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ESR STUDY OF MONOALKYLZINC-2,2'-BIPYRIDINE COMPLEXES, RZn · Bipy

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Summary

Paramagnetic species are formed when LiBipy is treated with various alkylzinc halides at —100°C and the ESR spectra are discussed. The observation that the half-life times of the radical species appear to depend only on the nature of the alkyl group bound to zinc proves that monoalkylzinc-2,2'-bipyridine complexes are formed. The nature of the bonding between zinc and 2,2'-bipyridine is discussed.

Introduction

The ability of 2,2'-bipyridine (Bipy) and related chelating heterocyclic nitrogen ligands to stabilize low oxidation states of metals is well-documented [1,2]. A large number of Bipy complexes of both transition- and main-group metals has been synthesized and characterized. As shown by ESR spectra, the complexes $M(Bipy)_2$ derived from Group II metals (Be [3], Mg [4]) and $SiCl_2$ [5] are even-electron triplet species. The boron complex $B(Bipy)_2$ [2] is a singlet-state molecule. In the complexes of the Group II metals and $SiCl_2$ the metal—ligand bonds are formulated as ionic rather than covalent as a result of electron transfer from the metal to the π-system of the ligands. However, the presence of boron coupling in the ESR spectrum of $B(Bipy)_2$ indicates covalent boron—ligand bonding.

A related type of complex, in which dialkyl- or diaryl-boron or -aluminium species are stabilized by coordination with pyridine or substituted pyridines, has been described by Köster [6,7]. These compounds were considered to be complexes of organoboron and organoaluminium radicals. The ESR spectra of the boron radicals show boron coupling, but have not been interpreted completely and no suggestions have been made as to the nature of the metal—ligand bonds in these compounds.

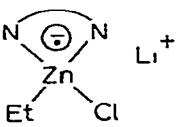
We have investigated the stabilizing effect of Bipy on hitherto unknown monoalkylzinc species.

Results and discussion

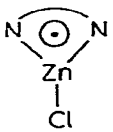
When lithium-2,2′-bipyridine, LiBipy [1] is treated at room temperature with an alkylzinc halide RZnX (R = Me, Et, i-Pr; X = Cl, Br, I) in diethyl ether or 2-methyltetrahydrofuran (MTHF), a deep-brown colour appears initially but vanishes within a second, and at the same time there is gas evolution and formation of a metallic deposit. When these reactions are carried out at —90°C in DME, THF or MTHF, stable red to brown solutions are obtained which show well-defined and superimposable ESR spectra. Computer simulation of the spectrum (Fig. 1) of the reaction product with ethylzinc chloride yielded hydrogen couplings $a_H = 3.48$ G (2H); $a_H = 2.17$ G (2H); $a_H = 0.63$ G (4H) and a nitrogen coupling $a_N = 2.85$ G (2N). The g-value was 2.0023. The identical coupling with both nitrogen atoms and the appearance of couplings with pairs of hydrogen atoms shows that the radical contains a symmetrical Bipy unit. No h.f.s. by zinc ($I = \frac{5}{2}$) or an alkyl group bound to zinc has been found.

We have compared our results with those of Takeshita and Hirota [8] on alkali metal—Bipy complexes in various solvents. Spin delocalization from the Bipy radical-anion onto the metal, and thus covalent bonding, increases in the series K < Na < Li < Zn (cf. Table 1). Assignments are those of Henning [9] and of Gooyer et al. [10].

The reaction of LiBipy with an organozinc halide may give one or more of the paramagnetic products I-IV. Structure IV can be excluded since it would give rise to a triplet spectrum, as observed by Brown and Weissman for a number of similar zinc complexes [4].



(I)



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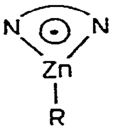

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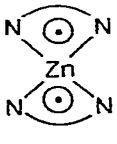

(IV)

(N⌒N = Bipy)

The spectral data obtained from the ethylzinc chloride reaction alone do not allow a choice between the remaining alternatives I, II and III. We have thus compared the ESR spectra of solutions resulting from reactions of LiBipy with the following compounds: Et_2Zn, $ZnCl_2$, EtZnX (X = Cl, Br, I), EtZnBr/EtZnI (1/1), MeZnCl, MeZnBr, MeZnBr/EtZnBr (1/1), and i-PrZnBr. Neither Et_2Zn nor $ZnCl_2$ give paramagnetic products, but in all the other cases fully identical ESR spectra, superimposable on that obtained from ethylzinc chloride and having equal g-values, were recorded. This similarity excluded structures I

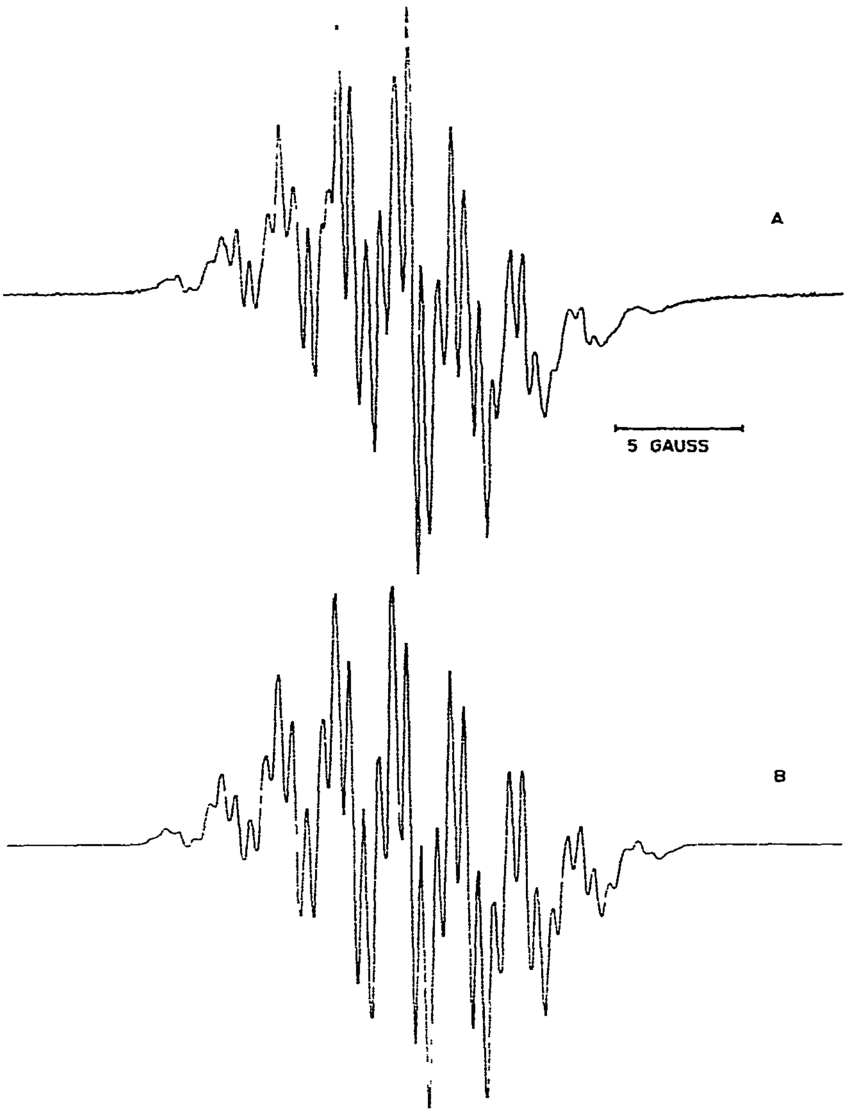

Fig. 1. ESR spectrum of the radical species formed from ethylzinc chloride and lithium 2,2'-bipyridine in MTHF at —76° C; (A) Experimental; (B) Simulated.

TABLE 1

ESR DATA FOR METAL-2,2'-BIPYRIDINE COMPLEXES IN 2-METHYLTETRAHYDROFURAN

Metal	Coupling constants (Gauss)				
	$a_N^{1,1'}$	$a_H^{4,4'}$	$a_H^{5,5'}$	$a_H^{3,3'}$	$a_H^{6,6'}$
K	2.60	1.07	4.67	1.21	0.57
Na	2.63	1.22	4.67	1.22	0.56
Li	2.77	1.74	4.28	0.69	0.47
Zn	2.85	2.17	3.48	0.63	0.63

TABLE 2

HALF-LIFE TIMES FOR THE THERMAL DECOMPOSITIONS OF SOME MONOALKYLZINC RADICAL SPECIES

Compound	Half-life time (sec)	
	at −76°C	at −62°C
MeZn · Bipy	500	—
EtZn · Bipy	2400	35
i-PrZn · Bipy	—	190

and II, since it is very likely that, if halogen were present in the radical, replacement of Cl by Br or I would change the *g*-value or couplings. On the other hand, alkyl group substitution might pass undetected if the effect were very small. Fortunately, a clear influence of the nature of the alkyl group on the thermal stability of the radical species could be established. Table 2 shows the half-life times for the thermal decomposition of some radical species obtained from different alkylzinc halides.

No difference in thermal stability was apparent for radical species generated from ethylzinc chloride, bromide or iodide. These results prove the presence of an alkyl group and the absence of a halogen atom in the radicals, leaving for the reaction products structure III, which we consider to be a σ-complex of a RZn^+ unit and a chelating Bipy radical anion.

The stability of the RZn · Bipy complexes increases with increasing electron-donating capacity as well as with increasing bulkiness of the alkyl group bound to zinc. The observation that the stability of a series of R_2Zn · Bipy complexes increases with increasing electron-donating capacity of R has been explained in terms of π-backbonding from zinc to Bipy [11]. However, for the RZn · Bipy complexes, backdonation of charge into the Bipy radical anion is unlikely.

Solvation of the cationic part of the complex by the strongly coordinating solvent MTHF will be hampered by bulky alkyl groups bound to zinc. However, in the absence of further information we hesitate to explain the observed stability sequence in terms of solvation effects.

Experimental

All experimental work was carried out under nitrogen using bench-top techniques. Solutions were transferred by syringes.

ESR spectra were recorded on a Varian E-4 ESR spectrometer using a modulation frequency of 100 kHz. *g*-Values were measured relative to solid DPPH ($g = 2.0036$). Computer simulations were carried out on a Varian 620-i spectrosystem.

The half-life times of the monoalkylzinc complexes were determined by plotting the amplitude of the central peak in the ESR spectra against time. The temperature in the microwave cavity was monitored with a Chromel/Alumel thermocouple.

Ethyl- and isopropyl-zinc halides were prepared by a published procedure

[12]. Methylzinc halides were prepared in situ by addition of a stoechiometric amount of zinc halide to a dimethylzinc solution in MTHF. LiBipy was made by Herzog's method [1] in MTHF.

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