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Trapping of the coordinatively unsaturated organosilicon anion radical $Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3^{\cdot-}$ by double ate-complex formation with AlR_3

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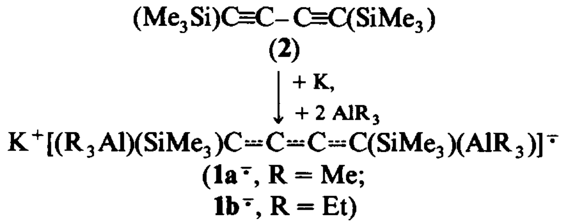
Abstract

Reaction of 1,4-bis(trimethylsilyl)-1,3-butadiyne with AlR_3 and potassium in THF has led to observation of the first examples of persistent radical di-ate complexes, $[(R_3Al)(Me_3Si)C{=}C{=}C{=}C(SiMe_3)(AlR_3)]^{\cdot-}$, which have been characterized by ESR spectroscopy.

Complexation of Lewis acidic aluminium compounds AlX_3 with radicals or radical ions has been observed in a number of cases where the coordination site is a heteroatom such as N [1], P [2], O [3,4], or S [5]. No such radical complexes have been reported in the case of carbanionic coordination centers, despite the fact that several remarkable compounds were isolated from reactions between alkali metals, unsaturated hydrocarbons, and aluminium alkyls [6–11]. In fact, there are only a few C-coordinated σ-complexes of anion radicals known at all [12], and those mainly involve diarylcarbenes [13].

Taking advantage of the facile reduction of 1,3-diynes and of the electron accepting ability of the trimethylsilyl group [14], we have obtained evidence for reaction (1), which leads to persistent radical di-ate complexes $\mathbf{1}^{\cdot-}$.



$$\begin{array}{c}(Me_3Si)C{\equiv}C{-}C{\equiv}C(SiMe_3)\\ (\mathbf{2})\\ \Big\downarrow{\scriptstyle +K,\ +2\,AlR_3}\\ K^+[(R_3Al)(SiMe_3)C{=}C{=}C{=}C(SiMe_3)(AlR_3)]^{\cdot-}\\ (\mathbf{1a}^{\cdot-},\ R = Me;\\ \mathbf{1b}^{\cdot-},\ R = Et)\end{array} \qquad (1)$$

Potassium metal reduction of 1,4-bis(trimethylsilyl)-1,3-butadiyne (**2**) in THF containing an excess of AlR_3 results in the formation of paramagnetic solutions, the ESR spectra of which (Fig. 1) clearly indicate hyperfine interaction of the unpaired electron with two ^{27}Al nuclei ($I = 5/2$, 100% natural abundance). Additional split-

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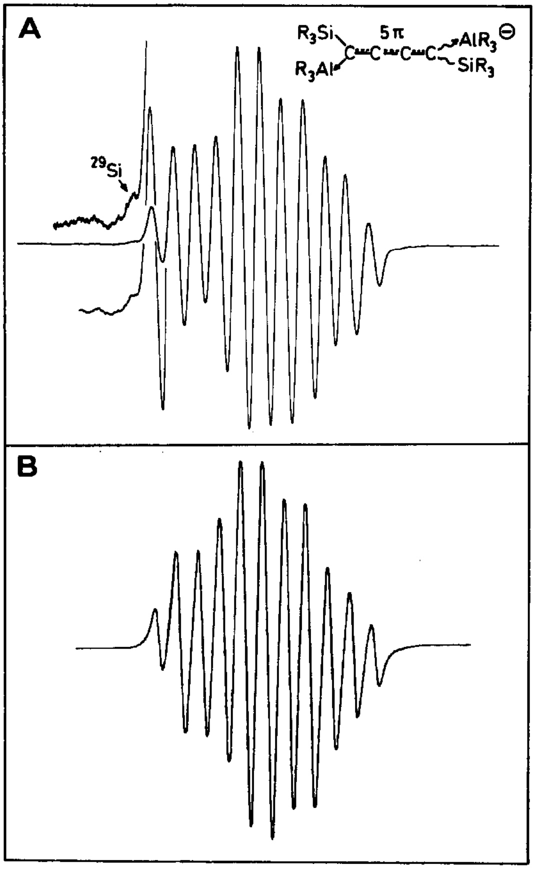
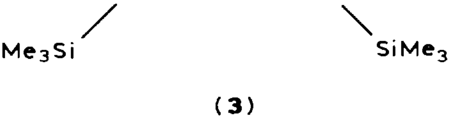


Fig. 1. ESR spectrum of the anion radical di-ate complex $[(Et_3Al)(Me_3Si)C{=}C{=}C{=}C(SiMe_3)(AlEt_3)]^{\cdot-}$ at 300 K in THF solution (A) and a computer simulated spectrum (B). The slight asymmetry is due to a paramagnetic impurity, ^{29}Si isotope coupling is visible as satellite feature of the amplified outermost ^{27}Al hyperfine line in the experimental spectrum.

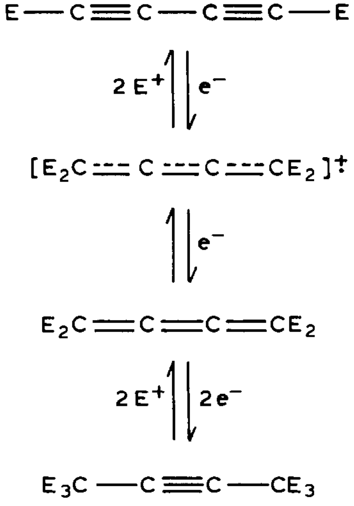
ting due to ^{29}Si isotopes in natural abundances (4.7%, $I = 1/2$) shows that there are only two silicon atoms present in the radical; there is no evidence for the formation of the anion radical of tetrakis(trimethylsilyl)butatriene (3) that was observed after reaction of **2** with potassium metal alone [14].



(3)

Despite earlier claims, the "free" anion radical of **2** itself could not be detected in solution, even at low temperatures [14]; formation of $\mathbf{1}^{\cdot-}$ and $\mathbf{3}^{\cdot-}$ suggests that coordinative unsaturation might be a reason for the instability of $\mathbf{2}^{\cdot-}$.

The 5 electron-4 center anion radicals $\mathbf{1}^{\cdot-}$ may be formulated in terms of a delocalized 1,2,3-butatriene structure (1); incidentally, the radical anion $\mathbf{1a}^{\cdot-}$ is isoelectronic [15] with the radical cation $\mathbf{3}^{\cdot+}$, which has been obtained by oxidative desilylation with $AlCl_3$ in CH_2Cl_2 of the fully reduced member in the redox/coordination scheme (eq. 2), viz., hexakis(trimethylsilyl)-2-butyne (**4**) [14].



(2)

(e.g. E = $SiMe_3$)

(**4**)

1,4-Coordination of electrophilic main group metal species to reduced 1,3-butadiynes is suggested by MO considerations, and is also in agreement with results for Li^+ [16] and organoaluminium complexes of doubly reduced systems [9–11]; incidentally, the work by Hoberg et al. contains a report on doubly reduced di-ate complexes related to $\mathbf{1}^{\cdot-}$, such as $[(AlR_3)PhC{=}C{=}C{=}CPh(AlR_3)]^{2-}$ [9].

Coupling constants of the radicals $\mathbf{1}^{\cdot-}$ and $\mathbf{3}^{\cdot-}$ as given in Table 1 show that the spin distributions are very similar (^{29}Si isotope couplings). Division of the measured splittings for the heteronuclei by the isotropic hyperfine coupling constants A_{iso} [17] reveals slightly higher spin densities at the positively charged silicon centers than at the more negatively charged (ate-complex!) ^{27}Al nuclei. The detailed geometry of the butatriene-type radicals $\mathbf{1}^{\cdot-}$, i.e. whether the *Z* or *E* configuration is preferred if there is a planar arrangement, cannot be established conclusively from the ESR data.

Table 1

ESR coupling constants a (mT) of organometallic butatriene radical ions [a]

Radical	$a(^{29}Si)$	$a(^{27}Al)$	a_{Si}/A_{iso} [b]	a_{Al}/A_{iso} [b]
$\mathbf{1a}^{\cdot-}$	0.55	0.301	0.0045	0.0031
$\mathbf{1b}^{\cdot-}$	0.55	0.309	0.0045	0.0031
$\mathbf{3}^{\cdot-}$ [c]	0.485		0.0040	
$\mathbf{3}^{\cdot+}$ [c]	1.210		0.0099	

[a] Measurements at 300 K in THF (anions) or CH_2Cl_2 (cation). [b] Isotropic hyperfine coupling constants A_{iso} from ref. 17. [c] From ref. 14.

Although a number of other reducible hydrocarbons, including cyclooctatetraene and aromatics, have also been studied under the conditions described here, they did not yield persistent radical ate-complexes, possibly because of their tendency to form exclusively (radical) π complexes [12]. The 1,4-bis(trimethylsilyl)-1,3-butadiyne system seems unique in that it provides strongly basic C-coordination sites in the 1,4-position, thereby facilitating the formation of persistent radical ate-complexes, before undergoing further reduction [10,11], elimination [18], or addition to C=C multiple bonds [19]. This result demonstrates for the first time that coordinative stabilization of radicals and radical ions [12,20] in organometallic chemistry can occur even in the absence of heteroatomic donor centers, but only a few stable carbon radicals, such as 1,3-butadiyne and diarylcarbene anions [13] or isonitriles [21] seem to provide sufficient space for σ coordination of organometallic fragments.

Experimental

Commercially available materials were used in the preparation of $\mathbf{1}^{\cdot-}$. The reactions between **2**, AlR_3, and distilled potassium in tetrahydrofuran solution were carried out in sealed glass tubes with capillaries for ESR measurements. Spectra were recorded on a Varian E9 spectrometer at 300 K, and calibrated by use of the perylene radical anion as reference [22]. Computer simulation of ESR spectra was carried out with a published program [23] on a PC system.

Acknowledgement

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