acyl 1, which produces, among other organics, HC(O)CH₂CMe₃ and a ditantalum monoacyl complex, which itself reduces to a variety of products. This decomposition prevents unambiguous determination of the reduction stoichiometry since the reduction rate of 1 decreases relative to the decomposition of 1 at low levels of reductant. An IR spectrum of the reaction mixture containing the tantalum product(s) shows broad Ta–O–Ta modes at 829 and 719 cm⁻¹ and a broad O–H mode at ~3250 cm⁻¹.

Reduction of the [¹³C]acyl (C₅Me₅)Ta[¹³C(O)CH₂CMe₃]Cl₃ yielded (CMe)₅(¹³CCH₂CMe₃), establishing that the unique arene ring carbon is derived from the acyl. At least two (by GC) of the three arene isomers (CMe)₄(CEt)(CCH₂CMe₃) were obtained from (C₅Me₄Et)Ta[C(O)CH₂CMe₃]Cl₃ reduction. A double label crossover experiment with labeled acyl and C₅R₅ groups supports a predominantly intramolecular mechanism for this unusual transformation. Reduction of an equimolar mixture of (C₅Me₅)Ta[¹³C(O)CH₂CMe₃]Cl₃ and (C₅Me₄Et)Ta[¹²C(O)-CH₂CMe₃]Cl₃ in toluene gave the direct arene products (CMe)₅(¹³CCH₂CMe₃) and (CMe)₄(CEt)(¹²CCH₂CMe₃) in 93% relative yield (eq 2), with only 7% combined cross-product arenes, (CMe)₅(¹²CCH₂CMe₃) and (CMe)₄(CEt)(¹³CCH₂CMe₃) isomers, observed by mass spectrometry.²¹
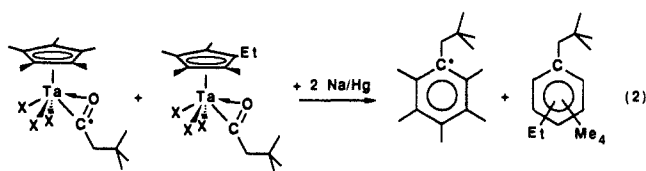
While a complete mechanism cannot yet be proposed, several experiments have yielded pertinent mechanistic information about this intramolecular reaction. No organic or inorganic intermediates are visible by ¹H or ¹³C NMR or IR spectroscopies during the reduction, and small molecule traps (H₂, CO, C₂H₄) do not affect the course of the reaction. The acyl/alkylidyne attack on the C₅Me₅ ring is highly selective, as there is no evidence for products from formal alkylidyne insertion into the C_{ring}–C_{methyl} or methyl C–H bonds. The ketone C₅Me₅C(O)CH₂CMe₃,¹⁴ potentially derived from acyl migration to the C₅Me₅ ring, is not a free intermediate since (1) ≤0.5% can be found by GC of the reaction mixture and (2) it is not visible during in situ NMR or IR spectral studies of the reduction. The lack of intermediates that are sufficiently long-lived to be detected or trapped during the reaction suggests the possibility of a concerted intramolecular process. Mechanistic possibilities include oxycarbenoid/carbenium²² addition to the C_{ring}–C_{ring} bond (with opening of the cyclopropyl to the arene) or acyl migration to the ring to form a lower valent C₅Me₅C(O)CH₂CMe₃ complex which is deoxygenated rapidly by the electrophilic tantalum. The role of the added electron(s) is presently unknown. While the LUMO in d⁰ Cp₂Ti[η²-C(O)CH₃]Cl is primarily C–O π* in character,²² the assignment of the LUMO in mono(η-C₅R₅) d⁰ η²-acyl complexes awaits extended Hückel and Fenske–Hall calculations.

The synthetic utility of reductive metal acyl deoxygenation and addition to other organic ligands will be addressed after more thorough studies are completed. In conclusion, our studies show that reductive acyl deoxygenation is possible and suggest that other organometallic ligands may exhibit unusual chemistry as the metal valency is formally altered.

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Supplementary Material Available: A description of a representative acyl reduction/arene isolation experiment and crystal data, measurement conditions, refinement details, and an ORTEP diagram of the molecular structure of C₆Me₅(CH₂CMe₃) (2 pages). Ordering information is given on any current masthead page.

Isomerization of the Cubane Radical Cation to the Bridged 1,4-Bishomobenzene (Bicyclo[3.3.0]octa-2,6-diene-4,8-diyl) Radical Cation†

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The electronic structure and the interconversion of the radical cations of the (CH)₈ group have recently attracted attention.¹⁻⁴ Among the (CH)₈ hydrocarbons, cubane⁵ has high symmetry (O_h) and the highest strain energy.⁶ Its physicochemical properties continue to attract experimental and theoretical interest.⁶⁻¹⁰ The cubane radical cation (1) was first studied in neon matrices at 4 K.¹ The observed nonet EPR spectrum ($|A_{8H}| = 3.2$ G) was explained by invoking a dynamic Jahn–Teller distortion of 1. Because of the narrow temperature range of neon matrices, further reactions of 1 were not observed.¹ Here we report isomerization of 1 to the bridged 1,4-bishomobenzene radical cation (2), which was first demonstrated to be formed by the ring-opening of the semibullvalene radical cation.³ A mechanism of this novel thermal rearrangement is suggested. Another highly strained compound in the (CH)₈ hydrocarbon family is cuneane.¹¹ We show here that radiolytic oxidation of cuneane also yields 2.

1 was generated by the radiolytic oxidation¹² of cubane in three Freon matrices (CFCl₃, CF₃CCl₃, and CF₂ClCFCl₂). Similar spectra of 1 were obtained in all three matrices. Figure 1a shows the EPR spectrum of 1 in CF₂ClCFCl₂ at 77 K. It is a broad

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(21) This result was shown by MS on the arene products. Control experiments showed that (1) acyl/cyclopentadienyl scrambling between the reactants does not occur in solution and (2) arene alkylidyne scrambling does not occur under mass spectrometric conditions.
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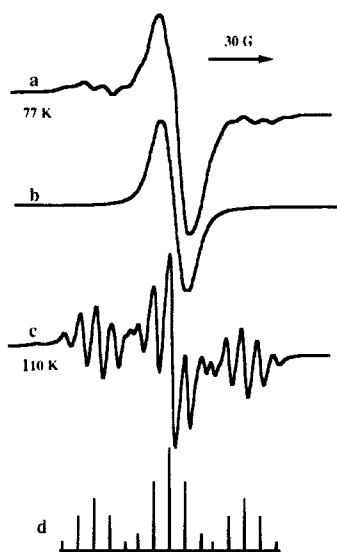
Figure 1. (a) First-derivative EPR spectrum of **1** at 77 K obtained from γ-irradiation (dose, 0.75 Mrad) of a solid solution of cubane (0.5 mol %) in $CF_2ClCFCl_2$ at 77 K and (b) its simulation by using $a(8H) = 3.2$ G and a Lorentzian line width of 4.5 G. (c) First-derivative EPR spectrum of **2** formed by thermal annealing of **1** to 110 K in $CF_2ClCFCl_2$ and (d) stick spectrum of spectrum c constructed by $a(2H_\beta) = 36.3$ G and $a(4H_\alpha) = 7.7$ G.

Scheme I
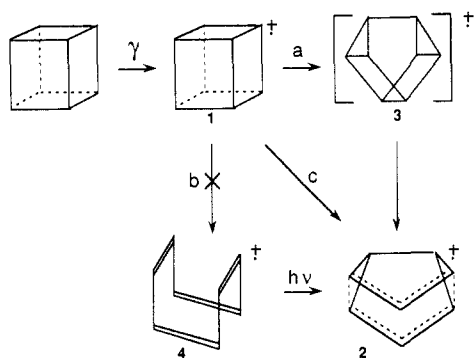
signal ($\Delta H_{pp} \approx 14$ G), less resolved than the EPR spectrum of **1** obtained in neon matrices.[1] The broader EPR line width observed is attributable to the weak interaction of the unpaired spin with the chlorine or fluorine atoms of Freon molecules observed in many other systems.[12] Figure 1a is satisfactorily simulated by the known coupling constant for **1**,[1] as shown in Figure 1b. From this assignment it is surmised that **1** undergoes dynamic Jahn–Teller distortion in Freon matrices at 77 K.

In addition to the broad signal assigned to **1**, Figure 1a exhibits some other weaker and wider EPR spectral features, which distort the EPR signal of **1**. On thermal annealing of the sample at 110 K, the singlet gradually and irreversibly decreases and disappears in a few minutes, and the wider EPR spectral features grow in. Figure 1c shows the EPR spectrum of the wider features at 110 K, which is analyzed as a triplet ($a(2H_\beta) = 36.3$ G) of quintets ($a(4H_\alpha) = 7.7$ G), as indicated by the stick spectrum in Figure 1d. The observed EPR data match exactly those for **2** under the same matrix and temperature conditions.[3,4] **1** also rearranges slowly to **2** at 77 K.

Several possible pathways for the rearrangement of the cubane radical cation (**1**) to the bridged 1,4-bishomobenzene radical cation (**2**) are shown in Scheme I.[13]

Pathway a involves the cuneane radical cation (**3**) as an intermediate, namely, the reaction follows the path **1** → **3** → **2**. Pathway b involves the ring-opening of **1** to the intermediate

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(13) Several other pathways of **1** to **2** are conceivable, e.g., via the syn-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene radical cation, as pointed out by one of the referees.
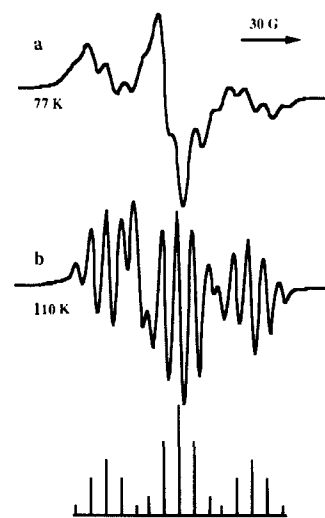
Figure 2. First-derivative EPR spectra recorded at 77 K (a) and 110 K (b) after γ-irradiation of cuneane (0.5 mol %) at 77 K in $CF_2ClCFCl_2$, showing features assigned to **2**. The dose is the same as in Figure 1.

cyclooctatetraene radical cation (**4**), followed by a 1,5-ring-closure of **4** to **2**. Pathway c assumes no stable intermediate like cuneane radical cation in the conversion of cubane radical cation **1** into **2**. Indeed, it may turn out that the radical cation **2** is the common intermediate involved in many transformations of the $(CH)_8$ radical cation family.

Pathway a is the preferred reaction route. The rearrangement of cubane to cuneane is known to be catalyzed by Ag(I),[14] which was proposed to involve the cyclobutyl carbonium ion as an intermediate formed by oxidative addition of Ag(I) to cubane. Cuneane can be further isomerized to semibullvalene by Rh(I),[15] and the oxidation of semibullvalene yields **2**.[3] These catalytic transformations of cubane to semibullvalene via cuneane suggest pathways for radical cation transformations, even though it is not clear whether comparison of structural features of the carbonium ion intermediate and cubane radical cation are meaningful. The suggestion that cubane radical cation (**1**) isomerizes to **2** via **3** is supported by the study of cuneane. Figure 2 shows the EPR spectra recorded at 77 K (a) and 110 K (b) after γ-irradiation of cuneane in $CF_2ClCFCl_2$ at 77 K. Both spectra possess the same features. The spectrum at 110 K is much better resolved. The hyperfine data ($a(2H_\beta) = 36.3$ G and $a(4H_\alpha) = 7.7$ G) measured from the spectrum at 110 K are the same as those of **2**, indicating that the rearrangement of **3** to **2** occurs at 77 K. This observation is consistent with the fact that no EPR signals from any intermediate such as **3** were detected in the transformation of **1** to **2** between 77 K and 110 K, since, if **3** is formed, it must promptly rearrange to **2**. A choice between pathways a and c is not feasible at this time.

Pathway b with **4** as intermediate is rejected by a comparison of our results with those of Williams and co-workers.[3,4] First, **1** is nearly colorless. We have carried out an optical absorption study of **1** in the $CF_2ClCFCl_2$ matrix at 77 K and found no absorption band in the region between 400 and 900 nm. However, **4** has a rich red color, absorbing strongly at 507 nm.[4] During the isomerization of **1** to **2**, no red color of the Freon solutions was observed, which means **4** cannot be a main intermediate. Secondly, and more importantly, Williams et al. demonstrated,[4] and we further confirmed, that **4** does not rearrange to **2** thermally, in contradiction to the observed thermal transformation of **1** to **2**.[16] Interestingly, **1** → **2** is also found to be driven by UV or visible light

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(at 90 K). Further experiments are being undertaken to clarify the photochemistry.

Lewis and Brønsted Acid Adducts in Ambient Temperature Chloroaluminate Molten Salts: NMR Observations

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In this report we show that when an organic base, *N,N*-dimethylaniline (DMA), is added to an acidic ambient temperature molten salt, an aluminum chloride adduct is formed; on addition of proton, which behaves as a superacid, the AlCl₃ is displaced in an equilibrium process.

It has recently been shown that the value of the Hammett acidity function for protons in acidic ambient temperature chloroaluminate molten salts indicates they are Brønsted superacids.[1,2] The molten salt, composed of a mixture of 1-ethyl-3-methylimidazolium chloride (ImCl) and AlCl₃, is acidic, basic, or neutral when the mole ratio of AlCl₃:ImCl is greater than, less than, or equal to unity, respectively.[3] The basic melts contain chloride ion, a Lewis base, while the acidic melts contain heptachlorodialuminate ion, $Al_2Cl_7^-$, a strong Lewis acid. The underlying Lewis acidity of the molten salt changes with melt composition; thus a variation of the Brønsted acidity with melt composition also results. Our interest is in the chemical and electrochemical behavior of solutes in these unusual Lewis/Brønsted acid solvents, and here we report NMR studies of the interaction of an organic base, DMA, with the Lewis and Brønsted components of this superacid medium.

The effect of melt composition on the ¹³C NMR resonance of the DMA methyl groups is shown in Figure 1.[4] The chemical shift remains essentially unchanged from neat DMA to DMA in a basic melt, where no AlCl₃ adduct forms. However, the methyl resonance shifts 6.5 ppm downfield when DMA is added to an acidic melt. Identical trends are observed in the ¹H NMR of DMA. The electrochemistry of DMA also shows marked dependence on melt composition. The oxidation potential for DMA shifts 1.75 V positive going from a basic to an acidic, proton free, melt.[5] These results indicate removal of electron density from the DMA molecule and are consistent with the formation of an AlCl₃ adduct in the acidic melt. This behavior is chemically reversible; changes observed are reversed moving from acidic to
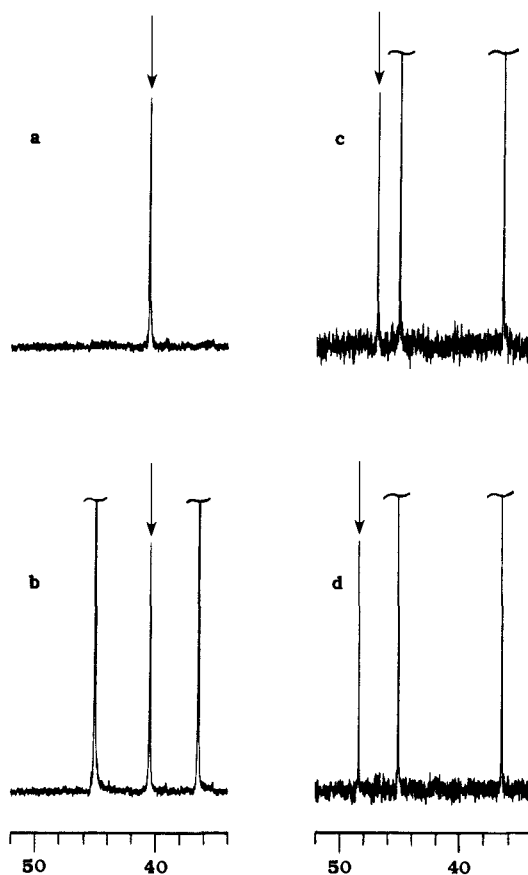

Figure 1. The effect of melt composition on the ¹³C NMR resonances for the DMA methyl groups at 20 °C: (a) neat DMA; (b) DMA in a basic melt; (c) DMA in an acidic melt; (d) DMA in an acidic melt containing excess ImHCl₂. (The chemical shifts are in ppm referenced to TMS in a coaxial tube. The peaks at δ 36 and δ 45 are due to the 1-ethyl-3-methylimidazolium cation.)

basic melts. DMA is a stronger base than $AlCl_4^-$ and is capable of displacing $AlCl_4^-$ from $Al_2Cl_7^-$ to form the adduct

$$Al_2Cl_7^- + DMA \rightarrow DMA{:}AlCl_3 + AlCl_4^- \qquad (1)$$

These conclusions are in agreement with suggestions in our previous electrochemical studies on DMA in a similar chloroaluminate molten salt system (a mixture of *n*-butylpyridinium chloride and AlCl₃).[6] Reaction 1 appears to be complete in a melt where $Al_2Cl_7^-$ is in excess over DMA. When the concentration of $Al_2Cl_7^-$ is less than that of the DMA, a mixture of DMA and DMA:AlCl₃ results. The ¹³C and ¹H NMR of the mixture of the two species at 20 °C show a single spectrum that is the population weighted average of the spectra for the DMA and DMA:AlCl₃, indicating that the exchange between DMA and DMA:AlCl₃ is fast on the NMR time scale ($k > 10^5$ s⁻¹).

The quantitative addition of protons to these molten salts can be achieved by use of 1-ethyl-3-methylimidazolium hydrogen dichloride (ImHCl₂).[4a] The addition of ImHCl₂ in excess of the DMA to acidic melts shifts the ¹³C resonance for the DMA methyl groups 1.5 ppm further down field (Figure 1d) and causes the ¹H resonance for the DMA methyl protons to be split into a doublet (³J_{H-H} = 5.3 Hz, Figure 2b). In addition, the ¹H spectrum shows a new broad peak at δ 7.8 (Figure 2a). Irradiation of this peak in a double-resonance experiment collapses the DMA methyl proton doublet, clearly showing coupling of the two peaks. Thus, we have assigned the peak at δ 7.8 ppm to the dimethylanilinium N–H proton. The addition of ImHCl₂ to an acidic melt containing DMA:AlCl₃ also results in a decrease in the DMA oxidation wave.[5] These observations support the displacement of AlCl₃ from

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