the values quoted should be reasonable. For association of two phenylalanyl side chains the free energy change is estimated to be −1.4 kcal/mol,[16] which yields the equilibrium constant $K_{NS}$ = 11 M$^{-1}$. Neither the free energy change nor $K_{NS}$ may be compared directly to quantities in the paper because the enhancement factor given by $1 + E_{LL}$ is unitless. However the ratio $(1 + E_{LL})/K_{NS}$ = [B] may be taken as the effective molar concentration of the second intramolecular reactant within our complexes. From Table V the optimum $1 + E_{LL} = 10^{0.67} = 4.7$ for the interaction between the phenylalanyl side chain and coordinated phenethylamine. The corresponding concentration [B] = 0.44 M corresponds to the effective concentration of the second intramolecular reactant. This concentration is greater than that of the complex which is in the mM range in our experiments. For the phenylalanyl–isoleucyl association, the estimated free energy change is −0.8 kcal/mol,[16] which corresponds to the equilibrium constant $K_{NS}$ = 3.9 M$^{-1}$. For the enhancement factor between the isoleucyl side chain and phenethylamine $(1 + E_{LL}) = 10^{0.27} = 1.9$, from which [B] = 0.48 M, similar to the concentration found above. Though approximate, these higher than experimental values for [B] are, like the chelate effect, a result of a high effective amine hydrocarbon concentration due to prior nitrogen coordination to Pd.

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(16) Nēmethy, G.; Scheraga, H. *J. Phys. Chem.* **1962**, *66*, 1773.

# Single Electron Transfer Reaction of Aluminum Hydride with N-Heterocycles. ESR Characterization of the Radical Products

**Wolfgang Kaim**

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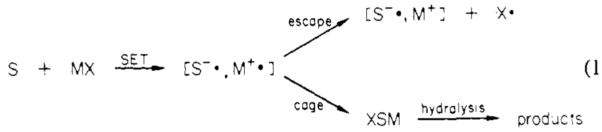
**Abstract:** The single electron transfer (SET) reactions $AlH_3$ and $AlD_3$ in THF with pyrazine (**1**), quinoxaline (**2**), phenazine (**3**), 4,4′-bipyridine (**4**), and 2,2′-bipyridine (**5**) have been studied by electron spin resonance (ESR) spectroscopy. Besides the conventional diamagnetic reduction products, persistent radical complexes are formed as escape products that could be fully characterized by ESR. The paramagnetic species obtained from the bridging systems **1**–**4** are binuclear radical anion complexes $[\mathbf{1}(AlH_3)_2]^{-\cdot}$–$[\mathbf{4}(AlH_3)_2]^{-\cdot}$, whereas the chelating 2,2′-bipyridine radical anion coordinates with one $^{+}AlH_2$ ion from the aluminum hydride dissociation equilibrium. A hyperconjugative model ($\pi_N/\sigma_{Al-H}$) is used to relate the aluminum hydride coupling constants with the coordination geometry in the radical complexes.

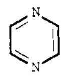
There is rapidly accumulating evidence that the reductions of organic compounds, S, by metal alkyls and hydrides may proceed via single electron transfer (SET) mechanisms (eq 1).[1]



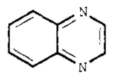
(1)

The frequent observation of relatively persistent radicals as "escape" products by electron spin resonance (ESR) has added evidence to substantiate this mechanism,[2–6] even though the identity of the radical products was not always clearly established (e.g., ref 3a).

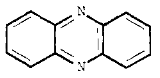
In the course of studies on organometallic radical complexes we have found that the radical anions of aromatic N-heterocycles such as various 1,4-diazines[7] pyrazine (**1**), quinoxaline (**2**), and phenazine (**3**) as well as those from bipyridines **4**[8a] and **5**[8b] are very suitable ligands for organoaluminum species.[9] Presented here is evidence that paramagnetic (open shell) complexes are also produced in SET reactions of aluminum hydrides with the neutral heterocycles,[4c–f] i.e., from diamagnetic (closed shell) precursors. The spectroscopic results obtained previously[9] have thus become very valuable for the analysis and identifications of these new radical complexes.



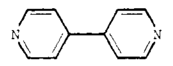
**1**



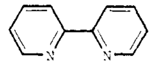
**2**



**3**



**4**



**5**

In this paper, the results of detailed ESR studies on the radical complexes formed from the simple hydride $AlH_3$ (or $AlD_3$) and substrates **1**–**5** will be presented. These new radical complexes offer the advantage that all relevant nuclei, $^{1}H$, $^{2}D$, $^{14}N$, and $^{27}Al$, have nonzero nuclear spins and exhibit ESR coupling constants large enough to be detected under conventional high-resolution

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(1) (a) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 17 and references cited. (b) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79. (c) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545. (d) Cf. also *Chem. Eng. News* **1981**, *59*, No. 15, p 26, and No. 30, p 38.

(2) For an early report on electron-transfer reactions of carbanions cf.: Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am Chem. Soc.* **1964**, *86*, 1807.

(3) (a) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 7779; **1981**, *103*, 5623. (b) Ashby, E. C.; Goel, A. B.; DePriest, R. N.; Prasad, H. S. *Ibid.* **1981**, *103*, 973. (c) Ashby, E. C.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 4783. (d) Ashby, E. C.; Goel, A. B. *J. Organomet. Chem.* **1981**, *221*, C15. (e) Ashby, E. C.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 1879; *J. Am. Chem. Soc.* **1981**, *103*, 4983; *J. Organomet. Chem.* **1981**, *214*, C1. (f) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Tetrahedron Lett.* **1981**, *22*, 4355; Ashby, E. C.; Park, W. S. *Ibid.* **1981**, *22*, 4209.

(4) (a) Kaim, W. *J. Am. Chem. Soc.* **1982**, *104*, 3833. (b) Kaim, W. *Angew. Chem.* **1982**, *94*, 150; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 140; *Angew. Chem. Suppl.* **1982**, 289. (c) Kaim, W. *Angew. Chem.* **1982**, *94*, 150; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 141; *Angew. Chem. Suppl.* **1982**, 298. (d) Kaim, W. *Z. Naturforsch.*, B **1982**, *37B*, 783. (e) Kaim, W.; Lubitz, W. *Angew. Chem.* **1983**, *95*, 915; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 892; *Angew. Chem. Suppl.* **1983**, 1209. (f) Lubitz, W.; Kaim, W., submitted for publication.

(5) Gause, E. M.; Rowlands, J. R. *Spectrosc. Lett.* **1976**, *9*, 219.

(6) (a) Stasko, A.; Malik, L.; Matasova, E.; Tkac, A. *Org. Magn. Reson.* **1981**, *17*, 74 and previous papers in that series. (b) Razuvaev, G. A.; Abakumov, G. A.; Klimov, E. S.; Gladyshev, E. N.; Bayushkin, P. Ya. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 1128.

(7) Kaim, W. *Angew. Chem.* **1983**, *95*, 201; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 171.

(8) (a) Kaim, W. *J. Organomet. Chem.* **1983**, *241*, 157; (b) *Chem. Ber.* **1981**, *114*, 3789.

(9) (a) Kaim, W. *J. Organomet. Chem.* **1981**, *215*, 325. (b) Kaim, W. *Ibid.* **1981**, *215*, 337.

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conditions. In addition, these radical complexes are relatively persistent at room temperature due to the stability of the parent radical $\pi$ systems.

## Experimental Section

**Materials.** The N-heterocycles **1**–**5** were obtained from Aldrich and used as purchased. $AlH_3$ solutions in THF (~0.5 M) were prepared by the method of Brown and Yoon from $LiAlH_4$ and 100% $H_2SO_4$.[10] $AlD_3$ was prepared accordingly, using $LiAlD_4$ (98% D, Aldrich).

**Procedures.** Reductions on the preparative scale were carried out under argon atmosphere. One equivalent of the heterocycle was reacted with approximately 2 molar (six hydride) equiv of $AlH_3$ in THF solution. After completion of the reaction, the solvent was evaporated, the residue carefully hydrolyzed, and the organic product extracted with ether. The identity of the major reaction products[11-14] was established by $^1H$ NMR and mass spectrometry.

For identification of the radical products, the reactions between the heterocyclic substrates and the hydride in THF were run in sealed-glass apparatuses. Colored solutions are formed in all instances, and a 1:3 molar ratio of substrate to $AlH_3$ was found to give satisfactory concentrations of radicals for ESR measurement. For optimum resolution, the concentration of the radicals had to be lowered by dilution. The persistance of the radical complexes at room temperature varies from a few hours (quinoxaline and phenazine radicals) to several days (pyrazine and bipyridine radicals).

**Electron spin resonance spectra** were recorded on a Varian E 9 instrument at 9.5-GHz microwave frequency, 330-mT magnetic field, and 100-kHz field modulation. The spectra were calibrated by using the perylene radical anion in DME.[15]

**ESR spectra simulation** was accomplished with the program ESR, which has been designated to handle a large number of lines.[16] The calculations were carried out at the Hochschulrechenzentrum Frankfurt.

## Results

**Cage Reaction.** The aromatic heterocycles **1**–**5** are reduced by strong hydride reagents such as $LiAlH_4$[3c,12,13] and bis(1,4-dihydro-1-pyridyl)zinc or -magnesium.[14] Products are obtained at various stages of the reduction. The following compounds have been isolated as major products from the reaction with $AlH_3$: piperazine from pyrazine (**1**),[11] 1,2,3,4-tetrahydroquinoxaline from quinoxaline (**2**),[12] 5,10-dihydrophenazine from phenazine (**3**),[12,13] 1,4-dihydro-4,4′-bipyridine from 4,4′-bipyridine (**4**),[14] and 1,4-dihydro-2,2′-bipyridine from 2,2′-bipyridine (**5**).[3c,14]

**Escape Reaction.** The reduction of the heterocycles **1**–**5** by $AlH_3$ (or $AlD_3$) at room temperature in THF is accompanied by the formation of persistent radicals. Highly resolved ESR spectra could be obtained from many of these reaction mixtures, and extensive hyperfine splitting from the interaction of the $^1H$ ($I = 1/2$), $^2D$ ($I = 1$), $^{14}N$ ($I = 1$), and $^{27}Al$ ($I = 5/2$) nuclei with the unpaired electron is evident (Figures 1–6). Analysis of these spectra and hence the identification of the radical complexes have been accomplished by computer simulation and deuteration. The ESR parameters are summarized in Table I, together with the data from reference radicals.[9]

## Discussion

**Reactivity.** Single electron transfer, as shown in eq 1, may be accompanied by the formation of stable paramagnetic products from diamagnetic precursors. SET processes require an electron-rich donor and an electron-poor acceptor.[1b] $AlH_3$ is a strong hydride reductant,[10] and electron-poor substrates such as polynuclear aromatic hydrocarbons,[3b] aromatic ketones,[3a] and complexes with metals in high oxidation states[17,18] can be reduced by $AlH_3$ (and $LiAlH_4$[3a,b,5,18]) via SET. Aromatic N-heterocycles such as **1**–**5** have proven to be exceptionally suitable electron transfer substrates[4] because (i) they have high reduction potentials,[19] (ii)

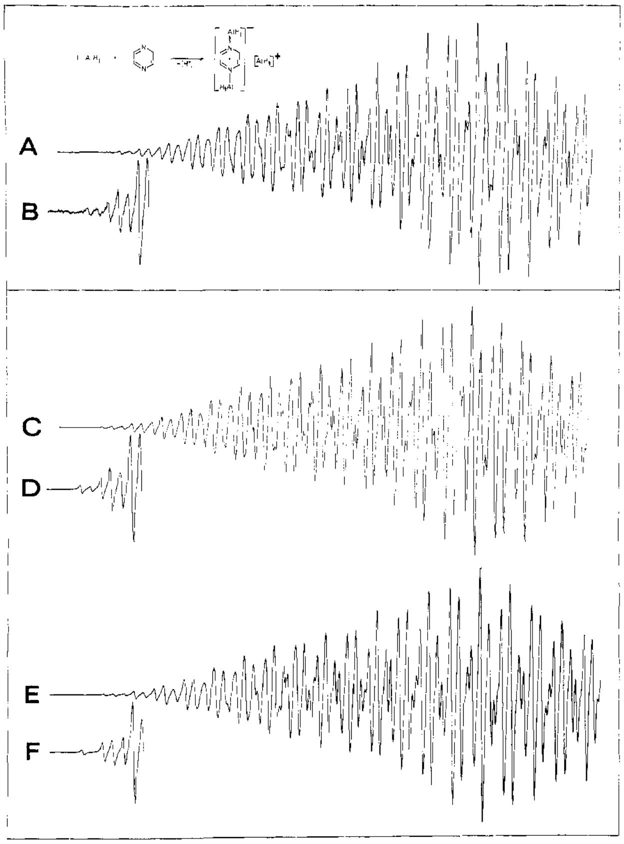

Figure 1. (A) Low-field part of the ESR spectrum of the radical product between pyrazine **1** and $AlH_3$ in THF at 300 K; (B) amplified wing section. Computer simulations distinguish between a complex $[\mathbf{1}(AlH_3)_2]^{-\cdot}$ with six AlH hydrogens (C, D) and a species $[\mathbf{1}(AlH_2)_2]^{+\cdot}$ with four AlH hydrogens (E, F); clearly, the first alternative is correct. Data for computer simulation are from Table I, line width 22 $\mu$T, 1925 theoretical lines for (C, D).

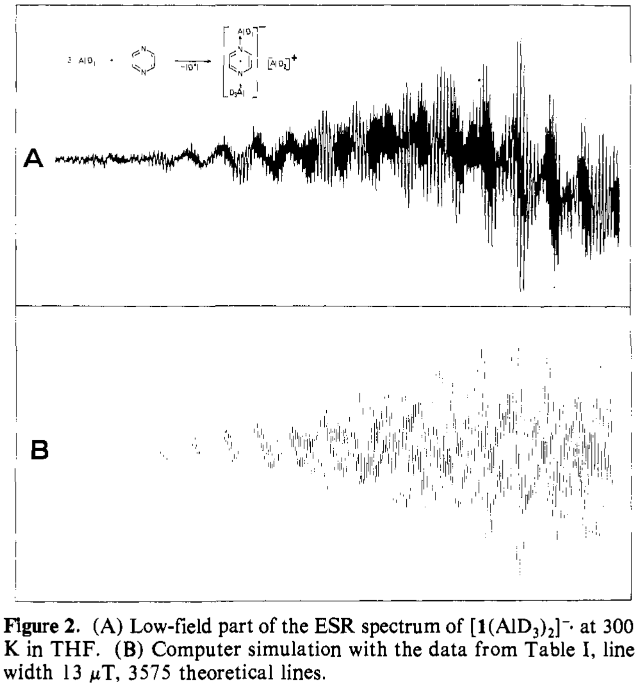

Figure 2. (A) Low-field part of the ESR spectrum of $[\mathbf{1}(AlD_3)_2]^{-\cdot}$ at 300 K in THF. (B) Computer simulation with the data from Table I, line width 13 $\mu$T, 3575 theoretical lines.

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(10) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464.

(11) Cf.: Cheeseman, G. W. H.; Werstiuk, E. S. G. *Adv. Heterocycl. Chem.* **1972**, *14*, 99.

(12) Bohlmann, F. *Chem. Ber.* **1952**, *85*, 390.

(13) Birkofer, L.; Birkofer, A. *Chem. Ber.* **1952**, *85*, 286.

(14) De Koning, A. J.; Budzelaar, P. H. M.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* **1980**, *199*, 153.

(15) Bolton, J. R. *J. Phys. Chem.* **1967**, *71*, 3702.

(16) Modification of the program ESPLOT (Kaim, W.; Bock, H. *J. Organomet. Chem.* **1979**, *164*, 281) by Dr. B. Roth, University of Frankfurt.

(17) Bulychev, B. M.; Kostenko, A. L.; Yakovleva, N. A.; Soloveichik, G. L. *Transition Met. Chem.* **1981**, *6*, 32, and literature cited.

(18) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.

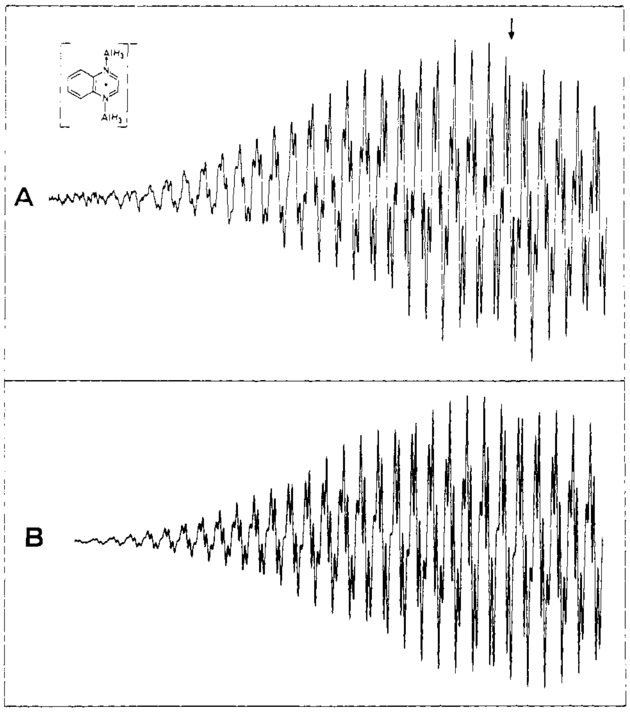

**Figure 3.** (A) Low-field section of the ESR spectrum of $[\mathbf{2}(AlH_3)_2]^{-\cdot}$ at 300 K in THF; the arrow denotes the center of the spectrum. (B) Computer-assisted spectrum synthesis with the data from Table I and a line width of 22 μT; 10395 theoretical lines.

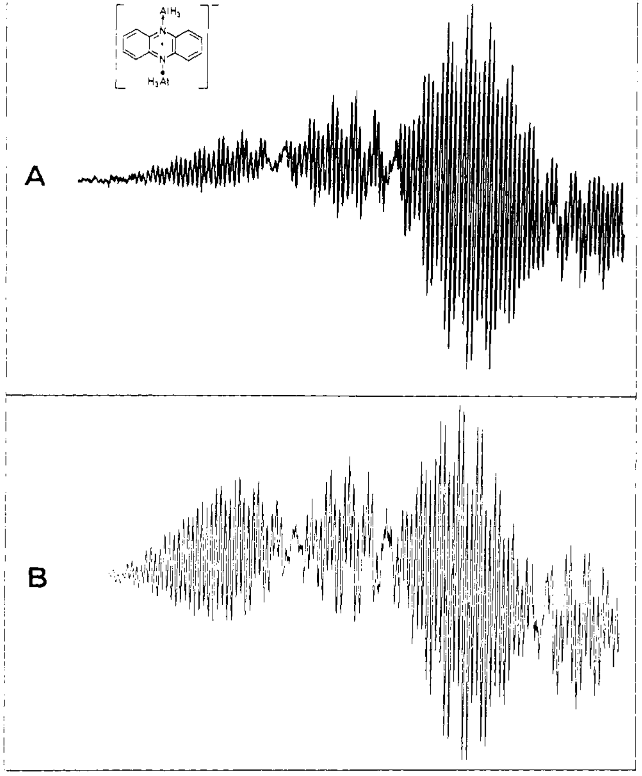

**Figure 4.** (A) Low-field section of the ESR spectrum of the radical complex $[\mathbf{3}(AlH_3)_2]^{-\cdot}$ at 300 K in THF. (B) Computer-assisted spectrum synthesis with the data from Table I and a line width of 22 μT; 9625 theoretical lines.

they form persistent anion radicals,[20] and (iii) they are good complex ligands, in the neutral as well in the reduced forms.[7,8]

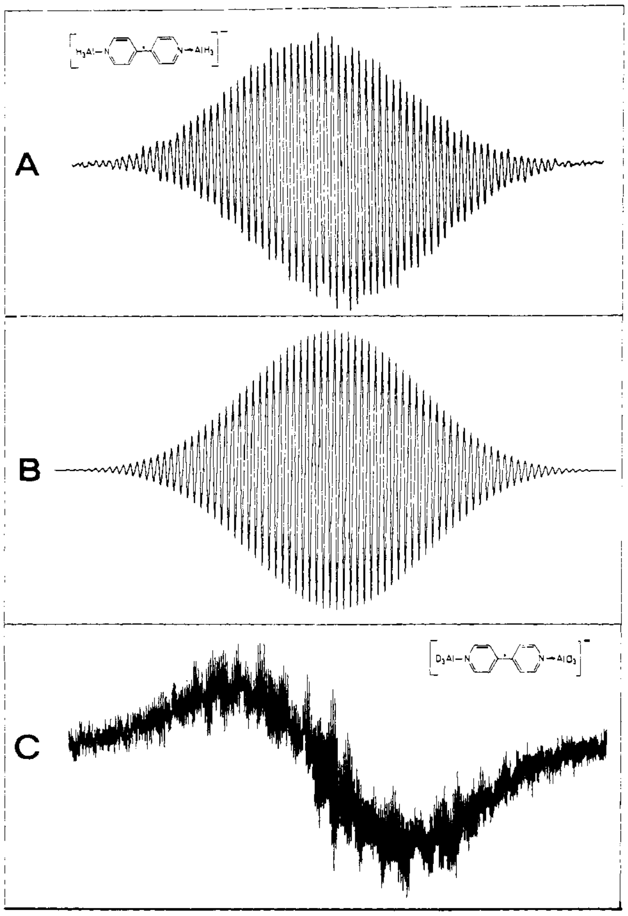

**Figure 5.** (A) ESR spectrum of the complex $[\mathbf{4}(AlH_3)_2]^{-\cdot}$ at 300 K in THF. (B) Computer simulation of spectrum A with the parameters from Table I and a line width of 15 μT; 9625 theoretical lines. (C) Highly resolved ESR spectrum of $[\mathbf{4}(AlD_3)_2]^{-\cdot}$ in THF at 300 K.

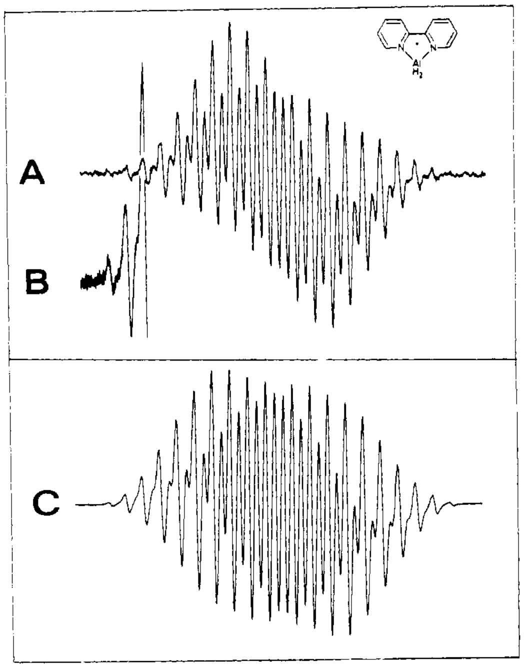

**Figure 6.** (A) ESR spectrum of the radical complex $[\mathbf{5}(AlH_2)]\cdot$ at 300 K in THF. (B) Amplified wing section. (C) Computer-assisted spectrum synthesis with the data from Table I and a line width of 75 μT; 810 theoretical lines.

The formation of radicals from SET reactions between unsaturated N-heterocycles and compounds with Al–H bonds was noted earlier; $LiAlH_4$[3c,4c,5] as well as diisobutylaluminum hydride

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(19) Cf.: Wiberg, K. B.; Lewis, T. P. *J. Am. Chem. Soc.* **1970**, *92*, 7154, or Tabner, B. J.; Yandle, J. R. *J. Chem. Soc. A* **1968**, 381.

(20) Carrington, A.; dos Santos-Veiga, J. *Mol. Phys.* **1962**, *5*, 21.

Table I, ESR Coupling Constants $a_X$($\mu$T) and $g$ Values of the Radical Complexes from SET Reactions of $AlH_3$ or $AlD_3$ with the N-Heterocycles **1-5**[a]

| radical | $a_{^1H}^{CH}$ [d] | $a_{^{14}N}$ | $a_{^{27}Al}$ | $a_{^1H}^{AlH}$ | $g$ |
|---|---|---|---|---|---|
| $[\mathbf{1}(AlH_3)_2]^{-\cdot}$ | 293 | 693 | 282 | 197 | 2.0034 |
| $[\mathbf{1}(AlD_3)_2]^{-\cdot}$ | 292 | 692 | 281 | 30[b] | 2.0034 |
| $[\mathbf{1}(AlMe_3)_2]^{-\cdot}$[a] | 289 | 694 | 245 | | 2.0034 |
| $[\mathbf{2}(AlH_3)_2]^{-\cdot}$[c] | 379 (2)<br>120 (5)<br>120 (6) | 618 | 238 | 145 | 2.0032 |
| $[\mathbf{2}(AlMe_3)_2]^{-\cdot}$[a] | 368 (2)<br>120 (5)<br>120 (6) | 611 | 203 | | 2.0032 |
| $[\mathbf{3}(AlH_3)_2]^{-\cdot}$[c] | 92 (1)<br>122 (2) | 584 | 150 | 122 | 2.0031 |
| $[\mathbf{3}(AlMe_3)_2]^{-\cdot}$[a] | 94 (1)<br>132 (2) | 592 | 132 | | 2.0031 |
| $[\mathbf{4}(AlH_3)_2]^{-\cdot}$ | 96 (2)<br>192 (3) | 347 | 149 | 96 | 2.0031 |
| $[\mathbf{4}(AlD_3)_2]^{-\cdot}$ | 96 (2)<br>192 (3) | 348 | 148 | 15[b] | 2.0031 |
| $[\mathbf{4}(AlMe_3)_2]^{-\cdot}$[a] | 96 (2)<br>192 (3) | 352 | 128 | | 2.0030 |
| $[\mathbf{5}(AlH_2)]\cdot$[c] | <40 (3,6)<br>~290 (4)<br>~290 (5) | ~290 | 460 | 630 | 2.0030 |
| $[\mathbf{5}(Al\text{-}i\text{-}Bu_2)]\cdot$[e] | 28 (3,6)<br>263 (4)<br>304 (5) | 304 | 437 | | 2.0030 |
| $[\mathbf{5}(AlMe_2)]\cdot$[a] | 26 (3,6)<br>259 (4)<br>304 (5) | 304 | 404 | | 2.0030 |

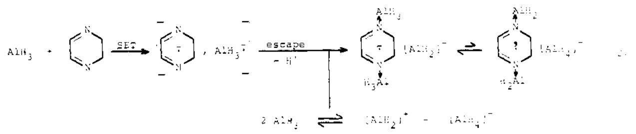
[a] Data from related aluminum alkyl radical complexes are given for comparison;[9] binuclear radicals are reformulated as anionic complexes with trialkylaluminum molecules. [b] $^2$D coupling ($I = 1$; $\mu_D/\mu_H = 0.1535$). [c] $AlD_3$ complexes did not exhibit resolved spectra. [d] Positions are assigned as given in brackets. [e] Reference 4d.

$i$-$Bu_2AlH$[4d] and sodium diethyldihydridoaluminate[4f] react in this way. In contrast, trialkylaluminum molecules do not yield radicals with the compounds **1–5** at room temperature.[21] The radical formation of $R_3Al$ with 2,2′-bipyridine (**5**) reported by Ashby and Goel[3d] is most likely due to the dialkylaluminum hydride impurities usually present in commercially available or redistilled aluminum alkyls.[22]

With respect to the cage reaction, 1,4-dihydro species are the expected reduction products. The formally antiaromatic (8 $\pi$) 1,4-dihydro-1,4-diazines[7,23] are, however, only stable in the case of the dibenzo derivative, 5,10-dihydrophenazine,[12] whereas the ethylenic moieties in 1,4-dihydroquinoxaline and 1,4-dihydropyrazine are susceptible to further rapid hydride reduction. Antiaromatic destabilization does not play a role for the pyridine systems, and 1,4-reduction to air-sensitive 1,4-dihydro systems[14] is observed.

**Radical Structure.** The structures of the complex paramagnetic species resulting from SET reactions of $AlH_3$ with hydrocarbon and carbonyl substrates have not always been fully elucidated. It was proposed by Ashby, Goel, and co-workers[3a] that the observed species would represent the primary pair of radical anion and radical cation (eq 1). Such an assertion, which would indeed imply a "direct" observation of SET,[24] is, however, unlikely since radical cations of simple metal alkyls and hydrides are not persistent at ambient temperatures.[1a] Furthermore, the highly resolved ESR spectra displayed[3a] are clearly indicative of isolated doublet radical species.[24]

When the small molecule pyrazine (**1**) is used as substrate, the structure of such a complex evolving from the escape process in an SET reaction is established here unambiguously (Figures 1 and 2). Computer simulation, deuteration, and the comparison with radicals described previously[9b] aid in determining the stoichiometry of the radical complex. The complex is clearly symmetrical; i.e., both coordination sites of the pyrazine radical anion are employed for complexation when excess $AlH_3$ is used. Careful spectral analysis allows a distinction to be made between two possible structures, viz., the coordination of the reduced pyrazine with two $AlH_3$ molecules or two $^+AlH_2$ cations, which are available from the dissociation equilibrium of $AlH_3$ (eq 2).[25] Meticulous



ESR analysis (Figure 1) shows the first alternative to be correct, a result that suggests a reformulation of the aluminum alkyl radical complexes described previously.[9] Unfortunately, the number of alkyl substituents on the metal cannot be determined either by ESR ($^1$H alkyl coupling constants are too small[4f]) or by ENDOR (electron nuclear double resonance) by which the number of coupling nuclei cannot be determined.[4e,f] Although eq 2 accounts for the stoichiometry of the reaction, the actual sequence of electron transfer and coordinative and dissociative steps is probably much more complex, especially since two nitrogen coordination sites are involved.

Interestingly, a different radical species is obtained when the complex hydride $LiAlH_4$ reacts with pyrazine in THF. In that reaction, as well as in the reaction of excess organolithium reagent with **1**, one observes the triple ion $[\mathbf{1}(Li)_2]^{+\cdot}$ as radical product.[4c,7] This species was described previously as resulting from lithium metal reduction of **1** in the presence of $LiBPh_4$.[26]

The 1,4-diazines quinoxaline (**2**) and phenazine (**3**) react with $AlH_3$ in a similar fashion to pyrazine; however, the radicals are less persistent (Figures 3 and 4). ESR identification of the $AlH_3$

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(21) Cf. the formation of chelate complexes reported by: Thiele, K. H.; Brüser, W. *Z. Anorg. Allg. Chem.* **1966**, *348*, 179; *Ibid.* **1967**, *349*, 33.

(22) Lehmkuhl, H.; Ziegler, K. "Methoden der Organischen Chemie (Houben-Weyl)"; Georg Thieme Verlag: Stuttgart, 1970; Vol. XIII/4, p 29.

(23) Kaim, W. *J. Am. Chem. Soc.* **1983**, *105*, 707.

(24) The formation of primary radical ion pairs in the triplet state by a photoinduced electron transfer reaction in the solid has been reported for quinones and organotin compounds: Emori, S.; Weri, D.; Wan, J. K. S. *Chem. Phys. Lett.* **1981**, *84*, 512.

(25) Nöth, H.; Wiberg, E. *Fortschr. Chem. Forschg.* **1967**, *8*, 321, or Nöth, H.; Ruländer, R. *Inorg. Chem.* **1981**, *20*, 1062.

(26) Al-Baldawi, S. A.; Gough, T. E. *Can. J. Chem.* **1970**, *48*, 2798.

complexes is again aided by the data obtained previously for the trimethylaluminum complexes.[9b]

An interesting alternative to the 1,4-diazines is created by the bipyridines **4** and **5**. 4,4′-Bipyridine behaves like pyrazine in many ways,[7] but as a pyridine derivative it exhibits significantly higher basicity.[27] With $AlH_3$ and $AlD_3$, the radical products formed are again of the ion–2(molecule) type (Figure 5).

Another more simple coordination behavior is observed with the bidentate chelating ligand 2,2′-bipyridine (**5**)

$$\mathbf{5} + AlH_3 \xrightarrow{SET} [\mathbf{5}^{-\cdot},AlH_3^{+\cdot}] \xrightarrow[-H\cdot]{escape} [\mathbf{5}(AlH_2)]\cdot \qquad (3)$$

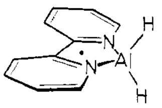
With aluminum hydride, reduced **5** forms a radical complex similar to the one obtained with diisobutylaluminum hydride.[4d] This time, however, a large hyperfine coupling from two additional protons is observed (Figure 6). Obviously, chelating ligands such as 2,2′-bipyridine impose a lower coordination number on the metal in their radical complexes,[28] so that, unlike with the nonchelating ligands **1**–**4**, the $^+AlH_2$ cation and not the $AlH_3$ molecule serves as coordination partner.

**ESR Parameters.** The $g$ values and the coupling constants of the nuclei of the heterocyclic ring system are virtually identical for the aluminum hydride radical complexes reported here and for the aluminum alkyl complexes described previously (Table I). This good agreement illustrates the usefulness of the prior data obtained on the aluminum alkyl complexes[9] and also reveals the nature of such complexes as radical anion–metal electrophile coordination compounds with very little spin transfer to the metal fragments.

The coupling constants $a_{^{27}Al}$ of the coordinated metal are, however, significantly different in both radical complex series; there is a 15% increase of $a_{^{27}Al}$ for the $AlH_n$ radicals relative to the $Al(CH_3)_n$ radicals (Table I).

Despite the fact that the additional hyperfine splitting by the hydrogens on aluminum makes the ESR spectra very complicated, these parameters have provided the information on the radical complex stoichiometry. Deuterium coupling constants could be determined in two instances (Figures 2 and 5). In accordance with theory, they amount to only 15% of the corresponding $^1H$ coupling constants.

The $^1H$(Al–H) coupling parameters also provide some clues for the spin-transfer mechanism in those complexes. Thus, the remarkably large H(Al–H) coupling constant for radical [**5**-($AlH_2$)]· is a consequence of the hyperconjugative spin transfer in a complex of structure I, where the $\sigma_{Al-H}$ bonds are parallel to the $\pi$ system and maximum $\sigma/\pi$ interaction results.



I

A quantitative approach to this H(Al–H) hyperfine splitting is available from a modified Heller/McConnell[29] eq 4, where $B$

$$a_H^{AlH} = B(\cos^2\theta)(\rho_N) \qquad (4)$$

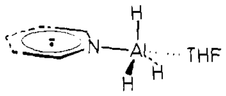
is a constant, $\theta$ is the angle between the $\pi$ system and the $\sigma_{Al-H}$ bond, and $\rho_N$ is the $\pi$ spin population at the nitrogen. An equation of this kind was originally derived to interpret $\beta$-hydrogen splittings in hydrocarbon radicals on the basis of $\sigma/\pi$ hyperconjugation;[29] recently, it has also been applied to heteroatomic systems.[30,31]

Table II. Hückel MO Spin Populations $\rho_N^{\pi}$ [a] and Hyperconjugation Constants $B$ As Calculated from Eq 4 [b]

| radical | $\rho_N^{\pi}$ | $B$, μT |
|---|---|---|
| $[\mathbf{1}(AlH_3)_2]^{-\cdot}$ | 0.246 | 1602 |
| $[\mathbf{2}(AlH_3)_2]^{-\cdot}$ | 0.207 | 1401 |
| $[\mathbf{3}(AlH_3)_2]^{-\cdot}$ | 0.197 | 1239 |
| $[\mathbf{4}(AlH_3)_2]^{-\cdot}$ | 0.122 | 1574 |
| $[\mathbf{5}(AlH_2)]\cdot$ | 0.520[c] | 1212 |

[a] Calculated with $h_N = 1$ and $k_{CN} = 1$. [b] $\cos^2\theta = 0.5$ for a freely rotating $AlH_3$ group; $\cos^2\theta = 1$ for the $AlH_2$ moiety in the fixed conformation (I). [c] The chelate arrangement requires $\rho_N^{\pi} = (2c_N)^2 = 4c_N^2$. See: Whiffen, D. H. *Mol. Phys.* **1963**, *6*, 223.

When $\pi$ spin populations $\rho_N^{\pi}$ from HMO calculations are used, the application of eq 4 to the aluminum hydride radical complexes at hand produces a series of constants $B$ (Table II), illustrating the validity of this approach as well as the expected breakdown of the model when steric effects such as peri interactions in the phenazine complex become important. This model cannot however, distinguish well enough between tetra- and pentacoordination at aluminum, $AlH_3$ is known to form both types of complexes with N-donors,[25,32] and it could be that there is additional coordination of one THF molecule in the axis for the $AlH_3$ complexes (II).



II

## Conclusion

Paramagnetic products from the reaction of $AlH_3$ and the N-heterocycles **1**–**5** have been identified by detailed ESR studies as radical anion complexes of either $AlH_3$ molecules or of the $^+AlH_2$ ion. Obviously, aspects of coordination play an important role in determining not only the selectivities in conventional hydride reductions[33] but also the radical product selectivity in SET reactions. It should, therefore, become a general practice to characterize not only the diamagnetic but also the paramagnetic reaction products in SET reactions as thoroughly as possible by using high-resolution ESR, ENDOR, or TRIPLE resonance.[4e,f] Although the radical anion complexes found in SET reactions may sometimes be side products rather than intermediates, the relatively rapid decay of the radicals described here as well as the fact that they still contain active hydride equivalents renders their function as true intermediates highly possible. Although the use of $AlH_3$ itself as a reductant is rather limited, a recent communication by Ashby and co-workers[34] has provided evidence that $AlH_3$ is the actual one electron transfer agent in the reduction of alkyl halides by $LiAlH_4$, thereby emphasizing the need to understand its SET reactivity.

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**Registry No.** $[\mathbf{1}(AlH_3)_2]^{-\cdot}$, 88525-64-8; $[\mathbf{1}(AlD_3)_2]^{-\cdot}$, 88525-65-9; $[\mathbf{2}(AlH_3)_2]^{-\cdot}$, 88525-66-0; $[\mathbf{3}(AlH_3)_2]^{-\cdot}$, 88525-67-1; $[\mathbf{4}(AlH_3)_2]^{-\cdot}$, 88525-68-2; $[\mathbf{4}(AlD_3)_2]^{-\cdot}$, 88525-69-3; $[\mathbf{5}(AlH_2)]\cdot$, 88525-70-6; $D_2$, 7782-39-0.

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(27) p$K_1$(**1**) = 0.65, p$K_2$(**1**) = −5.78: Chia, A. S.; Trimble, R. F. *J. Phys. Chem.* **1961**, *65*, 863. p$K_1$(**4**) = 4.82, p$K_2$(**4**) = 3.17: Krumholz, P. *J. Am. Chem. Soc.* **1951**, *73*, 3487.

(28) For other examples cf.: van Koten, G.; Jastrzebski, J. T. B. H.; Vrieze, K. *J. Organomet. Chem.* **1983**, *250*, 49.

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