

It is apparent that FR 900482 consists of the two tautomers with structures **1A** and **1B** which interconvert most likely via an intermediary keto form **C**. In the ^1H NMR spectrum of **1**, the major isomer showed a NOE between 9-H and one (δ_{H} 4.68) of $^{13}\text{C}-\text{H}_2$, while, in the minor one, a NOE was observed between 7-H and 9-H, indicating that, contrary to the case of the triacetates, the major isomer has the **A** form.¹¹ The tautomer **1A** is possibly favored by an intramolecular hydrogen bonding between the aziridine NH and the bridged oxygen.

FR 900482 is quite unique in containing a hydroxylamine function whose hydroxy group participates in a hemiketal moiety. The structure of FR 900482 is of interest in comparison with those of the mitomycin family of antibiotics. Thus, FR 900482 resembles mitomycins by having an aziridine and a carbamoyloxymethyl group but differs by lacking a quinonoid structure. FR 900482 exhibits powerful antitumor activity in a variety of transplantable murine tumors including mitomycin-resisted P388.¹²

Supplementary Material Available: Tables of fractional coordinates and thermal parameters, anisotropic thermal parameters, bond lengths, and bond angles (4 pages). Ordering information is given on any current masthead page.

(11) In an acidic solution, the equilibrium of **1** lies far toward **A**. The NMR spectra showed that in $\text{D}_2\text{O}-\text{DCI}$ **1** exists nearly quantitatively in the **1A** form: ^{13}C NMR ($\text{D}_2\text{O}-\text{DCI}$) δ 195.4 (d), 159.1 (s), 156.3 (s), 147.4 (s), 136.6 (s), 118.3 (s), 114.3 (d), 111.2 (d), 90.8 (s), 60.7 (t), 49.4 (t), 44.1 (d), 36.3 (d, 2 C); ^1H NMR ($\text{D}_2\text{O}-\text{DCI}$) δ 9.67 (s, 1 H), 7.0 (s, 2 H), 5.21 (dd, $J = 11, 6$ Hz, 1 H), 4.6 (d, $J = 11$ Hz, 1 H), 4.16 (d, $J = 17$ Hz, 1 H), 4.04 (dd, $J = 17, 5$ Hz, 1 H), 3.74 (m, 2 H), 3.65 (d, $J = 6$ Hz, 1 H).

(12) Antitumor activities in mice in comparison with those of mitomycin **C** (MMC) (shown by the highest T/C values). P388 (ip/ip, D1-5): **1**, 10.0 (mg/kg), T/C 305 (%); MMC, 1.0, 153. MMC-resisted P388 (ip/ip, D1), **1**, 18.0, 155; MMC, 3.2, 114. L1210 (ip/ip, D1-9): **1**, 10.0, 305; MMC, 1.0, 200. B16 (ip/ip, D1-9): **1**, 10.0, 350; MMC, 1.0, 223. Details will be reported: Shimomura, K.; Hirai, O.; Mizota, T.; Matsumoto, S.; Mori, J.; Shibayama, F.; Kikuchi, H. *J. Antibiot.*, in press.

Reaction of Aluminum Atoms with Ethylene: Formation of a Metallocyclopentane by Cyclodimerization of Ethylene at Low Temperatures¹

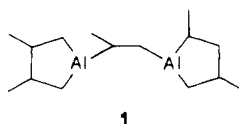
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Kasai^{2,3} has undertaken a detailed electron spin resonance (ESR) study of the reaction of aluminum atoms with ethylene in inert gas matrices at temperatures below 40 K and has concluded that addition to the $\text{C}=\text{C}$ double bond does not occur but that a π complex is formed. The free electron of this species is believed to reside mainly in the Al $3p_y$ orbital lying parallel to the $\text{C}=\text{C}$ bond with some spin population in the π^* orbital of the ethylene.

Skell and Wolf⁴ somewhat earlier found that Al atoms and propene at 77 K give, upon deuteration, products indicative of trivalent aluminum σ -bonded intermediates,⁵ e.g., **1**, which contain two alumino-substituted cyclopentane rings linked by a C_3 fragment. It was concluded that **1** is formed by ring opening of the initially formed aluminocyclopropane.



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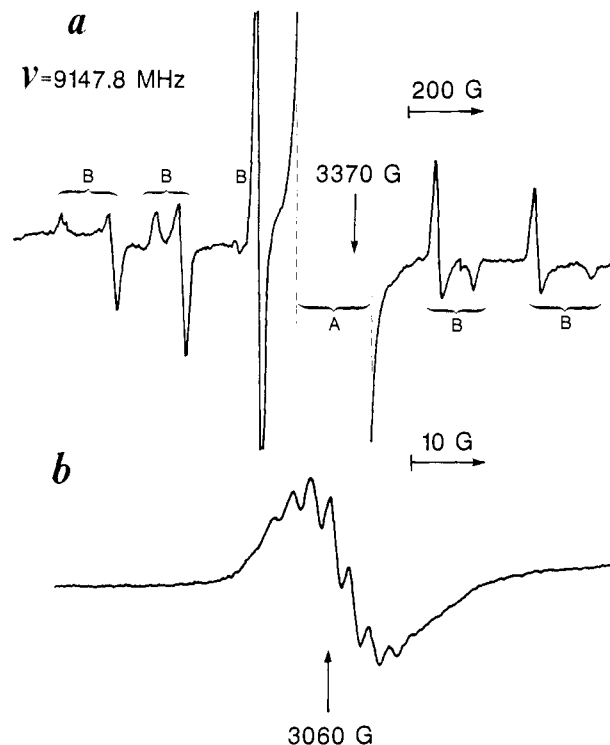


Figure 1. (a) ESR spectrum given by Al atoms and ethylene in cyclohexane at 77 K. (b) ESR spectrum of the $M_1 = +1/2$ line of species B at 210 K in adamantane.

We have recently shown that aluminum atoms react with buta-1,3-diene in hydrocarbon matrices at 77 K to form an alumino-substituted allyl and through a cheletropic cycloaddition to give an aluminocyclopentene in which the aluminum atom has adopted a hybridized sp^2 orbital configuration.⁶ In this latter species two of the sp^2 orbitals are used to covalently bond the aluminum to the terminal carbon atoms with the unpaired electron located mainly in the remaining sp^2 orbital. The 33% Al 3s contribution to the SOMO produces a large Al hyperfine interaction of 640 MHz. In this context we were interested to see whether the use of higher temperatures, hydrocarbon matrices, and the experimental conditions of the rotating cryostat might result in a σ -bonded species even in the case of ethylene, and we report here the results of our studies, which show that cyclodimerization to form aluminocyclopentane does indeed occur.

The rotating cryostat⁷ was used to react aluminum atoms, produced in a tungsten coil furnace, with newly deposited ethylene molecules trapped on the cold surface (77 K) of a continuously renewed matrix of adamantane or cyclohexane on the spinning drum containing liquid nitrogen. The resulting deposits were examined by ESR after transfer from the drum still at 77 K and under high vacuum.

The ESR spectrum shown in Figure 1a has two paramagnetic species A and B. Species A gives the more intense spectrum and will be fully discussed in a later publication; here we note only that its ESR parameters at low temperatures are similar to those reported by Kasai^{2,3} and assigned to the monoligand π complex $\text{Al}[\text{C}_2\text{H}_4]$. The absorption lines of species B are a textbook example of a species with axially symmetric g and A tensors. Its ESR parameters $a_{\parallel} = 798.3$ MHz, $a_{\perp} = 635.2$ MHz, $g_{\parallel} = 1.9986$, and $g_{\perp} = 1.9970$ are similar to those of aluminocyclopentene, suggesting that it has a structure similar to the product from Al atoms and buta-1,3-diene.⁶

Small hyperfine interactions were discernable on the aluminum lines, especially on the $M_1 = 1/2$ line, which became more evident

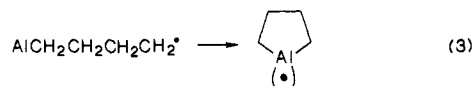
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on annealing (Figure 1b). No hyperfine lines were visible when C_2D_4 was used, showing that the interactions were with the protons of C_2H_4 . The $M_1 = 1/2$ line was an almost isotropic singlet, indicating that the $M_1 = 1/2$ interactions from C_2H_4/Al did not arise from the superposition of parallel and perpendicular features but from isotropic proton hyperfine interactions only. This line has been analyzed as a partially resolved quintet of quintets and was simulated with the ESR parameters, $a_H(4) = 4.0$, $a_H(4) = 2.5$, and $\Delta H_{pp} = 2.8$ G, identical with those of aluminocyclopentane.

The large aluminum hyperfine interaction and two sets of magnetically equivalent proton interactions of the same magnitude as those in aluminocyclopentene strongly indicate that the spectrum is due to aluminocyclopentane formed by a coupling of two ethylene molecules by the aluminum atom whose orbital composition is sp^x and not pure p as in the aluminum atom itself. Insertion of the $a_{||}$ and a_{\perp} aluminum values into the relationships $a_{||} = A_{iso} + 2A_{dip}$ and $a_{\perp} = A_{iso} - A_{dip}$ leads to $A_{iso} = 689.5$ MHz and $A_{dip} = 54.4$ MHz, assuming that $a_{||}$ and a_{\perp} are both positive. Combining these values with the predicted Al atomic parameters⁸ $A = 391$ l and $P = 83.4$ MHz gives s - and p -unpaired spin populations of 0.18 and 0.65, respectively, and a total spin population of ~ 0.83 on the Al atom. An sp^3 -hybridized orbital is indicated on the Al, but an sp^2 orbital cannot be excluded because of the inaccuracies in the predicted atom A and P parameters. The observation of two sets of four-proton interactions removes the possibility that the ESR carrier is a bridged aluminum monoethylene species but is consistent with the dimeric species in which the four protons on the two carbons adjacent to the aluminum have a 4-G interaction while the four protons of the β carbons have a 2.5-G interaction. As in aluminocyclopentene, aluminocyclopentane probably has an envelope-type structure of C_s symmetry with the Al atom below the C4 frame and is not a planar molecule of C_{2v} symmetry. The greater Al 3p orbital contribution to the SOMO in aluminocyclopentane is probably accompanied by more 3s character in the bonding orbitals directed toward the carbon atoms which itself may arise from smaller CCC bond angle at the central C-C single bond compared to those at the C=C double bond in aluminocyclopentene. The driving force for the involvement of the higher energy 3p orbitals of Al in this cyclometalation reaction is the formation of two strong C-Al σ bonds⁹ that more than compensate for the s to p promotional energy.

At least two mechanisms for the cyclodimerization reaction are possible: (i) a consecutive three-step radical process (reactions 1-3) or (ii) a concerted process involving the two ethylene molecules reacting simultaneously with the Al atom. If the reaction



proceeds via aluminoethyl and -butyl radicals, it is surprising that neither we nor Kasai^{2,3} see any trace of these radicals in matrix ESR spectra. Furthermore, the fact that no metal atom addition reaction to a simple alkene has yet been observed also tends to argue against this mechanism. Mechanism ii could involve the rearrangement of a bis-ethylene aluminum complex although a direct route not involving a complex is feasible.

There are numerous examples of such cyclodimerization of alkenes in the presence of transition-metal complexes,^{10,11} e.g., $Fe(CO)_5$, and the symmetry rules applicable to such reactions have been considered thoroughly by Stockis and Hoffmann.¹² The

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reactions usually require photoactivation and involvement of other ligands in addition to alkenes. We believe this is the first report of such a thermal reaction by a naked metal atom and provides direct evidence for the involvement of aluminocyclopentanes in aluminum-olefin reactions.⁵ In conclusion, it is worth noting that both species A and B are remarkably stable up to 343 K in adamantane.

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Determination of Relaxation Pathways in Coupled Spin Systems by Two-Dimensional NMR Exchange Spectroscopy with Small Flip Angles

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Two-dimensional exchange spectroscopy (NOESY) has proven to be a remarkably useful method for studying cross-relaxation (nuclear Overhauser effects).¹⁻³ In most applications, the multiplet structure due to scalar couplings is not explicitly taken into account, and the integrated signal amplitudes only yield information about cross-relaxation rates³⁻⁵ $\sigma_{ij} = W_{ij}^s - W_{ij}^0$ between spins I_i and I_j . This limitation makes it difficult to test various motional models,^{6,7} to ascertain the importance of correlation between pairs of dipolar interactions,⁸ and generally to study molecules with a correlation time $\tau_c \approx 1/\omega_0$, where the cross-relaxation rates σ_{ij} vanish.

It is the purpose of this communication to show that high-resolution 2D exchange spectra recorded with the "small flip angle NOESY" sequence $90^\circ-t_1-10^\circ-\tau_m-10^\circ-t_2$ allow one to determine separately the zero-, single-, and double-quantum relaxation rates W_0^s , W_1^s , and W_2^s between eigenstates $|r\rangle$ and $|s\rangle$. This method is related to zz -spectroscopy^{9,10} and to spy relaxation studies.¹¹ If $\tau_m = 0$, this experiment is equivalent to z -filtered COSY:^{12,13} only pairs of transitions that share a common energy level give rise to cross-peaks, which are positive or negative for progressive or regressive connectivities. Simple rules describe the amplitudes even in the presence of strong coupling.¹³

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