

can be thought of as providing the driving force behind the reduction of ketones to alcohols by labilizing the α hydrogen of the amide. The last three entries in Table III indicate that the complexation energy between reactants and between products is nearly equal since the enthalpy of reaction is nearly the same as for monomers.

Conclusion

The barrier for hydride transfer of a methyl hydrogen in LiNHCH_3 to formaldehyde has been calculated for the lithium amide-formaldehyde complex and for the complex of the lithium amide dimer model. While the former pathway has a lower barrier (17.8 kcal/mol, 3-21+G//MNDO) than the latter (30.6 kcal/mol, 3-21+G//MNDO), the latter pathway is strongly stabilized through complexation with the additional lithium amide. Unless solvent effects stabilize the former pathway by more than 43.5 kcal/mol relative to the latter, the reaction is predicted to proceed by way of the lithium amide dimer.

While the lithium amide was assumed to be dimeric, the hydride transfer actually may occur from an activated complex in a higher

degree of aggregation. The basic nature of the reaction, however, from such a reactant complex to a more stable product complex is not expected to change. In this regard, it is interesting to note that a recent NMR study²³ of butyllithium aggregates in THF has shown that the dimer is approximately 10 times as reactive as the tetramer toward benzaldehyde, while no evidence for a butyllithium monomer could be found even at low concentrations.

Further studies are under way to explore the mechanism of the reaction of other metalated bases with ketones, in particular the origin of C-substituted and N-substituted products formed from ambient anions.

Acknowledgment. Computer time for this study was donated by the Auburn University Computer Center. I thank Prof. Paul von Ragué Schleyer for making a preprint of his work available and for valuable suggestions as a referee.

Registry No. LiNHCH_3 , 37123-26-5; formaldehyde, 50-00-0.

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An ESR Study of the Reaction of Aluminum Atoms with Buta-1,3-diene: Cheletropic Cycloaddition and Substituted Allyl Formation¹

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Abstract: Electron spin resonance spectroscopic studies of the reaction of ground-state aluminum atoms with buta-1,3-diene in adamantane at 77 K in a rotating cryostat have demonstrated the formation of two major paramagnetic products, a σ -bonded aluminum cyclopentene and an aluminum-substituted allyl. The aluminum cyclopentene has the parameters $a_{\text{Al}} = 229.8$ G, $a_{\text{H}}(4) = 3.7$ G, $a_{\text{H}}(2) = 2.5$ G, and $g = 2.0025$. This is an example of a cheletropic reaction, and ab initio MO calculations place the aluminum atom below the plane of the butadiene carbon framework at an angle of about 42°. The aluminum-substituted allyl has the parameters $a_{\text{Al}} = 33.5$ G, $a_{\text{H}}(1) = 4$ G, $a_{\text{H}}(2) = 14$ G, $a_{\text{H}}(3) = 11$ G, and $g = 2.0023$ and is possibly a "bridged" species.

Uncertainty still surrounds the nature of the primary products from reaction of ground-state aluminum atoms ($3s^23p^1$) with alkenes and alkydienes. Electron spin resonance (ESR) studies of the reaction with ethylene in solid Ar at 4 K indicate a weak π -complex in which the C=C bond remains intact but in which some electron transfer occurs from the full π orbitals to an empty Al 3p orbital and in which the unpaired electron resides mainly in a 3p orbital parallel to the double bond.² On the other hand σ -bonded aluminocyclopropanes are indicated by the deuterolysis experiments of Skell et al., who reacted the condensates prepared at 77 K with D_2O .³ 3,4-Dideuteriobut-1-ene was formed from buta-1,3-diene, indicating interaction with only one double bond of the conjugated system. However, caution must be exercised in elucidating the structures of primary products from such experiments because of the many additional reaction steps from primary to final analyzed product. Differences between the ESR and deuterolysis results could be due, in part, to the large temperature difference in the two experiments which at these low temperatures will accentuate the effects of quite modest differences in energy barriers.

In the present paper we describe the results of our ESR studies of the reaction of Al atoms with buta-1,3-diene and some deuterated and ¹³C labeled derivatives in a rotating cryostat at 77 K under conditions more akin to those of the deuterolysis experiments. Our work shows the formation of an aluminum cyclopentene with an unusually large aluminum hyperfine interaction (HFI) and the addition of an aluminum atom to the conjugated system to form an aluminum-substituted allyl.

Experimental Section

The rotating cryostat, EPR spectrometer, and methods used to calibrate spectra and calculate spectral parameters have been described previously.⁵ The parameters in the Hamiltonian describing the spectra were obtained by diagonalization of the spin matrix and computer simulation of the spectra. Aluminum atoms in their ground electronic state were produced by resistively heating metallic aluminum in a molybdenum

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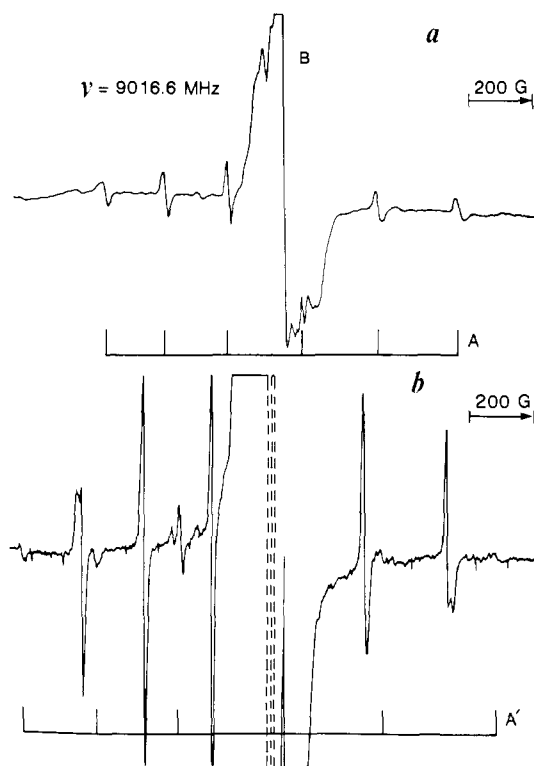


Figure 1. The ESR spectra from Al atoms and buta-1,3-diene in adamantane at 77 K; (a) $\text{CH}_2\text{CHCHCH}_2$ (b) $\text{CD}_2\text{CHCHCD}_2$.

furnace⁵ to $\sim 800^\circ\text{C}$. The rate of metal deposition was about 0.06 g/h.

Buta-1,3-diene (Research Grade) was obtained from Phillips, $\text{CD}_2\text{CHCHCD}_2$ and $\text{CD}_2\text{CDCDCD}_2$ were obtained from Merck, Sharpe and Dohme, Canada Ltd., and a mixture of CHDCDCDCD_2 and $\text{CD}_2\text{CHCDCD}_2$ was a gift from Dr. J. Worsfold (NRCC). The reactions were performed in adamantane (Aldrich).

Computational Details. Ab initio calculations were carried out with the GAUSSIAN 80 series of programs.⁶ Open-shell states were calculated by using the spin-unrestricted Hartree-Fock (UHF) formalism of Pople and Nesbet.⁷ Energy minimizations were accelerated by using Murtaugh-Sargent gradient procedures.⁸

Two basis sets were used in the calculations. An initial set of structural parameters was determined from minimal STO-3G^{9,10} calculations. The parameters were then refined by using the more flexible Huzinaga-Dunning's double- ζ (DZ) basis set¹¹ for C[9s5p/3s2p], H[4s/2s], and Al[11s7p/6s4p]. With the geometries thus determined, a set of five d-like functions (DZP) was added to the Al atom. Such polarization functions will be important in properly describing the spin density on the heavy atom.¹² Furthermore, the spin contamination in the UHF wave functions is found to be very small in all cases ($S^2 = 0.7529, 0.7537, 0.7543$ for STO-3G, DZ, and DZP basis sets, respectively), indicating that the predicted geometry should be reliable.¹²

Results

Adamantane containing Al atoms and buta-1,3-diene (C_4H_6) at 77 K gave a deposit which was light brown in color and which gave the ESR spectrum shown in Figure 1a. The spectrum consists of an almost isotropic sextet (A) with $a_{\text{Al}} = 229.8$ G and $g = 2.0025$ and a much more intense, multiplet central feature (B) shown in expanded scale in Figure 2a. Upon annealing to 100 K the $M_1 = 1/2$ line of the sextet (A) resolved into a quintet with a spacing of 3.75 G from the interaction of the unpaired

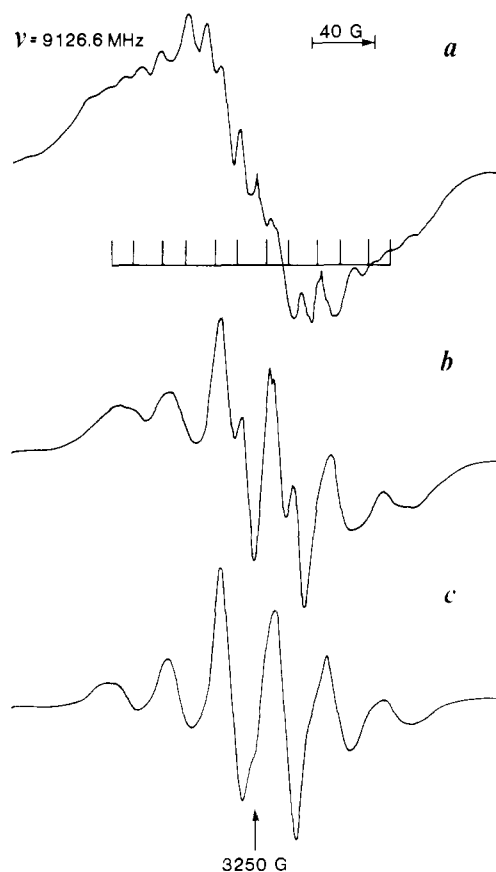


Figure 2. The central features from the ESR spectra given by Al atoms and buta-1,3-diene in adamantane at 77 K: (a) $\text{CH}_2\text{CHCHCH}_2$, (b) $\text{CD}_2\text{CHCHCD}_2$, (c) $\text{CD}_2\text{CDCDCD}_2$.

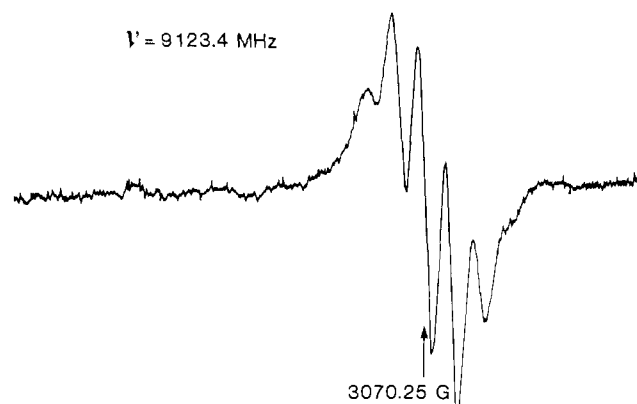


Figure 3. The $M_1 = 1/2$ line from the ESR spectrum of species A prepared from Al atoms and $\text{CH}_2\text{CHCHCH}_2$.

electron with four protons (Figure 3). The $M_1 = \pm 3/2$ lines were less well resolved but showed evidence for the 3.7 G splitting while the $M_1 = \pm 5/2$ lines were too broad to see these interactions. The $M_1 = -1/2$ line was lost in the central feature. In addition there was some evidence for a sextet (A') with a larger HFI than A.

Partially deuterated buta-1,3-diene, $\text{CD}_2\text{CHCHCD}_2$, gave the spectrum shown in Figure 1b. The sextet from A was more intense than in the previous case and clearly anisotropic. The $M_1 = 1/2$ line resolved into a triplet from two equivalent hydrogen atoms with a 2.5 G splitting. The sextet labeled A' was more evident and could be analyzed in terms of $a_{\text{Al}} = 299.4$ G and $g = 2.0032$. Spectrum B (Figure 2b) resolved into a sextet of doublets suggesting the interaction of one aluminum nucleus with one hydrogen nucleus. The sextet and doublet spacings were 33.5 and 14 G, respectively.

Perdeuteriobuta-1,3-diene gave a spectrum consisting of contributions from A, A', and B. The $M_1 = 1/2$ line of A was a singlet

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proving the previous HFI to be due to the protons of one butadiene ligand. The signal from this species was intense enough so that a ^{13}C HFI of 20 G could be observed at high gain. The spectrum from B is shown in Figure 2c and is a sextet with $a_{\text{Al}} = 33.5$ G and $g = 2.0023$.

Species A', whose intensity was somewhat variable from run to run, could either be A in a different trapping site or possibly AlO whose ESR parameters in neon are $A_{\parallel} = 311$ G, $A_{\perp} = 254.7$ G, $g_{\parallel} = 2.0015$, and $g_{\perp} = 2.0004$.¹³

Discussion

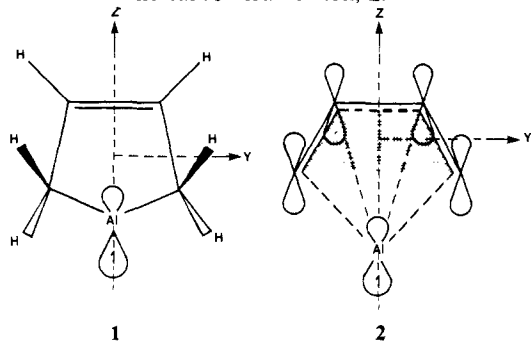
Reaction of Al atoms with buta-1,3-diene in a rotating cryostat at 77 K gives two major paramagnetic aluminum species with aluminum hyperfine interactions (HFI) of 229.8 G (species A) and 33.5 G (species B), respectively.

Species A: This species is not an aluminum atom-dialkene molecular complex in which the p orbital of the Al atom interacts with one C=C double bond since this would be analogous to $\text{Al}[\text{C}_2\text{H}_4]_2$ which gives an anisotropic ESR spectrum with $A_1(\text{Al}) = A_2(\text{Al}) = 0$, $A_3 = 44$ G, $g_1 = 2.014$, $g_2 = 2.002$, and $g_3 = 1.996$ and no resolved hydrogen HFI. The presence of four and two equivalent protons when $\text{CH}_2\text{CHCHCH}_2$ and $\text{CD}_2\text{CHCHCD}_2$ are used as ligands shows the species to contain one butadiene molecule and one aluminum atom. The magnitude of the Al HFI is noteworthy and we believe it is the largest yet observed for an organoaluminum species. It suggests a significant 3s orbital contribution to the semioccupied molecular orbital (SOMO) indicating hybridization of the Al valence orbitals. Spectra from the deuterated butadienes show that A has axial symmetry and a complete analysis of the spectrum gives $A_{\parallel} = 237.5$ G, $A_{\perp} = 222.6$ G, $g_{\parallel} = 2.0015$, and $g_{\perp} = 1.9971$. These values when inserted into the relationships $A_{\parallel} = A_{\text{iso}} + 2A_{\text{dip}}$ and $A_{\perp} = A_{\text{iso}} - A_{\text{dip}}$ lead to $A_{\text{iso}} = 227.6$ G and $A_{\text{dip}} = 5$ G, assuming A_{\parallel} and A_{\perp} to have the same sign. It is most likely that the SOMO at the aluminum atom has both s and p character, i.e.,

$$\phi = a\phi(3s) + b\phi(3p)$$

The values of a^2 and b^2 can be estimated by using the predicted values of $A_{\text{iso}} = 1395$ G and $A_{\text{dip}} = 29.5$ G for an electron in a 3s and a 3p orbital of aluminum.¹⁴ Thus $a^2 = 0.16$ and $b^2 = 0.16$, indicating an sp-hybridized orbital at aluminum with a total unpaired spin population of $\sim 32\%$ on the metal atom. However, the predicted values of A_{iso} and A_{dip} are not accurate enough to preclude an orbital with greater p character, e.g., sp^2 .

Two structures are possible for species A: a σ -bonded aluminumocyclopentene, **1**, and a π -complex with the aluminum atom below the butadiene carbon framework, **2**.



In **1** the aluminum has undergone sp^2 hybridization with two of these orbitals interacting with the two terminal CH_2 groups of butadiene to give a five-membered ring leaving a double bond located between C2 and C3. The unpaired electron on the aluminum would reside in an sp^2 orbital pointing away from the butadiene framework. Such a molecule of C_{2v} symmetry is consistent with the axial g and A tensors with the free electron in the sp^2 orbital along the C_{2v} axis and the symmetry plane tensor elements along the other two orthogonal axes being too close to

be differentiated. **1** is similar to the aluminumocyclopropanes suggested by Skell³ but would be less strained. Spin population at the protons will occur mainly by a spin polarization mechanism since the protons of the CH_2 group are not coplanar with the aluminum sp^2 free electron orbital. As discussed below the molecule could be distorted into an envelope shape with C_s rather than C_{2v} symmetry.

Structure **2** is a half-sandwich complex with bonding of the Dewar-Chat-Duncanson type.^{15,16} Electron donation could occur from the filled Ψ_1 and Ψ_2 orbitals of butadiene into the empty $3p_{xy}$ orbitals of aluminum with back-donation from the semioccupied $3p_z$ orbital to the antibonding Ψ_3^* orbital of the ligand. This species would have a $^2A'$ ground state in C_s symmetry with the unpaired spin population on Al located in a p_z orbital. The antibonding orbital is, however, close in energy to the 2B_2 antibonding orbital, and mixing between these orbitals would introduce Al s character into the SOMO.

The hydrogen HFI of the $\text{Al}/\text{C}_4\text{H}_6$ complex when compared with those for the butadiene radical anion are not consistent with such a complex. Thus the hydrogen HFI of the terminal and central hydrogens of C_4H_6^- are 7.7 and 2.8 G,^{17,18} respectively. Combining these values with the observed values of 3.75 and 2.5 G suggests unpaired spin populations on the terminal and central positions of the butadiene ligand of 0.48 and 0.89 compared to the values of 0.25 and 0.09 expected from the Al HFI and the same spin ratios on the central and terminal positions as in C_4H_6^- .

Furthermore, the Karplus-Fraenkel¹⁹ treatment of ^{13}C HFI shows that the SOMO on butadiene cannot be of a pure π character. The ^{13}C HFI at the terminal carbon atom, C, can be calculated from the equation

$$a_C = (S^C + 2Q_{\text{CH}} + Q_{\text{CC}})\rho_C^\pi + Q_{\text{C}'\text{C}}\rho_{\text{C}'\pi}$$

where $S^C = -12.7$ G and is the contribution from polarization of the 1s electrons, $Q_{\text{CH}} = 19.2$ G and $Q_{\text{CC}} = 14.45$ G and are the σ - π parameters resulting from interaction between the two CH bonds and the CC' bond and the π electron spin population on C (ρ_C^π), and $Q_{\text{C}'\text{C}} = -13.94$ G is the σ - π parameter resulting from interaction between the $\text{C}'\text{C}$ bond and π electron spin population on the adjacent carbon C' ($\rho_{\text{C}'\pi}$). If $\rho_C^\pi = 0.37 \times 0.68 = 0.25$ and $\rho_{\text{C}'\pi} = 0.13 \times 0.68 = 0.09$, a_C can be calculated to equal 8.8 G which is significantly less than the experimental value of 20 G. This suggests significant s character in the SOMO at the terminal carbons of the butadiene with rehybridization and bending of the CH_2 bonds out of the molecular plane.

The g -values in conjunction with the treatment of quenched aluminum atoms in inert gas matrices by Ammeter and Schlosnagle²⁰ can be used to give an estimate of the energy difference between the three orthogonal aluminum 3p orbitals in the butadiene complex, the 3s orbital contribution being assumed to have no effect on g variations from g_e . These authors have shown for large values of the ratio Δ/ξ that

$$g_{\perp} \approx g_e \text{ and } \Delta g_{\perp} = g_{\perp} - g_e = -4b^2\xi/3\Delta$$

where ξ is the spin-orbit coupling constant and Δ is the strength of the crystal field parameter, in the present case the energy difference between the energies of the perpendicular p orbitals. Inserting our value of $\Delta g_{\perp} = -0.00208$ and $\xi = 75$ cm^{-1} leads to an estimate of $\Delta \approx 7700$ to 15400 cm^{-1} , depending on whether $b^2 = 0.16$ or 0.32 (sp or sp^2). This compares with a value of 7540 cm^{-1} for the crystal field strengths around aluminum atoms trapped in krypton and shows clearly that there is a considerable perturbation of the p orbitals by the butadiene, i.e., chemical bonding has occurred.

Taking all of these factors into consideration leads us to the conclusion that species A has structure **1** formed by a cheletropic

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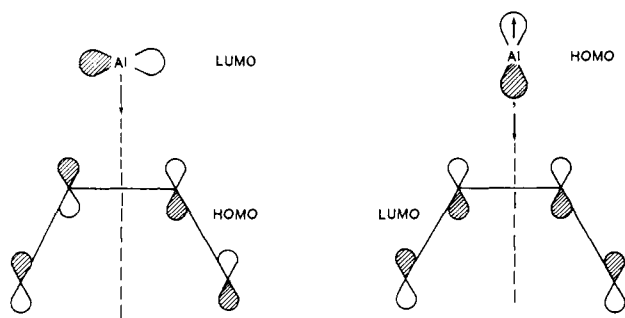


Figure 4. A frontier orbital diagram of the cheletropic reaction of Al atoms with buta-1,3-diene.

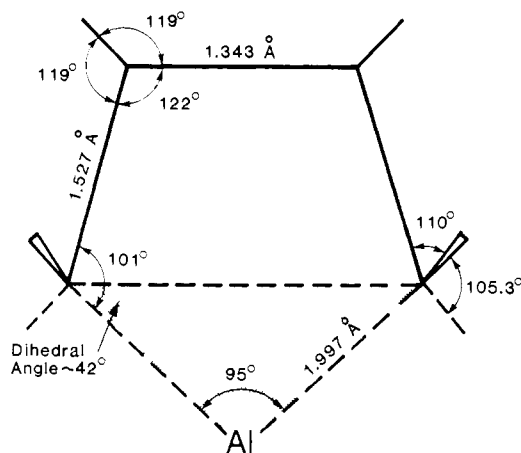


Figure 5. The theoretically predicted structure of $\text{Al}(\text{CH}_2\text{CHCHCH}_2)$.

addition of an Al atom to butadiene.²¹ It is pertinent to recall that aluminum forms quite strong Al-C bonds (e.g., $D(\text{Al}(\text{C}-\text{H}_3)_2-\text{CH}_3) = 68 \text{ kcal mol}^{-1}$) rather than π -complexes.²² Both cheletropic addition and π -complexing occurs for early transition metallocenes interacting with dienes.²³ A frontier orbital description of the reaction is given in Figure 4 which shows it to be symmetry allowed with the LUMO and HOMO orbitals in both participants being able to correlate. Such cheletropic reactions are known for species such as SO_2 and CH_2 .^{24,25} We think this is the first example of an atom cheletropic addition, the aluminum atom behaving not as a monovalent but as a trivalent species as it does in most aluminum compounds.

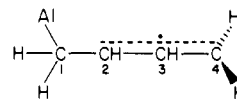
The theoretically predicted structure for the $\text{Al}(\text{CH}_2\text{CHCHCH}_2)$ complex is displayed in Figure 5. The predicted structures differ little at different levels of approximation, but the more accurate DZ basis set is used for further discussion. The equilibrium geometry adopts a puckered five-membered ring structure resembling cyclopentene. The electronic ground state (C_s symmetry) was found to be $^2A'$. The unpaired electron resides in a predominately Al sp-hybridized orbital pointing away from the ring. The total spin population on the Al atom is 0.8768 with 43% derived from the Al 3s orbital and the rest from the Al 3p orbital. The spin population on each terminal carbon atom is 0.0676 with almost negligible spin population on the other carbon atoms.

The s/p ratio of ~ 1 agrees with the empirical value calculated from A_{iso} and A_{dip} , but the predicted total spin population at the aluminum nucleus is too large by a factor of 2 to 3. Better

correspondence can be achieved by decreasing the dihedral angle between the C-Al-C and C-C-C planes from 42° toward zero, but the s/p ratio then also decreases. Because of the errors in the calculated atomic A_{dip} value we cannot preclude this possibility, but at the present time we prefer not to force fit the structure to the ESR parameters and vice versa.

The theory favors the formation of two Al-C bonds in a σ -bonded aluminum cyclopentene over a π -like complex. The Al-C bond distance of 1.996 Å may be compared with the experimental value of 1.957 Å found in monomeric trimethylaluminum.²⁶ It seems fair to conclude that the Al-C bond in the complex is a conventional single bond. The predicted C-C single and double bond distances are reasonable at this level of theory. The methylene C-H distance is 1.100 Å and the vinylic C-H distance is about 0.012 Å shorter. The C-Al-C angle of 95.2° is substantially smaller than those found in $\text{Al}(\text{CH}_3)_3$. This observation indicates that the bonding with the carbon atoms originates from overlap with the Al 3p orbitals. The ring strain is probably very small. The C-C-C bonding angle distribution indicates that the carbon atoms remain coplanar after the formation of the complex. However, the terminal carbon atoms of the butadiene molecule are rehybridized to sp^3 in order to optimize overlap with Al 3p orbitals. Furthermore, the valence angles at the terminal carbon atoms are very close to tetrahedral, a prediction consistent with the conclusion from the large ^{13}C HFI which also indicates a change from sp^2 to sp^3 at these carbons.

Species B: This is the most dominant species found in the aluminum-butadiene system, and it has an almost isotropic Al HFI of 33.5 G and a g value of 2.0023. The isotropic sextet with a 33.5 HFI observed for C_4D_6 clearly indicates the presence of one aluminum atom, the different peak-to-peak intensities of the six lines resulting from an M_1 effect on the line width. Both $\text{CD}_2\text{CHCHCD}_2$ and the mixture $\text{CHDCDCDCD}_2/\text{CD}_2\text{CHCDCD}_2$ show doublet HFI of 14 G on some of the sextet lines (most clearly seen on the $M_1 = \pm 1/2$ lines), indicating an allylic species. Unfortunately, the severe overlapping of many HFI manifolds and the low resolution ($\Delta H_{\text{pp}} \sim 7 \text{ G}$) only allow an approximate analysis of the B species. We have attempted many simulations and found the best, but not exact, fit with the following parameters which are also consistent with those determined from the C_4D_6 and $\text{C}_4\text{D}_4\text{H}_2$ spectra: $a_{\text{Al}} = 33.5 \text{ G}$, $a_{\text{H}}(1) = 4 \text{ G}$, $a_{\text{H}}(2) = 14 \text{ G}$, $a_{\text{H}}(3) = 11 \text{ G}$. Spectrum 2a clearly shows interaction with at least 3 protons with a spacing of $\sim 11 \text{ G}$ rather than the expected 13–14 G for an allylic species. The observation of hyperfine interaction with all the protons of the butadiene allows the aluminocyclopropane-type adduct to be excluded since only 3 hydrogens would be expected to interact. The alkyl $\text{CH}_2\text{CHCHAlCH}_2$ can also be discounted since the α and β protons would be expected to be $>20 \text{ G}$ not 14 G as found experimentally. The most likely species is the allyl



formed by addition of the aluminum atom to the terminal CH_2 group. We offer the following tentative assignment: two C4 protons, 11 G; C3 proton, 4 G; C2 proton, 14 G; one C1 proton, 14 G and one C1 proton 11 G. The inequivalence of the two C(1) protons is unusual but has been observed in mercapto allyls and ascribed to the preferential alignment of the RS group with the π system; this brings one of the protons into the nodal plane of the π orbital. A similar mechanism could operate for Al where overlap of its empty p orbitals with the π orbital would be favored. Such an overlap could explain the reduction of spin population at C4 over that usually found for allyls (11 G rather than 14 G proton HFI). It is a matter of semantics whether such a weak interaction can be taken as indicating bridging by the aluminum atom and RS group.

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The aluminum HFI is almost isotropic, indicating largely s character although it is likely that some p contribution must be present but almost undetectable. The spin population at the aluminum, using an A_{iso} value of 1395 G, for an aluminum atom¹⁴ is 0.024 and is remarkably close to the value of 0.028 for the methyl protons in methylallyl. Similar parallels exist for aluminum and hydrogens in vinyls^{27,28} and allyls²⁹ with Al at the central

carbon position.

Acknowledgment. J.A.H. and B.M. thank NATO for a research grant (No. 442/82) and B.M. thanks SERC for generous financial support.

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Angle-Selected ENDOR Spectroscopy. 1. Theoretical Interpretation of ENDOR Shifts from Randomly Orientated Transition-Metal Complexes

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Abstract: The NMR lines from ligand nuclei in paramagnetic transition-metal complexes are shifted because of the dipolar and Fermi contact interactions with the unpaired electron(s) of the metal ion. The dipolar interaction depends on the position of the nuclear spin with respect to the metal ion, and dipolar shifts can be analyzed to yield nuclear positions. This paper demonstrates how ESR spectra of randomly oriented molecules can be used to select molecular orientations. ENDOR spectra taken at orientations selected by ESR can then be used to determine nuclear positions and Fermi contact energies. A theoretical development of the equations for the shifts of ENDOR lines in randomly oriented solids is also given. This theory shows that the equations which have commonly been used to analyze ENDOR from these samples are incorrect and unable to account for many of the experimental features of the ENDOR spectra.

The electron spin of transition-metal ions interacts with ligand nuclear spins via dipolar and Fermi contact interactions, producing shifts in the NMR lines of the ligand nuclei.¹ The dipolar interaction depends on the relative position of the nuclear spin with respect to the metal atom, and the NMR spectra of solid samples can be analyzed to yield information about nuclear coordinates. NMR spectroscopy of solid paramagnetic samples has limited sensitivity so one can only examine relatively concentrated samples. Electron nuclear double resonance (ENDOR) is an alternative technique for obtaining nuclear resonance shifts of ligand nuclei in paramagnetic molecules. When nuclear and electron spin relaxation times are favorable, the technique yields a substantial sensitivity improvement and one can investigate magnetically dilute samples. ENDOR spectra are obtained by partially saturating an EPR transition and sweeping radio frequency radiation through nuclear resonance transitions.

EPR spectra of polycrystalline or amorphous samples reflect a "powder" average of all molecular orientations with respect to the magnetic field. If the \bar{g} and hyperfine tensors are known, one can associate distinct sets of molecular orientations with a given resonant field value. This set of molecular orientations is thereby selected for nuclear resonance by the fixed field setting of the ENDOR experiment.²⁻⁴ The result is an ENDOR spectrum that reflects the angular dependence of the hyperfine energies of ligand nuclei. Once this angular dependence is known, the geometric location of a ligand nucleus and spin density at that nucleus can be determined.

This idea has been applied in a variety of ENDOR studies of metal complexes to yield qualitative results. Much of the work done in powder ENDOR has not made full use of the angular selection which is provided by anisotropy in the EPR spectrum. The traditional equations used for powder ENDOR shifts have assumed that the electron and nuclear spins are quantized along the same axis and that the spin-only g value of the electron can be used to determine the dipolar field at the nucleus. These equations yield nearly correct answers in some limiting cases but are generally incorrect. We take a more complete approach, carefully considering the influence of angular selection on ENDOR powder spectra and making few simplifying assumptions in calculation of ligand nuclear resonant frequencies. With these methods, peak assignment is facilitated and accurate measurement of ligand nuclear coordinates in randomly oriented magnetically dilute paramagnetic samples is possible.

In this paper, we demonstrate more comprehensive techniques for using EPR spectra to select fixed molecular orientations for ENDOR investigations. ENDOR spectra have usually been taken only at the turning points of the EPR spectrum so that angular selection is limited to a few specific orientations. When frequency modulation of the swept rf radiation is employed, one is able to obtain ENDOR spectra throughout the EPR spectrum, thereby increasing the range of angular orientations which are selected. A theoretical development of the equations for ENDOR shifts in randomly oriented samples is also given, and results from this equation are compared with results from more commonly used equations for the analysis of ENDOR spectra. Techniques through which one can obtain information about molecular structure from angle-selected ENDOR experiments are illustrated for a typical copper complex. The equations are general, however, and can be used to determine local geometries of ligand nuclei near transition-metal ions in a variety of types of metal complexes. The

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