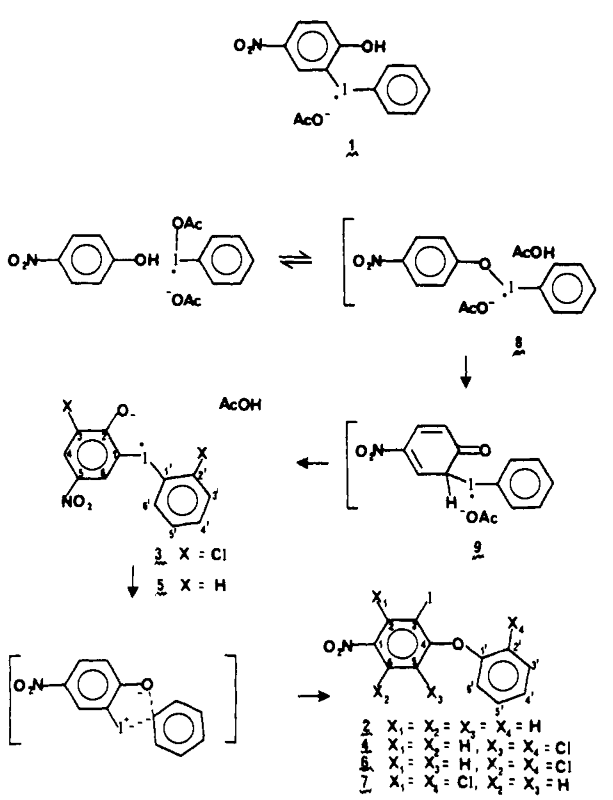

Figure 2. Mechanism for the formation of (3-chloro-2-hydroxy-5-nitrophenyl)(2′-chlorophenyl)iodonium hydroxide inner salt.

the basis of (i) substantial observed shielding of ortho carbons in phenolic systems[10] and (ii) the less extensively coupled signal for C(1) in the fully coupled spectrum. The latter consideration also suggested that the less extensively coupled resonance line at 144.0 ppm was due to C(5) whereas that at 139.7 ppm was due to C(2′). The remaining quaternary signals due to chlorine-bearing carbons were assigned by comparison with resonance lines of corresponding methine carbons (C(3), C(2′), and C(6′)) in the inner salt **5**. Essentially all of the signals due to methine carbons in each of the four compounds listed in Table I could be assigned by proton homonuclear spin decoupling experiments together with a series of four proton decoupler-stepped off-resonance decoupling experiments.[11,12]

Some preliminary observations on the nature of this reaction have been noted. Under the same experimental conditions, no reaction occurred between 4-nitroanisole and phenyliodine diacetate. Reaction of 2,6-dichloro-4-nitrophenol with phenyliodine diacetate at 45 °C for 50 days was reported to give 2,6-dichloro-1,4-benzoquinone (47%).[2] In all cases examined in the chlorinated dibenzofuran syntheses, no unexpected rearrangements were observed (i.e., for the chlorinated phenyliodine diacetates, ipso displacement of the iodine occurred) and rearrangement of the iodine was always ortho to the original phenol carbon. In the reaction of 3-chloro-4-nitrophenol with 2-chlorophenyliodine diacetate, a 3:1 mixture of **6** and **7**, respectively, resulted.

With the demonstrated stability of the inner salt in cases where the nitrophenol contains no electron-donating functionality, the mechanism originally proposed,[2] with revision of the structure of the intermediate salt (see Figure 2), is supported. The reported[2] formation of 5-iodo-2-methoxy-4-phenoxy-nitrobenzene from 3-methoxy-4-nitrophenol under identical conditions with the formation of the inner salt from 4-nitrophenol suggests that, for nitrophenols with electron-donating substituents, either a concerted rearrangement of **9** (from **8**) or a rapid rearrangement of the inner salt (analogous to **5**) occurs.

The mechanism and general synthetic utility of this reaction are under investgation.[13]

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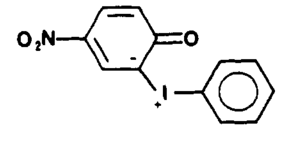

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Aluminum Atom–Benzene Molecular Complex: Matrix Isolation Electron Spin Resonance Study

Sir:

Recently we have shown that the Al atom ($3s^2$ $3p^1$) forms a π-coordination complex with ethylene and that the complex results from the dative interaction between the vacant antibonding π orbital of ethylene and the semifilled p orbital of Al parallel to the double bond.[1] We report in this communication the generation and the detection by ESR of the Al atom–benzene molecular complex stabilized in neon matrices. The lowest, vacant π orbitals of benzene belong to the irreducible representation e_2 (doubly degenerate) of the C_{6v} symmetry group. The semifilled p orbital of Al located along the symmetry axis of benzene would belong to either a_1 (p_z) or e_1 (p_x and p_y), and hence cannot effect the dative interaction with

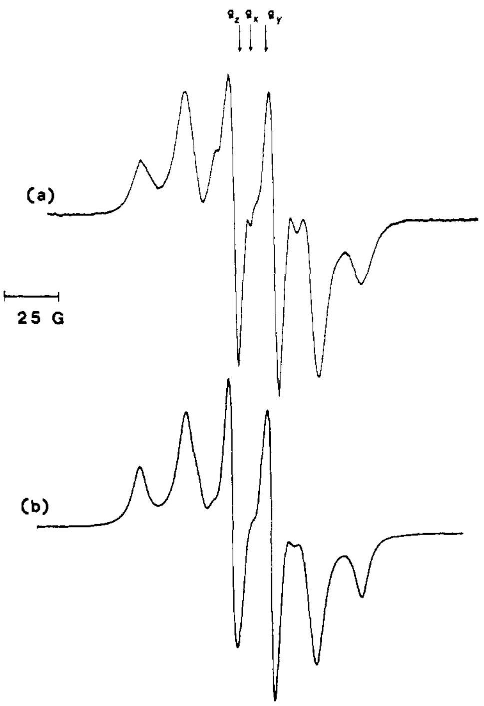


Figure 1. (a) ESR spectrum observed from neon matrix containing Al and C_6D_6. (b) Computer-simulated spectrum based upon the parameters given in the text.

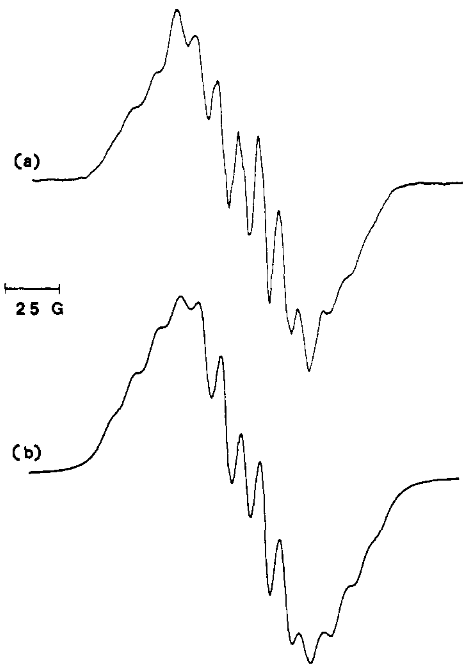


Figure 2. (a) ESR spectrum observed from neon matrix containing Al and C_6H_6. (b) Computer-simulated spectrum based upon the parameters given in the text.

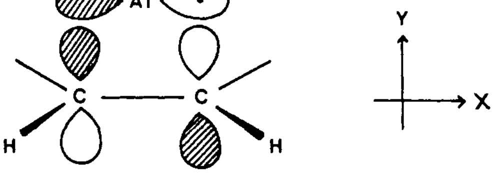
the lowest, vacant π orbitals of benzene. One thus anticipates the Al atom-benzene complex to be of symmetry lower than C_{6v}. The present study revealed unequivocally that the Al atom complexes with benzene through only one C=C unit of the ring.

The experimental setup designed to trap high-temperature vapor-phase species in a rare gas matrix at liquid helium temperature and to observe the ESR of the resulting matrix has been described earlier.[2] In the present study, Al atoms were vaporized from a tantalum cell resistively heated to ~1050 °C and trapped in neon matrices together with benzene introduced through a separate gaseous sample inlet. The concentrations of Al and benzene in the resulting matrices were estimated to be ~0.1 and 2 mol %, respectively. The frequency of the spectrometer locked to the sample cavity was 9.410 GHz and all the spectra were observed while the matrices were maintained at ~4 K.

A neon matrix containing Al atoms ($3s^2\,3p^1$) alone appeared white and showed no ESR signal. The absence of a signal attributable to Al atoms is ascribed to the extreme broadening caused by the degeneracy of the p orbitals.[3] When Al atoms were condensed together with benzene, the matrix appeared purple, and a strong ESR signal possessing a unique pattern appeared centered about the position corresponding to $g = 2.00$. Figures 1a and 2a show such spectra obtained when C_6D_6 (perdeuteriobenzene) and C_6H_6 (normal benzene) were used, respectively. We propose to assign these spectra to Al atom-benzene molecular complexes randomly oriented within the matrices.

The sextet structure conspicuously resolved in Figure 1a must result from the hyperfine interaction with the ^{27}Al nucleus (natural abundance = 100%, $I = \frac{5}{2}$). The unique intensity pattern and line shape were realized to be caused by the uniaxial symmetry of the Al coupling tensor, $|\mathbf{A}_x| \gg |\mathbf{A}_y| \simeq |\mathbf{A}_z|$ and the orthorhombic **g** tensor indicated in the figure. Resorting to the method of computer simulation (of the ESR spectrum of randomly oriented radicals)[4] the following **g** tensor and the Al coupling tensor were determined from Figure 1a: $\mathbf{g}_x = 2.002 \pm 0.001$, $\mathbf{g}_y = 1.998 \pm 0.001$, $\mathbf{g}_z = 2.005 \pm 0.001$; $|\mathbf{A}_x(\mathrm{Al})| = 21.0 \pm 0.5$, $|\mathbf{A}_y(\mathrm{Al})| = 7.5 \pm 2.0$, $|\mathbf{A}_z(\mathrm{Al})| = 7.5 \pm 2.0$ G. The computer-simulated spectrum based upon these parameters and a Lorentzian line shape with the line width of 8 G is shown in Figure 1b. A careful comparison of Figures 1a and 2a then revealed that the latter spectrum is an overlapping sextet of triplets, the sextet pattern being that of the former and the triplet pattern being that expected from the coupling interaction of ~10 G with two equivalent protons. Figure 2b shows the computer-simulated spectrum based upon the **g** tensor and the Al coupling tensor given above and the following additional parameters: $|A(\mathrm{H}_1)| = |A(\mathrm{H}_2)| = 10.0$ G.

The Al coupling tensor of uniaxial symmetry and the coupling interaction of the observed magnitude with two equivalent protons are most compatible with the bonding scheme in which the Al atom complexes with benzene through one C=C unit of the ring. We further envisage that the coordination plane C-Al-C is perpendicular to the benzene ring and that the complex is formed by dative interaction between the semifilled p orbital of Al parallel to the C-C link and the orbital given by the antibonding combination of the p_π orbitals of the two carbon atoms as shown. The proposed bonding scheme is then identical with that shown for the Al atom-ethylene complex,[1] and the semifilled orbitals of both complexes are given by



$$\Phi = a[\mathrm{p}_x(\mathrm{Al})] + b[\mathrm{p}_y(\mathrm{C}_1) - \mathrm{p}_y(\mathrm{C}_2)] \qquad (1)$$

The Al coupling tensor should reflect the uniaxial symmetry of the $\mathrm{p}_x(\mathrm{Al})$ orbital and be given by $\mathbf{A}_x = A_{\mathrm{iso}} + 2A_{\mathrm{dip}}$ and $\mathbf{A}_y = \mathbf{A}_z = A_{\mathrm{iso}} - A_{\mathrm{dip}}$.[5] Here, A_{iso} represents the isotropic interaction induced through polarization of the filled core orbitals, and A_{dip} represents the anisotropic interaction related to the spin density in $\mathrm{p}_x(\mathrm{Al})$. Let us assume that all of the elements of the Al coupling tensor determined above are positive. They then yield $A_{\mathrm{iso}} = 12.0$, $A_{\mathrm{dip}} = 4.5$ G. The value of A_{dip} for a unit spin density in the Al 3p orbital has been calculated to be 21 G.[5] The coefficients in eq 1 for the Al-benzene complex are thus assessed to be $a^2 \simeq 0.2$, $b^2 \simeq 0.4$. The McConell relation[6] and the spin density, b^2, in the p_π orbital of carbon then predict the proton coupling constant of 9 G in close agreement with the observed value. In the case of Al-ethylene, it has been shown that $a^2 = 0.7$ and $b^2 = 0.15$. It is interesting that the electron migration occurs to a much further extent for the Al-benzene complex.

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Hydrogenation and Degradation of Carbon Disulfide by Organometallic Cluster Hydride Complexes. Reaction of Carbon Disulfide with $(\mu\text{-H})_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$

Sir:

It has recently been proposed that transition metal cluster compounds may form the basis for the development of a valuable new class of homogeneous catalysts. This idea is based on the principle that the cooperative interaction of several metal atoms with a given substrate or substrates can produce new and unusual forms of reactivity.[1,2] We have recently been examining the ability of triosmium-hydride cluster complexes to effect the hydrogenation of small molecules[3] and have found that $(\mu\text{-H})_2Os_3(CO)_{10}$ reacts with CS_2 via an unusual dicluster reaction to produce the molecule $(\mu\text{-S}_2CH_2)[(\mu\text{-H})Os_3(CO)_{10}]_2$.[3b] In this reaction each cluster has transferred one hydrogen atom to the carbon atom of the CS_2 molecule and produced a dithiomethylene ligand which then links the two cluster units. In an effort to gain further insight into the mechanism of this unusual reaction we have examined the reaction of $(\mu\text{-H})_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ with CS_2. To our surprise, we have found an entirely new reaction in which a single cluster complex reacts with one molecule of CS_2, transfers both its hydrogen atoms to the carbon atom, cleaves a single sulfur atom from the original CS_2 unit, and ultimately produces a fractured cluster complex containing inorganic sulfide and a bridging thioformaldehyde ligand.

In a typical reaction 0.12 g of $H_2Os_3(CO)_9[P(CH_3)_2C_6H_5]$ was refluxed in 25 mL of CS_2 solvent for 3 h. The color of the solution changed from purple to orange. The solvent was removed in vacuo, and the product I was isolated (16% yield) by chromatography over alumina.[4] The details of the molecular structure of I have been established through an X-ray crystal structure analysis.[5,6] The molecular structure of I is shown in Figure 1. An inorganic sulfide ligand S(2) is found bonded to all three osmium atoms. The group C(10)-S(1) is a thioformaldehyde ligand which is formally π bonded to atom Os(2), while sulfur atom S(1) simultaneously serves as a bridge between atoms Os(1) and Os(2). Although the hydrogen atoms of the thioformaldehyde ligand were not observed crystallographically, their presence was confirmed by the observation of an AB quartet resonance pattern in the ^{1}H NMR spectrum.[7] We are not aware of any other structural characterizations of a thioformaldehyde ligand and find here that the C-S bond distance at 1.79 (1) Å is very long and approaches that of a single bond.[8,9] There is a metal-metal bond between atoms Os(1) and Os(3), Os(1)-Os(3) = 2.855 (1) Å, but none between Os(1) and Os(2), Os(1)··Os(2) = 3.780 (1) Å, and Os(2) and Os(3), Os(2)··Os(3) = 4.033 (1) Å.

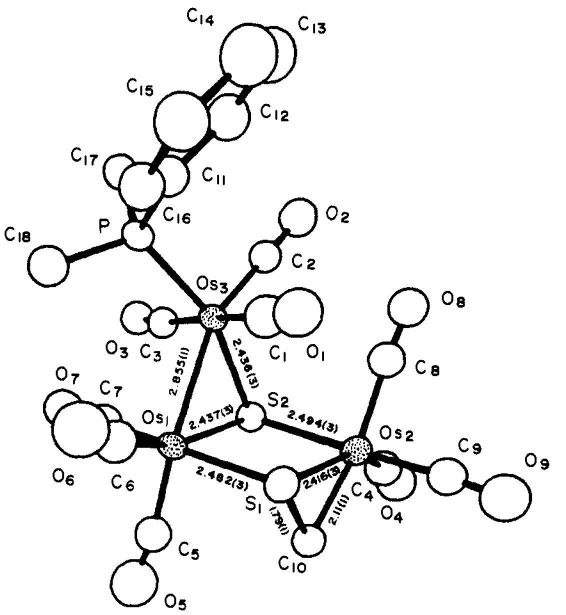

Figure 1. A perspective ORTEP drawing of $(\mu\text{-SCH}_2)(\mu_3\text{-S})Os_3(CO)_9[P(CH_3)_2C_6H_5]$ showing 50% probability ellipsoids and selected bond distances.

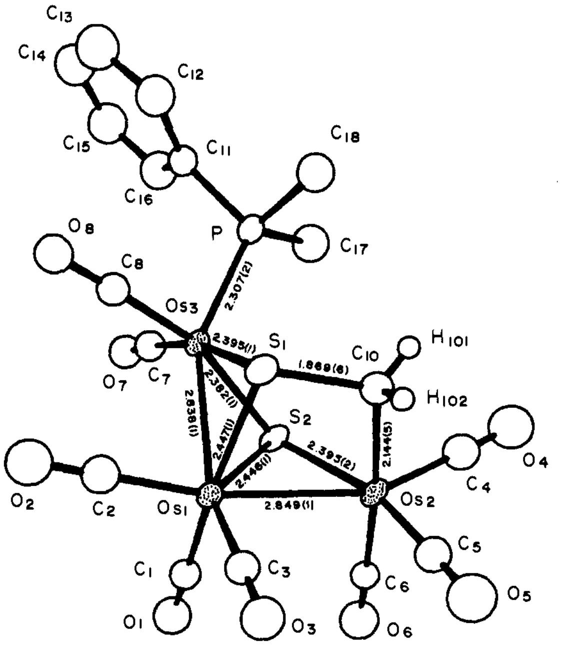

Figure 2. A perspective ORTEP drawing of $(\mu_3\text{-SCH}_2)(\mu_3\text{-S})Os_3(CO)_8[P(CH_3)_2C_6H_5]$ showing 50% probability ellipsoids for all nonhydrogen atoms and selected bond distances.

When refluxed in hexanes solvent, I readily loses 1 mol of carbon monoxide to form the complex $(\mu_3\text{-SCH}_2)(\mu_3\text{-S})Os_3(CO)_8[P(CH_3)_2C_6H_5]$, II (yield 74%).[11] II was also analyzed crystallographically and its molecular structure is shown in Figure 2.[12,13] This compound also contains an inorganic