(1) The fragment ions observed from $(C_2H_2)_3{}^+$ are identical with those from other stable $C_6H_6{}^+$ isomers.

(2) The AE of $C_4H_4{}^+$ from $(C_2H_2)_3$ was found to be lower in energy than the IE of $(C_2H_2)_2$.

(3) The measured AE's for the formation of $C_4H_3{}^+$ and $C_4H_2{}^+$ from the $(C_2H_2)_3$ in the total energy scale are in agreement with the AE's of these two ions from 2,4-hexadiyne, 1,5-hexadiyne, and benzene.

(4) The relative intensities of the $C_6H_5{}^+$, $C_6H_4{}^+$, and $C_3H_3{}^+$ ions from $(C_2H_2)_3$ and those reported previously from benzene, 2,4-hexadiyne, and 1,3-hexadiyne in the total energy range 16.87–17.17 eV were found to be in fair agreement.

Acknowledgment. We would like to thank Mr. J. Erickson and Mr. S. H. Linn for their assistance in obtaining part of the data for this experiment. The authors also wish to thank the referees for their comments which have led us to perform a more thorough analysis of our experimental data.

Registry No. $C_6H_6{}^+$, 34504-50-2; $C_6H_5{}^+$, 17333-73-2; CH_2CHCCH^+, 59699-48-8; $C_3H_3{}^+$, 26810-74-2; $C_4H_4{}^+$, 79105-72-9; $C_6H_4{}^+$, 70220-84-7; 2,4-hexadiyne, 2809-69-0; 1,5-hexadiyne, 628-16-0; benzene, 71-43-2; 1,3-hexadiyne, 4447-21-6.

Electronic Structure of Bridged Dialuminum Compounds

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Abstract: Geometry-optimized 3-21G ab initio calculations were performed on the $[R_3Al\cdots H\cdots AlR_3]^-$ ion with R = H or R = CH_3. The lowest energy was obtained with a linear Al···H···Al structure. Small rotational barriers and bending energies are also reported. In addition, the structure of $[H_3Al\cdots Cl\cdots AlH_3]^-$ was calculated for comparison and found to be bent.

Atwood[2] et al. have reported an X-ray diffraction study of several electron-deficient species that possess a linear, singly hydrogen-bridged $[(CH_3)_3Al\cdots H\cdots Al(CH_3)_3]^-$ structure. This is particularly important, since it has been widely recognized that direct metal-to-metal bonding, resulting in a nonlinear structure (such as in the $[Cl_3AlClAlCl_3]^-$ ion) may be significant.[3] The bonding present in such electron-deficient compounds has been widely discussed in the literature.[4]

We wish to report ab initio geometry-optimized calculations on the $[R_3Al\cdots H\cdots AlR_3]^-$ ion, where R = H and R = CH_3, and, for comparison, $[H_3AlClAlH_3]^-$. The calculations were performed with the GAUSSIAN-80 program with a 3-21G basis set. The optimized geometry parameters are given in Table I. The linear Al···H···Al bond is of importance and reproduces the experimental data. That the bridging Al···H is longer than the terminal Al–H bond is expected by considering either the resonance structures in **1** or on the basis of the bonding molecular orbital fragment shown in **2**, which makes up the electron-deficient bond.

$$H_3\bar{A}l\text{—}H \quad AlH_3 \longleftrightarrow H_3Al \quad H\text{—}\bar{A}lH_3$$

1

2

Table I. Geometry-Optimized Parameters and Energies for $[R_3Al\cdots H\cdots AlR_3]^-$ Species

	R = H, 3-21G	R = CH_3[a], 3-21G[a]	R = CH_3, exptl[2]
Al···H, Å	1.720	1.731	1.665
R–Al, Å	1.632	2.030	
Al···H···Al, deg	180.0	180.0	
R–Al···H, deg	104.4	104.0	
energy, au	−485.226	−718.2540	

[a] The H–C length and H–C–Al angle optimized to 1.091 Å and 111.4°, respectively.

Table II. Geometry-Optimized Parameters and Energy for $[R_3Al\cdots Cl\cdots AlR_3]^-$ Species

	R = H, 3-21G	R = Cl, exptl[3]
Al···Cl, Å	2.467	2.24
R–Al, Å	1.621	2.10
Al···Cl···Al, deg	132.6	110.0
R–Al···Cl, deg	103.0	
energy, au	−942.0464	

On examination of the nature of the Al···H···Al central bond, it is found to exhibit a similarity to a hydrogen bond where the electron-donating atom would be the hydrogen while the formally vacant aluminum sp^3 hybrid would be functioning as an acceptor orbital constituting what we would call an "aluminum bond". Similar bonding has been found in organolithium compounds to exist between oligomers.[5]

The rotational barriers, calculated as being less than 1 kcal/mol, are predictably small. This might be interpreted as being due to negligible direct interaction between the AlH_3 units. The Al–Al distance is in excess of 3.4 Å. An additional cause may be that the central hydrogen bears only an s-type orbital. We have also performed optimized 3-21G calculations on ethane-like Al_2H_6 in D_{3h} and D_{3d} geometries and again obtained a barrier of <1 kcal/mol even though the Al–Al distance now optimizes to approximately 2.76 Å. Another point concerning interaction is that

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(1) (a) Brooklyn College. (b) John Jay College. (c) Queensborough College.

(2) (a) Atwood, J. L.; Rogers, M. J.; Zaworotko, M. Y.; Hunter, W. E.; Hrncir, D. C., presented at the Tenth International Conference on Organometallic Chemistry, Toronto, August, 1981. (b) Atwood, J. L.; Hrncir, D. C.; Rogers, M. J.; Howard, J. A. K.; *J. Am. Chem. Soc.*, in press.

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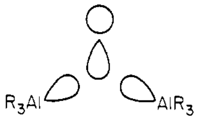
the R–Al···H angle optimizes to nearly the same value for both R = H and R = CH_3.

We have calculated the energy required to produce small deformations from linearity around the Al···H···Al bond by using our best structure and inducing angles of 5° and 10°, without performing any further geometry optimization. The energy required for these excursions was 0.04 and 0.14 kcal/mol, respectively.

For purposes of comparison, we have studied the $[H_3AlClAlH_3]^-$ analogue of the $[Cl_3AlClAlCl_3]^-$ ion, which is known to have a nonlinear Al–Cl–Al bond. We have performed the 3-21G optimization of the structure of $[H_3AlClAlH_3]^-$. The results are shown in Table II along with experimental data obtained for $[Cl_3AlClAlCl_3]^-$ ion. We ascribe the nonlinearity of the central three-center bond to an increased stabilization that occurs for a molecular orbital of a_1 symmetry (C_{2v}) upon bending (see **3**).



3

The orbital energy of the MO shown in **3** is found to decrease as the bend increases (a change of −0.6 kcal/mol occurs in going from a 180° to a 140° angle). Gimarc[6] and, earlier, Walsh[7] have studied such deformations. Clearly, the participation of the occupied p orbitals is important in producing a nonlinear structure.

Acknowledgment. We wish to acknowledge Professor Atwood for kindly providing us with a copy of his paper prior to publication.

Registry No. $H_3AlHAlH_3^-$, 65856-39-5; $(CH_3)_3AlHAl(CH_3)_3^-$, 81523-03-7.

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CIDNP and Triplet-State Reactivity of Biradicals

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Abstract: From an analysis of magnetic-field-dependent (mfd) CIDNP effects obtained during cycloalkanone photolysis, it is concluded that the self-reactions of the intermediate biradicals occur not only from the singlet state but also from the triplet state. Triplet-state reactivity is presumably mediated by spin–orbit coupling, allowing transitions to occur directly from the triplet-biradical manifold to singlet product states. As the product selectivity of the triplet-state reactions in general will be different from that of the singlet reactions, this provides a new spin-sorting pathway, allowing T_0–S type CIDNP effects to be generated in biradical products. These effects have indeed been observed for 1,4, 1,5, and 1,6 biradicals. A previously developed theory for biradical CIDNP based on the stochastic Liouville equation is extended to include product formation from triplet-state biradicals. The theory can satisfactorily account for ^1H mfd CIDNP curves obtained for cyclohexanone (**1**) and bicyclo[3.2.1]octan-2-one (**2**). Furthermore, simulations of ^{13}C mfd curves recently obtained by Doubleday for 2-phenylcycloalkanones yielded both triplet- and singlet-state-reactivity parameters for the intermediate acyl–alkyl biradicals. It can be concluded that the direct reaction from the triplet state for these biradicals leads predominantly to ketene product; cyclization to the parent ketone is also relatively favorable whereas formation of alkenal is negligible. These reactivities are quite different from those of singlet-state biradicals. The effects of spin–orbit coupling in acyl–alkyl biradicals are qualitatively discussed, and an attempt is made to rationalize the observed trends by considering biradical conformations in which this interaction is maximized.

Introduction

Biradicals constitute an important class of reaction intermediates, but because of their short lifetimes, remain an elusive species. Only recently has a true biradical intermediate (the one that occurs in the Norrish type II photoreaction of valerophenone) been directly observed in a flash photolysis experiment.[2] A somewhat less direct but often more simple way of detecting biradicals is provided by the chemically induced dynamic nuclear polarization (CIDNP) method. Here, the nuclear-spin polarization patterns observed in reaction products and the magnetic-field dependence thereof give information on the intermediacy of biradicals and on their dynamic behavior and magnetic parameters (hyperfine couplings, exchange interaction, etc.).[3–6]

Most high-field CIDNP spectra of biradicals generated from triplet-state precursors show exclusively emission effects[3–6] as opposed to the mixtures of emission and enhanced absorption that are characteristic for radical-pair CIDNP.[7] The fact that nuclear-spin polarization is observed in a biradical product indicates that electron–nuclear hyperfine coupling contributes significantly to the intersystem crossing in the biradical. The emission effect is easily explained by noting that in the presence of an exchange interaction between the "unpaired" electrons, hyperfine induced triplet–singlet (T → S) transitions from *one* of the three triplet states (the T_- state) favored. Provided the biradical has a singlet ground state, this leads to overpopulation of the higher nuclear-spin levels in the products. This effect was first reported by Closs[8] and has subsequently been observed for many biradicals with relatively long flexible chains.[3–6] We have recently developed a quantitative theory based on the stochastic Liouville equation to account for this effect and its magnetic-field dependence.[5] In the early seventies, however, anomalies had already been observed in several laboratories, especially for the short-chain biradicals.[9]

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