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Preliminary communication

PARAMAGNETIC ORGANOALUMINUM COMPLEXES

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Summary

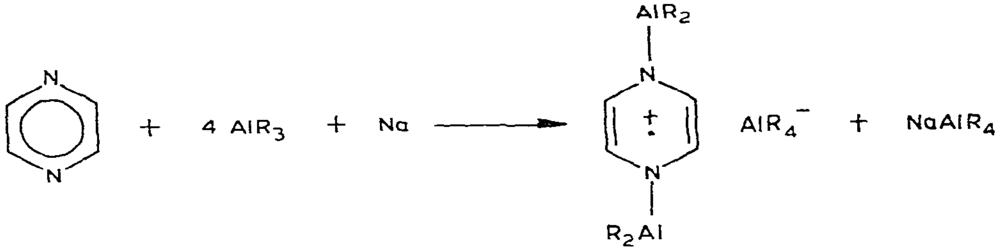
Alkylaluminum compounds react with some aza-aromatics and alkali metals to yield persistent paramagnetic species. Depending on the solvent and the coordinating ability of the azine, radical anions, neutral radicals or radical cations are formed. ESR spectroscopy has been used to elucidate the nature of the radical species.

Paramagnetic organoaluminum compounds are not well known, while radicals such as $R_3Al^{\cdot -}$ or $R_2C^{\cdot}—AlR_3$ [1] could only be generated by high energy irradiation of solids, the reaction of aluminum halides with alkali metals and pyridine was reported to give persistent radicals [2,3], but these have not been adequately characterized [4]. More recently, the detection of a stable $(C_2H_5)_3AlK$ radical was postulated [5], but analysis of the ESR spectrum and the reported data suggest the presence of the biphenyl anion radical instead [6,7].

Current investigations [7] have demonstrated the ability of radical ions with "free" electron pairs to form complexes with acceptor molecules, including alkylaluminums. Variation of the reaction conditions and subsequent ESR analysis have now revealed a remarkable variety of products.

Starting with pyrazine (pz), an azine of high symmetry (D_{2h}), the reaction with AlR_3 and K or Na yielded two different radicals, depending on whether benzene or THF was used as solvent. In both cases, the correct ESR spectrum for a species with two coordinated organoaluminum groups is found, but the ESR coupling constants differ in a distinct way. While the ^{14}N splitting remains almost unchanged, the ^{27}Al and, in particular, the ^{1}H coupling constants are significantly higher when the reaction is performed in THF.

In order to understand this difference it is necessary to take into account the fact that alkylaluminums are partly dissociated in ethers into AlR_4^- and AlR_2^+ ions, whereas there is much less such dissociation in benzene solution [8—10]. Different reactions are also observed when alkylaluminums and electropositive metals are treated with substrates in a variety of solvents [11]. It thus seems likely that the paramagnetic species formed in benzene is the radical anion of the complex $(R_3Al)_2p\dot{z}$, while in THF the pyrazine anion reacts with the stronger acceptor R_2Al^+ to form a radical cation:



(1)

The ESR spectrum of the $(Me_2Al)_2pz^{\cdot+}$ radical cation is shown in Fig. 1, and the spectroscopic parameters of the pyrazine radicals are listed in Table 1 together with those of appropriate reference compounds.

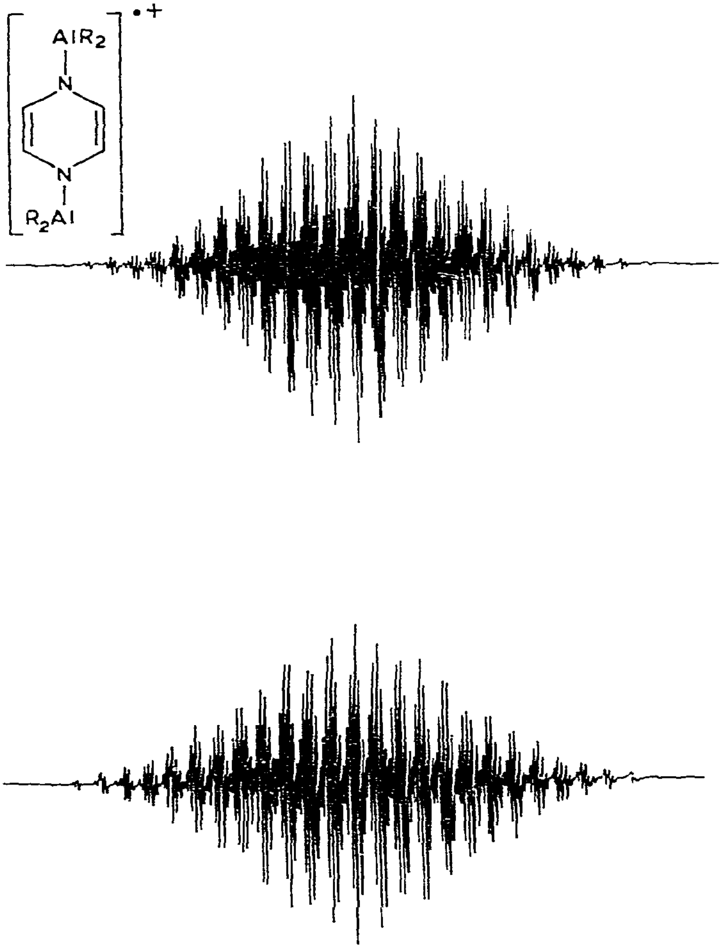
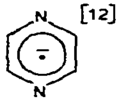
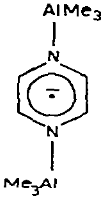
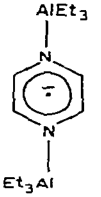
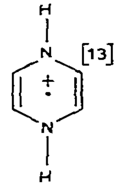
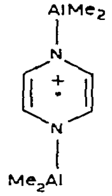
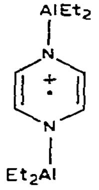


Fig. 1. ESR spectrum of the radical cation $(Me_2Al)_2pz^{\cdot+}$ in THF at room temperature and its computer simulation (lower spectrum).

TABLE 1

ESR PARAMETERS OF PYRAZINE RADICAL ANIONS AND CATIONS AND THEIR ORGANO-ALUMINUM COMPLEXES, THE COUPLING CONSTANTS (mT) WERE DETERMINED AT 300 K

	 [12]			 [13]		
a(N)	0.718	0.687	0.70	0.745	0.694	0.694
a(H)	0.264	0.262	0.262	0.316	0.289	0.290
a(Al)	—	0.221	0.234	—	0.245	0.253
g	2.0035	2.0035	2.0035	2.0034	2.0034	2.0034

There is strong evidence for both structure assignments based on the ESR data. The radical anions $(R_3\,Al)_2\,pz^{\overline{\bullet}}$ have proton coupling constants almost identical to that of pyrazine anion, the ^{14}N splitting being reduced by the coordination. On the other hand, the species found in THF resemble more closely the 1,4-dihydropyrazine radical cation, both the ^{14}N and ring-proton coupling constants showing decrease which could be attributed to delocalisation of spin towards the metal centers.

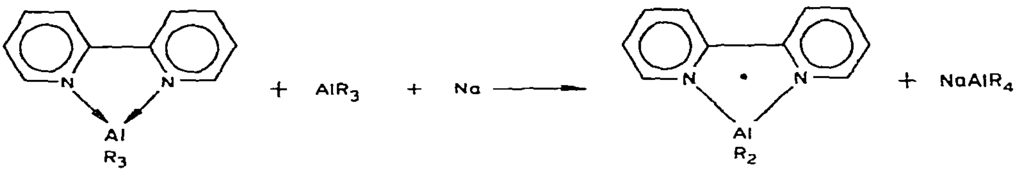
Another representative aza-aromatic compound, one which can coordinate in a bidentate fashion, is 2,2′-dipyridyl (dipy). 1/1 complexes R_3 Al-dipy are well known [10,14], and 2/1 adducts can be obtained in pentane [10]. The reaction of 2,2′-dipyridyl and alkali metals with AlR_3 or $ClAlR_2$ in THF, benzene or heptane yields only one radical, which is considered to be the neutral complex $dipy(AlR_2)^{\bullet}$ for the following reasons:

(1) A relatively large ^{27}Al coupling constant for only one aluminum atom is observed, indicating a chelate structure for the radical.

(2) Formation of the radical and ESR resolution is almost unaffected by the solvent, as would be expected for a free, uncharged radical.

(3) A comparison of the coupling constants with those of the dipy radical anion [15] and the corresponding diquat radical cation [16] (Tab. 2) reveals an intermediate position for the Al-containing radicals.

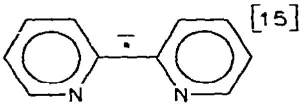
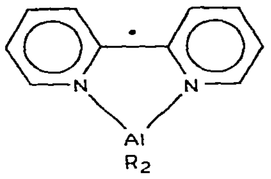
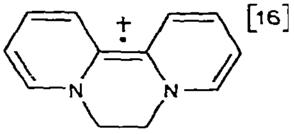
The reaction of 2,2′-dipyridyl with alkylaluminums and alkali metals can thus be represented by eq. 2, the ease of formation of the radical corresponding to its high persistency.



(2)

TABLE 2

ESR PARAMETERS OF PARAMAGNETIC 2,2′-DIPYRIDYL SPECIES, COUPLING CONSTANTS (mT) WERE DETERMINED AT 300 K

		 (R = CH_3 , C_2H_5)		
a(N)	0.241	0.30	0.30	0.408
$a(H_3)$	0.057	0.025	0.030	0.058
$a(H_4)$	0.491	0.30	0.30	0.254
$a(H_5)$	0.166	0.255	0.27	0.290
$a(H_6)$	0.071	0.025	0.030	0.036
a(Al)	—	0.404	0.436	—
g		2.0030	2.0030	

Thus, despite the lack of success in previous attempts [2,3,5] to characterize stable organoaluminum radicals, it is clear that these species can be obtained very readily, identified unambiguously by ESR, and persist over unusually long periods [4].

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