# Electron Spin Resonance Spectra and Structure of Al(C₆H₆) in Hydrocarbon Matrices[1]

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Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9. Received April 10, 1989
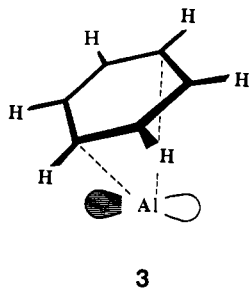
Abstract: Reactions of Al atoms with benzene at 77 K in benzene and inert hydrocarbon matrices on a rotating cryostat have been studied by ESR spectroscopy. A monoligand complex, Al(C₆H₆), is the only paramagnetic product, and at 4 K the ESR spectrum shows resolvable hyperfine interactions with one aluminum and two equivalent protons and has the following magnetic parameters in adamantane: $a_x(\text{Al}) = 56$ MHz, $a_y(\text{Al}) = a_z(\text{Al}) = 14$ MHz, $a_x(2\text{H}) = a_y(2\text{H}) = a_z(2\text{H}) = 27$ MHz, $g_x = 2.0010$, $g_y = 1.9970$, and $g_z = 2.0060$. The spectrum changes with an increase in temperature and at 220 K is more consistent with an interaction with six equivalent protons with parameters $a_{\text{Al}} = 9.5$ MHz, $a_{\text{H}}(6) = 5.3$ MHz, and $g = 2.0010$. Two alternative bonding schemes are discussed: (i) a η^2 complex with the Al positioned above one of the carbon–carbon bonds with hyperfine interaction to the two ortho protons and (ii) a η^2 complex in which the Al lies along the C_{6v} axis and bridges two para carbons with hyperfine interaction to the two para protons. The latter alternative is considered more likely since it explains more readily the spectral changes with temperature. At 4 K the Al bonds are across the para carbons in a rigid structure while at 220 K the molecule is fluxional with the Al to carbon bonds moving from one para position to the next at a higher rate than the proton hyperfine frequency so as to simulate a η^6 complex.

Kasai and McLeod[3] were the first to report the ESR spectrum of monobenzenealuminum from reaction of ground-state Al atoms $(3s^2 3p^1)$ with benzene in a neon matrix at ~4 K. Rather unexpectedly, the spectrum revealed interaction with only two of the six protons of benzene with an unpaired spin population of ~0.2 in the 3p orbital of Al and ~0.4 on the ring. These authors suggested a structure **1** with Al complexed to one C=C unit by

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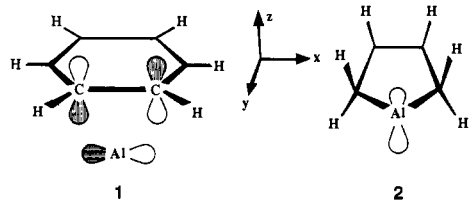
dative bonding of the semioccupied $3p_x$ orbital and two antibonding p_π orbitals on two ortho carbon atoms. Recently, Mitchell et al.[4] using time-resolved resonance fluorescence spectroscopy have measured a binding energy in Al(C₆H₆) of 49 kJ mol⁻¹ in the gas phase and have argued on thermochemical grounds that a π complex is more feasible than aluminocyclohexadienyl.

Reaction of Al atoms with the related conjugated molecule buta-1,3-diene at 77 K in hydrocarbon matrices gave, in addition to an alumino-substituted allyl, a cheleotropic cyclization product, aluminocyclopentene (**2**) where a 1,4-addition of the Al across the terminal CH₂ groups had occurred.[5] It seems feasible that a similar 1,4- or para-addition could occur in the case of benzene to give **3** in which the two interacting protons are disposed para

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(2) NSERC Postdoctoral Fellow, 1987–1988.
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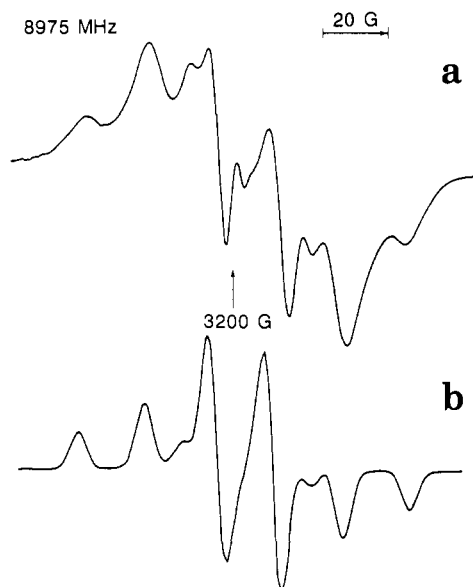
not ortho to each other; i.e., the benzene is localized in one Kekule resonance form (cyclohexatriene) and behaves like butadiene.[6,7]

Studies of the reaction of Al atoms with ethylene in matrices[8-10] and in the gas phase[4] have shown the formation of an unusually tightly bound monoligand complex, Al(C₂H₄), with $D[\text{AlC}_2\text{H}_4] > 30$ kJ mol⁻¹. It has, however, proved difficult to provide a theoretical basis for such strong bonding even in this simple system with only the most sophisticated calculation being able to predict binding energies greater than those resulting from van der Waals dispersive interactions.[11-13] The bonding and structures for arene-aluminum products are even more difficult to predict with any confidence. In an attempt to shed more light on the unusual bonding of group 13 atoms with alkenes and arenes, we have investigated the products of the reaction of Al atoms with benzene in hydrocarbon matrices at 77 K on a rotating cryostat by ESR spectroscopy and report the results here.

Experimental Section

The rotating cryostat, instruments, and computational methods used to record, calibrate, and analyze ESR spectra have been described previously.[14] Aluminum was evaporated from a tungsten basket (No. 12070, Ernest F. Fullam, Inc., Schenectady, NY) suspended from the molybdenum electrodes of the furnace. Adamantane (Aldrich), benzene (Anachemia), and perdeuteriobenzene (MSD, Canada Ltd.) were used as received after thorough degassing.

Results

Reaction of Aluminum Atoms and Benzene-d_6 (C₆D₆) in Benzene-d_6. The ESR spectrum at ~4 K given by reaction of Al atoms with C₆D₆ in a C₆D₆ matrix at 77 K is shown in Figure 1a and is similar to that of Al(C₆D₆) in neon at 4 K. The spectrum consists of six absorption-like powder ESR lines with a spacing of ~52 MHz centered at g = 2.0016. It is that expected from a 7-electron benzenealuminum(0) species with axial symmetry

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Figure 1. (a) ESR spectrum of $Al(C_6D_6)$ in C_6D_6 at 4 K. The extra line at g = 2.0023 is attributed to a trace of $C_6D_6^-$. (b) Computer-simulated spectrum based on the parameters given in the text.

in which most of the unpaired spin on Al is located in a 3p orbital.

An acceptable computer simulation of the experimental spectrum (Figure 1b) was obtained with the following parameters: $a_x(Al)$ = 55 MHz, $a_y(Al)$ = $a_z(Al)$ = 14 MHz, $a_x(2D)$ = $a_y(2D)$ = $a_z(2D)$ = 4 MHz, g_x = 2.0014, g_y = 1.9982, and g_z = 2.0034. An orthorhombic **g** tensor was necessary for good simulation though the **a** tensor was axial. There is a broad absorption underlying the spectrum, which we have not added to the simulation.

At 77 K the resolution of the ESR spectrum was poorer because of line broadening. However, further careful annealing of the sample to 121 K resulted in a much sharper spectrum indicative of motional averaging. The experimental spectrum at 121 K could be simulated with the following parameters: $a_x(Al)$ = 45 MHz, $a_y(Al)$ = $a_z(Al)$ = 12 MHz, $a_x(2D)$ = $a_y(2D)$ = $a_z(2D)$ = 5.6 MHz, g_x = 2.0015, g_y = 1.9970, and g_z = 2.0047.

Reaction of Aluminum Atoms and C_6D_6 in Adamantane. Reaction of Al atoms with C_6D_6 in an adamantane matrix at 77 K gave the powder spectrum at 4 K shown in Figure 2a. The ESR parameters that gave the best simulation of the experimental spectrum were: $a_x(Al)$ = 59 MHz, $a_y(Al)$ = $a_z(Al)$ = 16 MHz, $a_x(2D)$ = $a_y(2D)$ = $a_z(2D)$ = 4 MHz, g_x = 2.0039, g_y = 1.9970, and g_z = 2.0040 (Figure 2b). The aluminum and deuterium coupling tensors were similar to those found in benzene and neon matrices, suggesting that the same carrier had been formed.

Temperature affected spectral resolution in adamantane in a similar fashion to that in benzene. Again the spectrum at 77 K was poorly resolved compared to that at 4 K while careful annealing produced a progressively more solutionlike spectrum until at 232 K the isotropic sextet shown in Figure 2c was observed. This spectrum yielded the isotropic parameters: a_{Al} = 9.5 MHz and **g** = 2.0011, the latter being close to one-third the trace of the **g** tensor in benzene (2.0016).

The observation of both rigid and motionally averaged spectra enabled the sign of $a_\perp(Al)$ to be determined by comparing the value of a_{Al} calculated from eq 1 to the experimental value of a_{Al}

$$a_{Al} = (a_\parallel + 2a_\perp)/3 \tag{1}$$

= 9.5 MHz. Thus, if $a_\parallel$ (59 MHz) and $a_\perp$ (16 MHz) are both positive, a_{Al} = 30 MHz, whereas if $a_\perp$ is negative, a_{Al} = 9 MHz. Clearly, a negative value of $a_\perp$ gives a calculated a_{Al} closer to the experimental value.

Computer simulation of the isotropic spectrum assuming that the electron coupled with two equivalent deuterons yielded the magnetic parameters a_{Al} = 9.4 MHz, $a_D(2)$ = 0.8 MHz, and **g** = 2.0005. It should, however, be noted that an equally good computer simulation of the isotropic spectrum at 232 K was
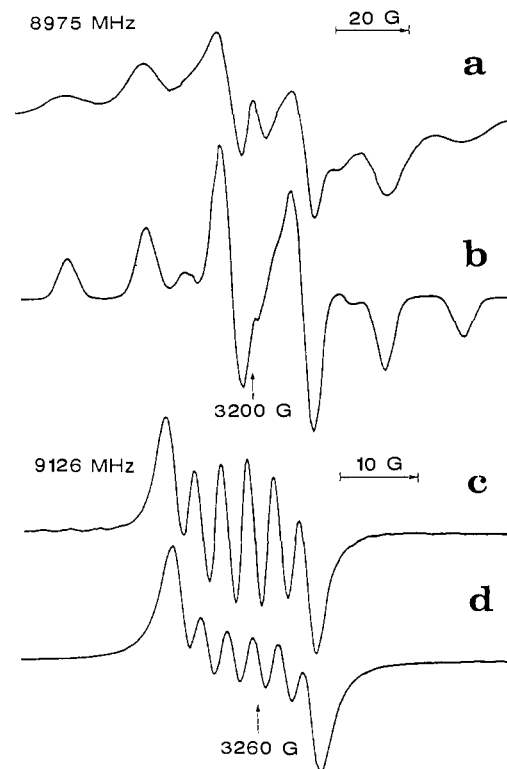

Figure 2. (a) ESR spectrum of $Al(C_6D_6)$ in adamantane at 4 K. (b) Computer-simulated spectrum based on the parameters given in the text. (c) ESR spectrum of $Al(C_6D_6)$ in adamantane at 232 K. (d) Computer-simulated spectrum based on parameters given in the text.
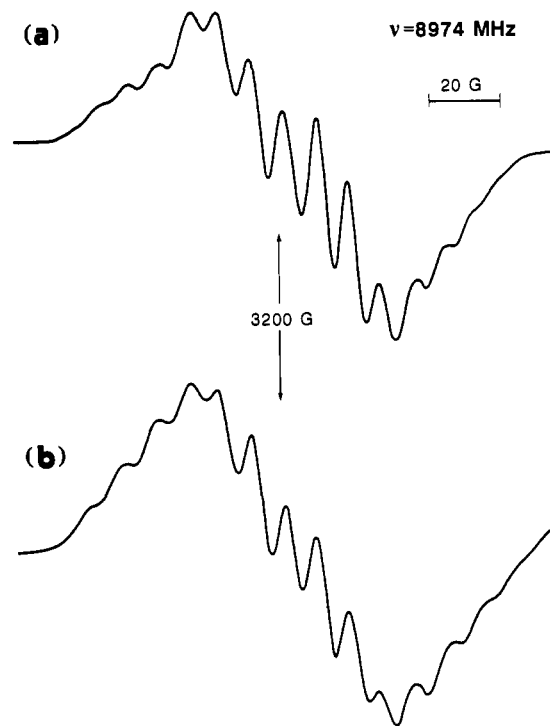

Figure 3. (a) ESR spectrum of $Al(C_6H_6)$ in C_6H_6 at 4 K. (b) Computer-simulated spectrum based on the parameters given in the text.

obtained if the same parameters were used, but interaction with six rather than two deuterons was invoked: i.e., $a_D(6)$ = 0.8 MHz. This aspect is discussed below.

Reaction of Aluminum Atoms and C_6H_6 in C_6H_6. Al atoms in solid C_6H_6 at 77 K gave a broad powder ESR spectrum having distinct Al hyperfine interactions but poorly resolved proton interactions. Spectral resolution improved at 4 K (Figure 3a), the more normal powder spectrum resulting from the greater rigidity

Table I. ESR Parameters of Al(C_6H_6) and Al(C_6D_6) in Benzene, Adamantane, and Neon Matrices[a]

	$a_{\parallel}$(Al)	$a_{\perp}$(Al)	a_{Al}	$a_{H/D}$	g_x	g_y	g_z
Al(C_6D_6)[b,c]							
4 K	55	−14	9	4	2.0014	1.9982	2.0034
121 K	45	−12	7	5.6	2.0015	1.9970	2.0047
Al(C_6D_6)[b,d]							
4 K	59	−16	9	4	2.0039	1.9970	2.0040
232 K			9.4	0.8			
Al(C_6H_6)[b,c]							
4 K	55	−19	5.7	27	2.0014	1.9969	2.0047
Al(C_6H_6)[b,d]							
4 K	56	−14	9	27	2.0010	1.9970	2.0060
220 K			9.5	5.3			
Al[C_6H_6][e,f]							
4 K	58.9	−21	5.6	28	2.002	1.998	2.005

[a] Hyperfine interactions in MHz. [b] This work. [c] In benzene. [d] In adamantane. [e] Reference 3. [f] In neon.
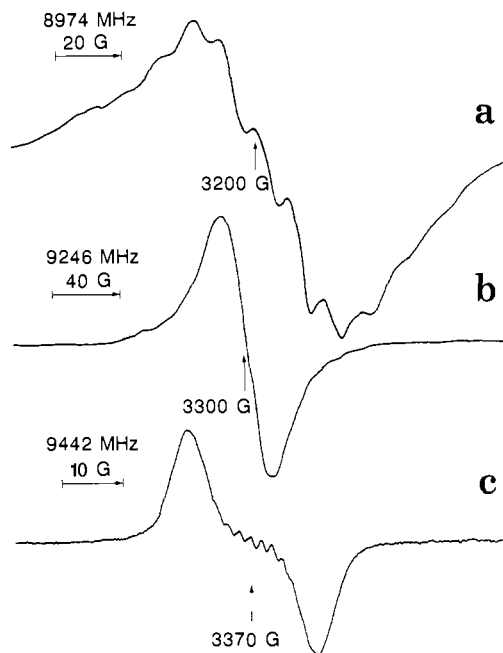

Figure 4. ESR spectrum of Al(C_6H_6) in adamantane given at (a) 4 K, (b) 77 K, and (c) 220 K.

of the matrix. A good computer simulation (Figure 3b) resulted for a carrier with an axial Al hyperfine tensor, an orthorhombic **g** tensor, an isotropic coupling with two protons and the following parameters: a_x(Al) = 55 MHz, a_y(Al) = a_z(Al) = 19 MHz, a_x(2H) = a_y(2H) = a_z(2H) = 27 MHz, g_x = 2.0014, g_y = 1.9969, and g_z = 2.0047. These parameters were consistent with those from Al and C_6D_6 and were similar to those found by Kasai and McLeod in neon.[3] As expected from its larger gyromagnetic ratio the proton coupling was 6.5 times larger than the deuteron coupling in Al(C_6D_6) at 4 K.

Reaction of Aluminum Atoms and C_6H_6 in Adamantane. The ESR powder spectra recorded at 4, 77, and 220 K for reaction of aluminum atoms and C_6H_6 in adamantane at 77 K are shown in parts a–c of Figure 4. It is interesting to note that the best resolved spectra were at 4 and 220 K. Acceptable simulations at these two temperatures were obtained assuming electron interaction with two equivalent protons and the parameters: a_x(Al) = 56 MHz, a_y(Al) = a_z(Al) = 14 MHz, a_x(2H) = a_y(2H) = a_z(2H) = 27 MHz, g_x = 2.0010, g_y = 1.9970, and g_z = 2.0060 at 4 K and a_{Al} = 9.5 MHz, a_H(2) = 5.3 MHz, and **g** = 2.001 at 220 K. The similarity between the average and isotropic aluminum coupling constants calculated from the ESR parameters at 4 and 220 K suggests that the same species is responsible for the spectra at both temperatures. However, the large difference in a_H(2) at the two temperatures is not entirely consistent with this conclusion.

The spectrum at 220 K can also be simulated reasonably well on the basis of an isotropic interaction of 9.5 MHz with Al and
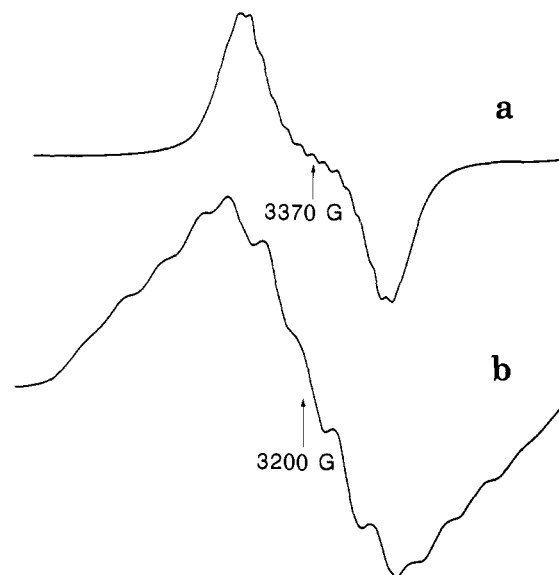
5.3 MHz with six equivalent protons (Figure 5a). Similarly, a good simulation of the spectrum at 4 K can be obtained by including an unresolved 5 MHz coupling to the four remaining protons of the benzene in addition to the 27 MHz coupling with two protons (Figure 5b). It is, therefore, not possible to use spectral simulations alone to distinguish between interaction of the unpaired electron with two or six protons in Al(C_6H_6) at 220 K. These alternatives are discussed in detail below.

Discussion

The EPR parameters given by Al(C_6H_6) and Al(C_6D_6) in benzene, adamantane, and neon matrices are summarized in Table I.

Spectral Assignment. It is apparent from the Al hyperfine interaction in the two hydrocarbon matrices at the various temperatures that the carrier of the spectrum contains one Al nucleus and is not a trapped Al atom, which has for example $a_{\parallel}$ = 142.8 MHz and $a_{\perp}$ = −98.7 MHz in site II of argon.[15] All the ESR parameters are in fact similar to those that have been assigned to the aluminum monobenzene complex Al(C_6H_6) in neon at 4 K.[3] We therefore conclude that the same species is formed in adamantane and benzene at the higher temperature of 77 K. Clearly, Al(C_6H_6) is a bonafide complex that is formed in widely different matrices over a range of temperatures.

Structure of Al[C_6H_6]. Mainly because of the observation of hyperfine interaction with only two out of the six protons of benzene, Kasai and McLeod[3] suggested that Al(C_6H_6) is a π-

Figure 5. (a) Computer-simulated spectrum of Al(C_6H_6) in C_6H_6 at 220 K assuming a six-proton interaction. (b) Computer-simulated spectrum of Al(C_6H_6) in C_6H_6 at 4 K assuming interaction with six protons.

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coordination complex in which the $3p_x$ orbital of Al, which contains the unpaired electron, interacts with one C=C unit through the 2p orbital components of the LUMO of benzene ($1e_{2u}$) as shown in structure 1.

This is analogous to the bonding that has been proposed for monoethylenealuminum(0), $Al(C_2H_4)$.[8,9] However, as was pointed out by Kasai and McLeod,[3] there is significantly more transfer of spin to the benzene than to the ethylene. This is confirmed when we use our values of A_{iso} and A_{dip} (determined knowing that $a_\perp(Al)$ is negative) to estimate unpaired spin populations in the 3s and 3p orbitals of Al. Division of the measured value of the isotropic Al hfi (9.5 MHz) in adamantane by the 1-electron parameter $A = 3911$ MHz for an electron in the 3s orbital of aluminum[16] gives a 3s spin population (ρ_{3s}) of 0.0024 (cf. 0.0014 for neon). The value of A_{dip} calculated from the relationship

$$A_{dip} = \frac{a_{\parallel} - a_{\perp}}{3} \quad (2)$$

is ~24 MHz (cf. 26.6 MHz in neon recalculated with $a_\perp$ negative). Dividing this value by αP, where the most recent value for unit spin population in the Al 3p orbital P is 178.4 MHz[17] and α is 0.4, gives $\rho_{3p} = 0.34$ (cf. 0.37 in neon). Hence, the remaining unpaired spin population of ~0.7 resides on the benzene ring compared with ~0.88 on the ethylene ligand of $Al(C_2H_4)$.[8–10]

These values for ρ_{Al} are not consistent with the two-proton interaction of 27 MHz with no spin population of opposite sign at the other protons of the benzene ring if the McConnell relation[18]

$$\rho_C(\pi) = \frac{a_H}{Q} \quad (3)$$

is obeyed, where $\rho_C(\pi)$ is the unpaired spin population at the two carbon atoms and Q is a proportionality constant and has a value of 63 MHz, since this predicts a spin population of 0.86 instead of 0.66 on the arene ligand. It should be noted that the major proton interaction will be negative if it is induced by spin polarization from the carbon p orbital.

This discrepancy as well as the marked differences between the hyperfine coupling to the two unique protons observed at 4 K (27 MHz) and that observed at 220 K (5.3 MHz) casts doubt that 1 is the best representation of the structure of $Al(C_6H_6)$. The difference can be resolved if we assume that at 4 K there is unresolved hyperfine coupling of opposite sign to the four remaining protons of the benzene while at 220 K there is equal interaction with all six protons with a coupling of $^1/_6$th the algebraic sum of the couplings at 4 K. The equality

$$[2(a_{H_1}) + 4(a_{H_2})]_{4K} = 6(a_H)_{220K}$$

is satisfied if the unresolved coupling at 4 K, $a_{H_2} = -5$ MHz. As already indicated in the Results, the experimental spectrum at 4 K can be simulated equally well on the basis of a coupling of 27 MHz with two protons and an unresolved coupling of 5 MHz with four protons. These changes with temperature could arise from a subtle change in the bonding of $Al(C_6H_6)$ with temperature. We suggest that at 4 K the bonding between Al and benzene is rigid and involves bridging of the two para positions by the Al atom, which lies on the C_{6v} axis (structure 3). At higher temperatures the bonding becomes fluxional as the barrier to rotation about the C_{6v} axis is overcome by the increase in temperature, the CAlC bridge clicking from one pair of para positions to the next. At 77 K the fluxional frequency matches the proton hyperfine frequency with a resultant broadening of the lines. At 220 K the motion across the para position is at higher frequency so that all six protons become equivalent on the ESR time scale. This is readily accommodated by the cheleotropic model 3. Although we are not able to produce definitive evidence in favor of structure 3, it is difficult to envisage the physical migration
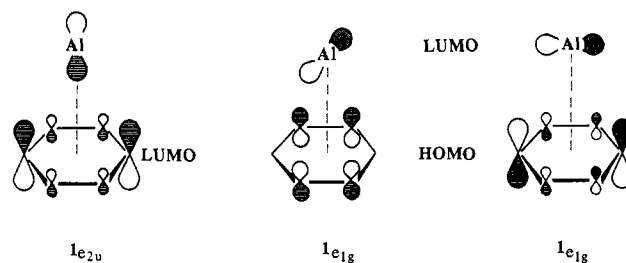

Figure 6. Frontier orbital diagram of the cheleotropic reaction of Al atoms with benzene.

of the Al atom beneath the benzene ring from one double bond to the other, which is required to explain the equivalence of the six protons in the ortho π structure 1. It should however be noted that interaction of a transient or metal center with one double bond of the benzene ring is not unprecedented since reaction of benzene with CH_2 to give cycloheptatriene[19,20] proceeds via a norcaradiene intermediate, and in a novel class of penta-ammineosmium(II) compounds, the metal center coordinates to the 1,2-position of benzene.[21]

Structure 3 is reminiscent of the products previously observed for the cheleotropic addition of Al atoms to conjugated dienes[5] and for the addition product resulting from the cocondensation of difluorosilylene with benzene at -196 °C.[22] The Frontier orbital description of the reaction given in Figure 6 shows it to be symmetry allowed with the LUMO and HOMO orbitals of both reactants able to correlate. Recent extended Hartree–Fock ab initio calculations[23] (in which the basis sets included polarization functions of C and F) of the interaction of benzene with hydrogen fluoride suggest the optimal geometry of the complex has the HF molecule lying along the C_{6v} of the benzene moiety in accordance with our findings.

The proton hyperfine of 27 MHz is twice that of the terminal CH_2 protons in aluminocyclopentene [c-$Al(C_4H_6)$], aluminocyclopentane [c-$Al(C_4H_8)$], and aluminoethylene $Al(C_2H_4)$, but this is expected since the unpaired spin population at aluminum is less in $Al(C_6H_6)$. The SOMO at the Al nucleus of $Al(C_6H_6)$ is quite different in that it has only 3p character unlike the sp or sp² hybridization occurring in c-$Al(C_4H_6)$ and c-$Al(C_4H_8)$. This may be indicative of the relative weakness of the C–Al bond and may also be associated with the presence of two flanking C=C bonds in the benzene case. In neither structure 1 nor 3 need there be a considerable loss of the delocalization energy although there is participation of antibonding π orbitals in both cases. The bonding in $Al(C_6H_6)$ is weaker than in $Al(C_2H_4)$, $Al(c$-$C_4H_8)$, and $Al(c$-$C_4H_6)$ since it decays in adamantane above 278 K whereas $Al(C_2H_4)$, $Al(c$-$C_4H_8)$, and $Al(c$-$C_4H_6)$ decay above 323 K. The weak nature of the C–Al bonds formed in the $Al(C_6H_6)$ complex is also consistent with the finding of equal coupling to the six benzene protons at 220 K. The energy barrier to rotation of the bonding across the para positions around the ring is estimated to be 4–8 kJ mol⁻¹ from the averaging that occurs at 220 K and implies a loosely bound complex. This motion of the bonding is not unlike the rotation about η^6-arene–metal bonds in compounds such as *bent*-terphenylenechromium tricarbonyl.[7] Hoffmann and co-workers[6] have considered the bonding and rotational barriers in arene transition-metal complexes for the two extreme cases of localizing the arene π system in one Kekule canonical form (cyclohexatriene) and the completely delocalized aromatic sextet and have concluded that, although there is some localization, the energy barriers to rotation are very small in complexes such as benzene tricarbonylchromium. Recently a

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barrier of 39.4 ± 2.1 kJ mol⁻¹ has been reported for rotation in the extremely asymmetric terphenylenechromium tricarbonyl.[7]

A recent IR study by Manceron and Andrews[24] of the products resulting from the cocondensation of lithium atoms with benzene led the authors to propose a structure for $Li(C_6H_6)$ similar to that which we suggest for $Al(C_6H_6)$ with the Li along the C_{6v} axis of the benzene ring.

Conclusion

The same monoligand aluminum(0) complex is formed in benzene and inert hydrocarbon matrices at 77 K as is produced in solid neon at 10 K. The temperature dependence of the proton couplings of $Al(C_6H_6)$ and its stability at ambient temperatures are consistent with a 1,4 cheleotropic adduct at low temperatures, which becomes fluxional at higher temperatures, with the Al atom bonding clicking from one 1,4-position of the benzene ring to the next. A 1,2 π-complex in which the six protons become equivalent by migration of the aluminum atom from one C=C unit of the benzene ring to the next appears less probable.

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In-Trough Cyclic Voltammetric Studies of Langmuir–Blodgett Monolayers of a Surfactant Derivative of Ru(bpy)₃²⁺ at an Indium–Tin Oxide Electrode

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Abstract: Langmuir–Blodgett (L–B) monolayers of a surfactant derivative of ruthenium tris(bipyridine) complex, Ru-(bpy)₂(bpy-C₁₉)²⁺, where bpy = 2,2′-bipyridine and C₁₉ = CH₂NHOC(CH₂)₁₆CH₃, confined to the surface of an indium–tin oxide electrode have been studied by cyclic voltammetry (CV) carried out in a Langmuir trough. The surfactant monolayer spread on an electrolyte subphase solution was brought to contact with the electrode by either vertical dipping under a surface pressure or horizontal touching at arbitrary surface concentrations. In the horizontal touch experiment, the surface tension was used to sustain contact of the subphase solution with the electrode, which was held at a position slightly above the air/water interface. In this arrangement the exact electrode alignment with the surfactant layer is not important. The data obtained from in-trough CV measurements reveal that the spread surfactant molecules at submonolayer concentrations were highly aggregated at the air/water interface rather than distributed homogeneously as a two-dimensional gaseous state, and a major cause for the incomplete electrochemical recovery of deposited L–B monolayers frequently observed is the relaxation of the compressed surfactant molecules toward the limiting molecular area in an ionic aqueous solution. The CV measurements performed also provided information concerning electron transfer in the organized monolayer assemblies, the physical and chemical changes of the spread surfactant layer at the air/water interface, and the mass transfer of solution species across the L–B monolayer films.

In a previous paper we reported for the first time the observation of the electrogenerated chemiluminescence (ECL) from an organized monomolecular layer of a surfactant derivative of Ru-(bpy)₃²⁺ consisting of a single stearamidomethylene chain linked to one bipyridine unit at the 4-position (abbreviated Ru(bpy)₂-(bpy-C₁₉²⁺) on the surface of indium-doped tin oxide (ITO), Pt, and Au electrodes.[1] The surfactant monolayer was coated on the substrate electrodes by the L–B method and the ECL was generated in an electrochemical cell containing an aqueous oxalate solution by applying a positive potential to the electrode modified by the monolayer of Ru(bpy)₂(bpy-C₁₉²⁺).[2] The ECL observation revealed that a Ru(bpy)₂(bpy-C₁₉)²⁺ monolayer confined to a conductive surface by the L–B technique was excitable through an electrochemical route and that the radiative decay of the excited states could compete with the nonradiative ones. While this concept of immobilizing luminescent molecules on electrode surfaces led to the development of a new class of ECL systems that can be useful for a variety of purposes,[3] it also motivated us to characterize these organized monolayers at electrodes by electrochemical techniques. Although monolayer assemblies of Ru(bpy)₃²⁺ derivatives formed by L–B and other methods have been the subject of extensive photochemical and spectroscopic studies,[4] their electrochemical studies have been limited.[5]

In this paper we describe the application of cyclic voltammetry(CV) carried out in a Langmuir trough to the characterization of the L–B monolayer films of Ru(bpy)₂(bpy-C₁₉)²⁺. There have been a number of reported studies about the electrochemical behavior of organized assemblies of surfactant molecules on electrode surfaces.[5–8] In particular, two previous reports have

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(2) For the proposed mechanism of this ECL system, see: (a) Chang, M.; Saji, T.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 5399. (b) Rubinstein, I.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 512.

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(5) Daifuku, H.; Aoki, K.; Tokuda, K.; Matsuda, H. *J. Electroanal. Chem.* **1985**, *183*, 1.
(6) (a) Fujihira, M.; Araki, T. (a) *Chem. Lett.* **1986**, 921. (b) Fujihira, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2379.