

Organoaluminum Radical Complexes from the Single Electron Transfer Reaction of Diisobutylaluminum Hydride with N-Heterocycles

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Electron Transfer, N-Heterocycles, Diisobutylaluminum Hydride, Radical Complexes, ESR Spectra

Diisobutylaluminum hydride $i\text{Bu}_2\text{AlH}$ reacts with N-heterocycles L (L = pyrazine, 2,2'-bipyridine, 4,4'-bipyridine) *via* single electron transfer to yield 1:1 radical complexes $[\text{L}(\text{Al}^i\text{Bu}_2)]^\cdot$.

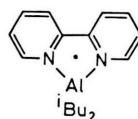
The single electron transfer (SET) reactivity of metal alkyls and hydrides is currently receiving growing attention [1–3]. Thus, it has been demonstrated that aluminum species AlX_3 (X = R [4], H [5], Cl [6]) can react with reducible carbonyl compounds to form aluminium containing radical complexes [4–6]. Besides carbonyl compounds, certain N-heterocycles can also be used as electron transfer substrates [2, 3, 7]; however, molecules such as pyrazine (1), 2,2'-bipyridine (2), and 4,4'-bipyridine (3) do not form radical complexes with trimethylaluminum unless an alkali metal is used for reduction [8, 9].

This report shows that the replacement of one alkyl substituent in AlR_3 by hydrogen permits a single electron transfer to occur in the reaction with the substrates 1, 2 and 3. The reagent used was diisobutylaluminum hydride (DIBAH) which has already found wide application in organic synthesis as a selective reductant [10, 11].

Results and Discussion

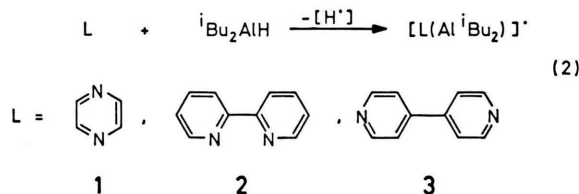
Diisobutylaluminum hydride reacts with the heterocycles 1–3 in THF to yield coloured paramagnetic solutions. These solutions exhibit ESR spectra which prove the formation of organoaluminum complexes (^{27}Al : 100%, $I = 5/2$). The spectrum of the 2,2'-bipyridine complex is shown in Fig. 1. The species can be identified as a chelate complex

$[\text{2}(\text{Al}^i\text{Bu}_2)]^\cdot$ (1) with ESR coupling constants very similar to those of the radical $[\text{2}(\text{AlEt}_2)]^\cdot$ [8, 12].



$$\begin{aligned} a_{\text{N}} &= 0.304 \text{ mT} \\ a_{\text{H}(3,6)} &= 0.028 \text{ mT} \\ a_{\text{H}(4)} &= 0.263 \text{ mT} \\ a_{\text{H}(5)} &= 0.304 \text{ mT} \\ a_{^{27}\text{Al}} &= 0.437 \text{ mT} \end{aligned} \quad (1)$$

The ESR spectra observed after reacting the bridging ligands 1 and 3 with DIBAH are more complex and suggest the coordination of only *one* organoaluminum fragment to the reduced substrate (2).



1:1 complex formation has already been observed in the reactions of 1, 2 and 3 with Grignard reagents [3, 13]; in contrast, the lithium compounds LiR and LiAlH_4 react with pyrazine to yield the 1:2 complex $[\text{1}(\text{Li})_2]^\cdot$ [2]. These differences reflect a decrease of the reducing ability along the series $\text{LiR} > \text{MgR}_2 \sim \text{AlR}_2\text{H} > \text{AlR}_3$.

In analogy to the observations made with organo-magnesium complexes [3, 13], additional alkali metal reduction of the solutions containing DIBAH and 1 or 3 leads to symmetrical 1:2 radical complexes $[\text{1}(\text{Al}^i\text{Bu}_2)_2]^\cdot$ and $[\text{3}(\text{Al}^i\text{Bu}_2)_2]^\cdot$, respectively. Their ESR spectra are identical to those of the corresponding diethylaluminum complexes $[\text{L}(\text{AlEt}_2)_2]^\cdot$ [8, 9]. This ESR spectroscopic similarity of radical complexes with AlEt_2 and Al^iBu_2 fragments is not unexpected since both substituents, ethyl and i butyl, have methylene as the first hydrocarbon group of the alkyl chain in common.

The ability of DIBAH to react in a SET process and to lose the hydrogen in that reaction illustrates the general use of this reagent for reductive hydrogenation [10, 11]. These ESR results add further evidence to the significance of SET processes in reactions involving organometallics [1–3].

Experimental Part

The spectrometer and the techniques used have been described earlier [8]. The radical complexes were obtained by adding diisobutylaluminum hydride (Alfa) to a THF solution of the corresponding heterocycle.

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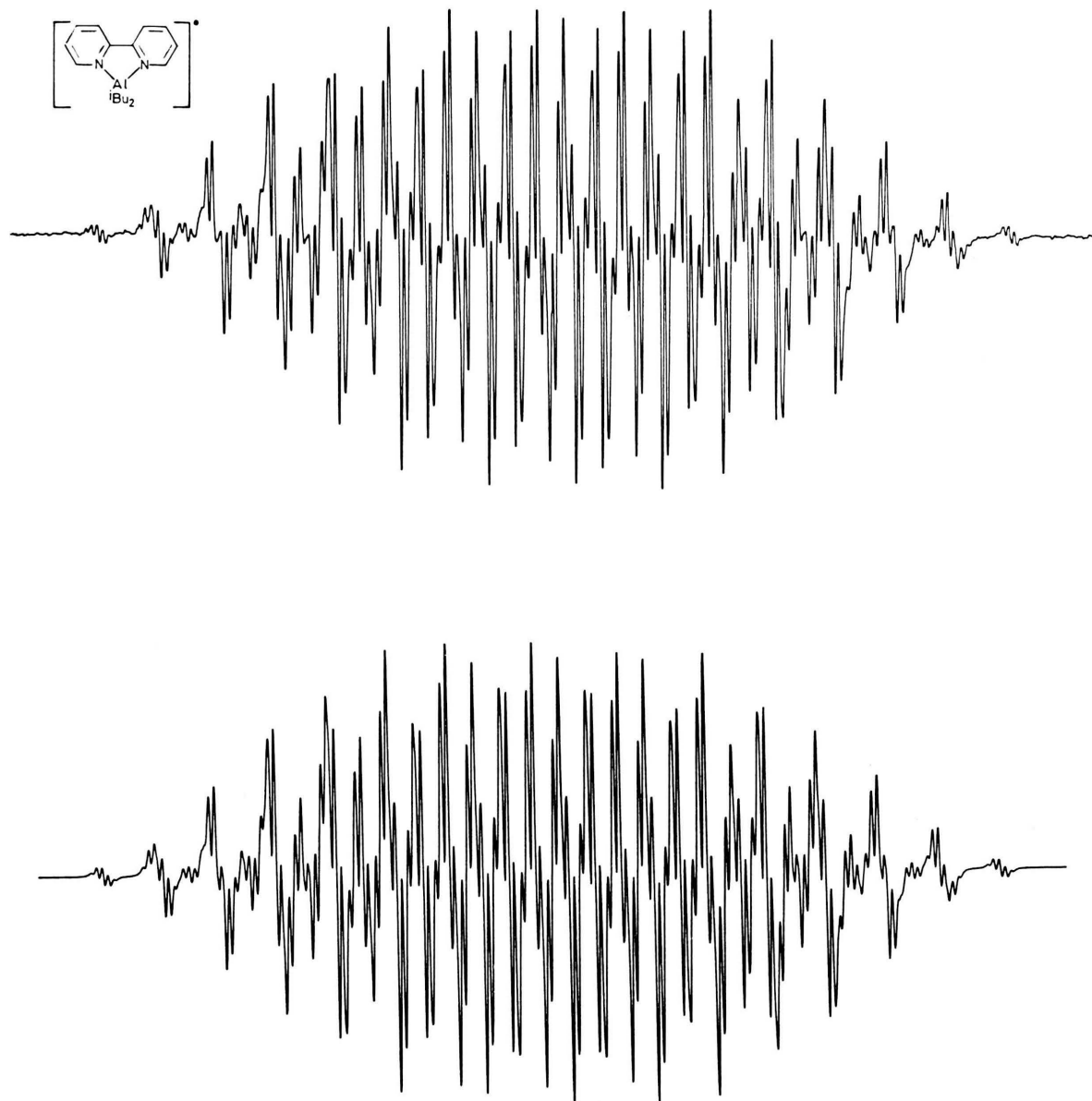


Fig. 1. ESR spectrum of the radical complex formed in the reaction of 2,2'-bipyridine and DIBAH in THF at 300 K. Below: Computer simulation, line width 0.017 mT.

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- [12] The presence of a paramagnetic species with an Al-H bond can be excluded because such a radical would be expected to exhibit $^1\text{H}(\text{Al}-\text{H})$ splitting as well as an essentially different ^{27}Al coupling constant [2].