 orbital as the LUMO [8].

Our current interest [9] in the electron transfer ability [10] and the co-
ordination chemistry of Grignard reagents led us to study the reaction of 1,10-
phenanthroline [11] with various organomagnesium compounds in solvating
ethers such as THF or DME. These reactions result in paramagnetic red solu-
tions which display well resolved ESR spectra upon dilution. Different organo-
magnesium reagents RMgBr or R_2Mg (R = CH_3, C_2H_5, i-C_3H_7, C_6H_5) lead to
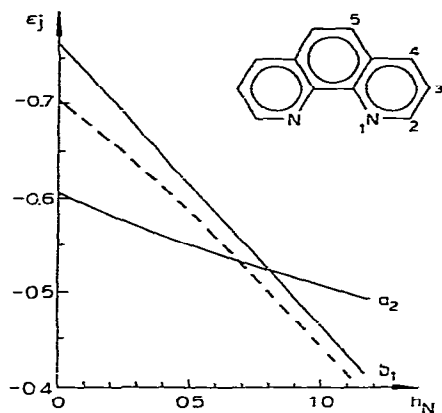
Fig. 1. Hückel MO energies $\epsilon_J(\beta)$ of the two lowest unoccupied molecular orbitals of 1,10-phenanthroline (solid lines) and of the LUMO of 2,2'-bipyridine (broken line), depending on the Coulomb integral parameter h_N.
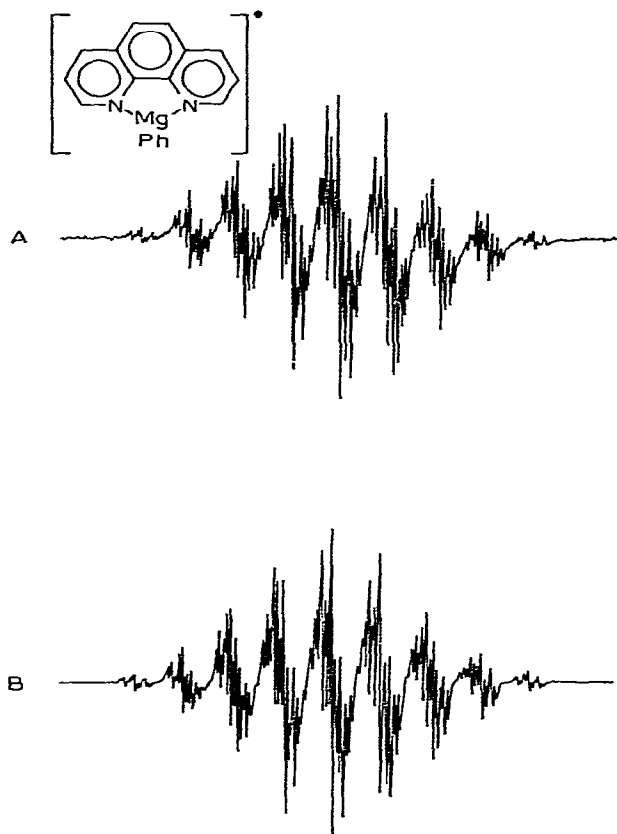

Fig. 2. (A) ESR spectrum of the radical complex formed in the reaction of 1,10-phenanthroline with diphenylmagnesium in THF at 300 K. (B) Computer assisted spectrum synthesis with the data from Table 1 and a line width of 0.014 mT.
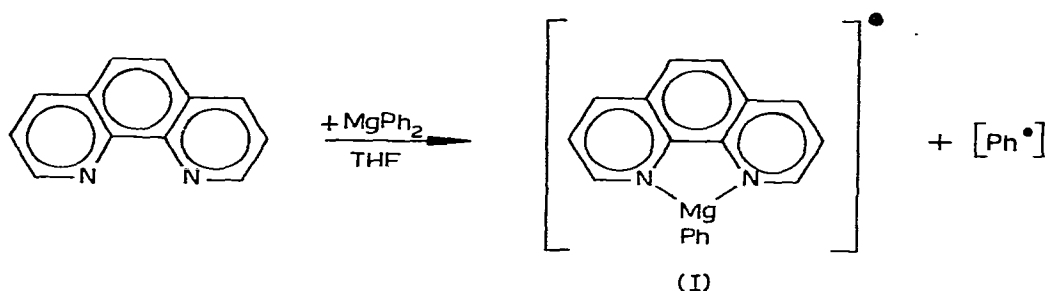
(I)

TABLE 1

ESR COUPLING CONSTANTS a_X (mT) OF ORGANOMAGNESIUM RADICAL COMPLEXES FROM 1,10-PHENANTHROLINE (phen) AND 2,2'-BIPYRIDINE (bipy) TOGETHER WITH THE PARAMETERS OF THE ISOCONJUGATED RADICAL ANIONS OF PHENANTHRENE AND BIPHENYL (numbering scheme according to Fig. 1)

	Phenanthrene[.-] [4]	[phen(MgPh)][.-] [a]	[bipy(MgPh)][.-] [a] [9]	Biphenyl[.-] [12]
a_1	0.070	0.290 [b]	0.293 [b]	0.273
a_2	0.288	0.021	0.031	0.043
a_3	0.030	0.290	0.387	0.546
a_4	0.356	0.326	0.194	0.043
a_5	0.428	0.064	0.067	0.273
Singly occupied MO assignment	a_2	b_1	b_1	b_{1u}

[a] ^{1}H assignments according to HMO spin populations; metal isotope coupling (^{25}Mg: 10%. $I = 5/2$) could not be detected because of low natural abundance, cf. however ref. [9]. [b] ^{14}N coupling constant.

only marginally different ESR spectra. Figure 2 shows the spectrum of the phenyl derivative together with its computer simulation.

When comparison is made with data for other pertinent radicals, as shown in Table 1, the ESR data for the phen complex I indicate that its spin distribution is similar to that of the corresponding bipy radical complex, but completely different from that of the isoconjugated radical anion of phenanthrene. This is most conclusively demonstrated by the large a_1(^{14}N) splitting constant of the organomagnesium radical complexes, contrasting with a small value a_1(^{1}H) in the phenanthrene anion radical. The fact that the complexation of the phen radical anion with a simple organomagnesium fragment results in a spin distribution according to molecular orbital b_1, as in the bipy anion radical, makes it clear why phen and bipy ligands can often be interchanged in complexes with only minor changes of the properties of the complexes.

References

1 W.R. McWhinnie and J.D. Miller, Adv. Inorg. Radiochem., 12 (1969) 135.
2 Cf. the references in P. Hanson, Adv. Heterocycl. Chem., 25 (1979) 236 or W. Kaim, Chem. Ber., 114 (1981) in press.
3 Cf. E.W. Stone and A.H. Maki, J. Chem. Phys., 39 (1963) 1635; "probable" coupling constants were reported by R.E. Dessy, J.C. Charkoudian and A.L. Rheingold, J. Am. Chem. Soc., 94 (1972) 738; cf. also M.F. El-Shazly, Inorg. Chim. Acta, 26 (1978) 173.
4 K. Möbius, Z. Naturforsch. A, 20 (1965) 1102.
5 C. Gooijer, N.H. Velthorst and C. MacLean, Mol. Phys., 24 (1972) 1361.

6 A similar reversal in the energy sequence of the two lowest antibonding orbitals upon increase of the nitrogen Coulomb integral was studied for 2,7-diazapyrene: J. Bruhin and F. Gerson, Helv. Chim. Acta, 58 (1975) 2422.

7 C.L. Honeyburne, Mol. Phys., 21 (1971) 1057.

8 R. Heid, F. Dietz and P. Thomas, Z. Chem., 12 (1972) 304; O. Gürtler, K.P. Dietz and P. Thomas, Z. Anorg. Allg. Chem., 396 (1973) 217; J. Reinhold, R. Benedix, P. Birner and H. Hennig, Z. Chem., 17 (1977) 115; A. Rusina, A.A. Vlcek and S. Zalis, Z. Chem., 19 (1979) 27.

9 W. Kaim, Angew. Chem., 93 (1981) in press.

10 Electron transfer by organomagnesium compounds has been reported previously; the ESR spectra obtained were described as those of "free" ketyls, cf. E.C. Ashby, A.B. Goel and R.N. DePriest, J. Am. Chem. Soc., 102 (1980) 7779.

11 Electron transfer to 1,10-phenanthrolines has been observed in the reaction with $Cp_2Ti(CO)_2$: D.R. Corbin, W.S. Willis, E.N. Duesler and G.D. Stucky, J. Am. Chem. Soc., 102 (1980) 5969.

12 A. Carrington and J. dos Santos Veiga, Mol. Phys., 5 (1962) 21.