this laboratory dealing with reactions between pentafluorosulfur halides and olefins,[3] we have investigated reactions of SF_5Br with selected acetylenes in an attempt to synthesize new SF_5-substituted acetylenic monomers. In this paper, we describe the synthesis and characterization of the novel compounds, bis(pentafluorosulfur)acetylene, $SF_5C\equiv CSF_5$, and (pentafluorosulfur)trifluoromethylacetylene, $SF_5C\equiv CCF_3$.

Millimole quantities of SF_5Br and $SF_5C\equiv CH$, the only previously known (pentafluorosulfur)acetylene,[4] reacted readily in sealed Pyrex vessels at 105 °C for 3 h to give a 75% yield of the 1:1 addition product $SF_5CBr{=}CHSF_5$ (I). This compound, which is the first example of a bis(pentafluorosulfur)ethylene, is a clear liquid with a vapor pressure of ~11 Torr at 25 °C. It was isolated by vacuum distillation through a trap at −23 °C into a collection trap at −45 °C. The infrared spectrum contained the characteristic absorptions of olefinic C—H and C=C stretching vibrations at 3115 and 1610 cm^{-1} and the very intense absorptions of S–F vibrations at 895, 890, and 605 cm^{-1}. The mass spectrum, recorded on a CVC TOF instrument, showed two weak, but distinct, peaks at 360 and 358 mu corresponding to the parent ions with the bromine isotopes. Additional principal peaks were found at 233 and 231 ($SF_5C_2HBr^+$), 127 (SF_5^+), 106 and 104 (C_2HBr^+), and 89 (SF_3^+). In the ^{19}F NMR spectrum, two pairs of complex doublets and an 18-line pattern appeared downfield from the internal Freon-11 resonance. The doublets (δ −64.7 and −60.4 ppm; $J \approx 155$ and 154 Hz)[5] were assigned to the four equatorial fluorine atoms whose resonances were split by coupling with the axial fluorine atom in each SF_5 group. The 18-line pattern, whose most intense peak had a chemical shift of −73.2 ppm, was an overlap of two 9-line resonances arising from AB_4 coupling of the axial fluorines with those in the equatorial positions. These data were consistent with the expected presence of two nonequivalent SF_5 groups in the molecule and further suggested that only one isomer was formed. Additional support for this conclusion was obtained from ^1H NMR data which contained a regular pentet (τ 2.30, $J = 6.8$ Hz) originating from coupling with a geminal SF_5 group. The lack of coupling between the hydrogen atom and the second SF_5 group suggested a cis relationship between H- and SF_5-, leading to the conclusion that the SF_5 groups are trans to each other.

Dehydrobromination of I by KOH occurred readily at ambient conditions to give a 64% yield of the novel bis(pentafluorosulfur)acetylene, $SF_5C\equiv CSF_5$ (II), which is of particular interest as the SF_5 analogue of hexafluorobutyne. The identity of the material was confirmed by gas-phase molecular weight measurements (found, 278.5; theory, 278.1) and spectroscopic data. In the gas-phase infrared spectrum, a weak absorption at 2220 cm^{-1} was assigned to the C≡C stretching vibration, and the very strong bands at 930, 920, and 605 cm^{-1} to S–F vibrations. The ^{19}F NMR spectrum in Freon-11 contained only one AB_4 pattern (δ_A −67.1 and δ_B −79.7 ppm ($J \approx 148$ Hz))[5] which was consistent with equivalent SF_5 groups. A relatively simple mass spectral fragmentation pattern contained a very weak parent ion at 278 mu, together with major fragments at 259 ($S_2F_9C_2^+$), 151 ($SF_5C_2^+$), 127 (SF_5^+), and 89 (SF_3^+). The experimentally determined vapor-pressure equation, $\log P(\text{mm}) = 7.76 - (1582/T)$, yielded an extrapolated boiling point of 51.0 °C, $\Delta H_{\text{vap}} = 7.24$ kcal/mol, and $\Delta S_{\text{vap}} = 22.3$ cal/K.

The mixed (pentafluorosulfur)trifluoromethylacetylene, $SF_5C\equiv CCF_3$ (III), was synthesized by a route similar to that of II. We found, as did Gard and co-workers,[6] that SF_5Br reacted with 1,1,1-trifluoropropyne to give the monoaddition product $SF_5CH{=}CBrCF_3$ (IV). This, in turn, underwent dehydrobromination readily with KOH at ambient conditions to give the desired $SF_5C\equiv CCF_3$ (III). A molecular weight of 220.9 (theory, 220.1) was determined by gas density measurements and was in good agreement with a weak parent ion observed at 220 mu in the mass spectrum. The remainder of the spectrum contained a simple fragmentation pattern with major peaks at 201 ($SC_3F_7^+$), 127 (SF_5^+), 112 ($C_3F_4^+$), 108 (SF_4^+), 93 ($C_3F_3^+$), 89 (SF_3^+), and 69 (CF_3^+). The gas-phase infrared spectrum contained a weaker C≡C stretching vibration at 2295 cm^{-1} than that observed in the bis(SF_5) compound II, along with very intense bands at 1270, 1200, 945, 920, 850, and 625 cm^{-1} resulting from C–F and S–F vibrations. ^{19}F NMR data were also consistent with the presence of an SF_5 and a CF_3 group within the molecule as evidenced by the AB_4 pattern (δ_A −68.0 and δ_B −78.8 ppm ($J \approx 149$ Hz) relative to internal Freon-11),[5] and a regular pentet at δ +53.7 ppm arising from coupling of the CF_3 resonance with the SF_4 portion of the SF_5 group. At ambient conditions, the compound is a gas with a boiling point of 14.4 °C, and an enthalpy and entropy of vaporization of 5.12 kcal/mol and 17.8 cal/K as calculated from the vapor pressure equation, $\log P(\text{mm}) = 6.77 - (1118/T)$. It is interesting that the boiling point of this compound is about halfway between that of 51.0 °C for the bis(SF_5) compound II and −24.6 °C for the bis(CF_3) molecule, hexafluorobutyne. From this, it can be seen that the replacement of a CF_3 with an SF_5 group in this series of acetylenes is responsible for an increase of 35–40 °C in the boiling point of the compound.

We are continuing our investigations of these unique compounds to gain some insight into their chemistry and into the nature of polymeric materials that may be derived from them.

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A Dynamical Equilibrium between Ion Pairs of Aromatic [9]Annulene Anion and of Olefinic Nonafulvene Structure, Respectively

Sir:

The ion-pair character of organometallic compounds R^-M^+ [1] and of enolates $R_2C{=}CRO^-M^+$ [2] has been extensively studied in recent years. Since the structure (and the reactivity) of these species is a function of the solvent S, the temperature, the concentration, the gegenion M^+, and the nature of groups R, one is usually faced with a rather complex situation. Furthermore, differentiation of the various ion pairs can be difficult because of their structural similarity.

We report the case of a compound which exists in tetrahydrofuran (THF) in the form of two ion pairs which are entirely different structurally and easily detectable by means of ^1H NMR spectroscopy: the sodium enolate (**1**) with its olefinic nonafulvene structure and the $CH_3C(O)$-substituted sodium cyclononatetraenide (**2**) which is aromatic. The dynamic equilibrium **1** $\rightleftharpoons$ **2** is shifted from **1** to **2** on lowering the tem-

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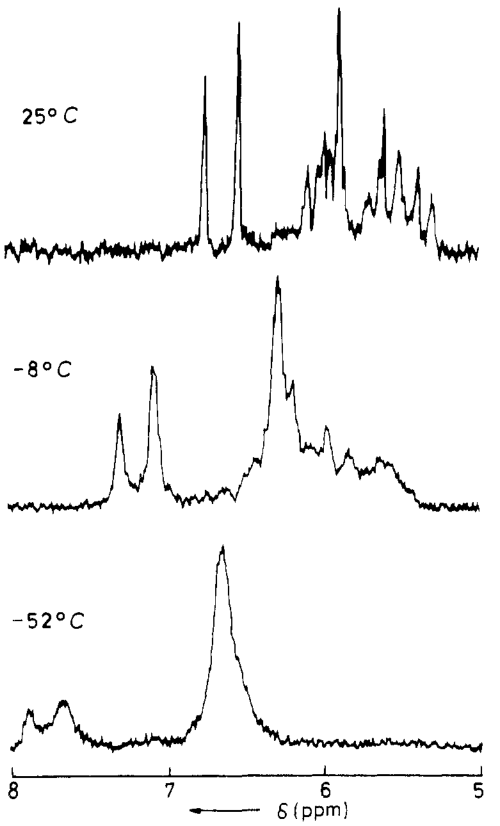
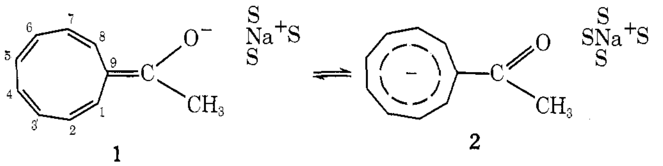


Figure 1. ^{1}H NMR spectral characteristics of the equilibrium $1 \rightleftharpoons 2$ in THF at 25, −8, and −52 °C. Chemical shifts are in parts per million from Me_4Si.



1 **2**

S = THF

perature from 25 to −52 °C. **1** and **2** are prepared from 9-acetyl-*cis,cis,cis,cis*-cyclonona-1,3,5,7-tetraene and sodium bis(trimethylsilyl)amide or sodium hydride in THF. Figure 1 shows the ^{1}H NMR spectrum at *25 °C* (δ_{rel} (Me_4Si internal standard) 5.25–6.10 (m, H^2–H^7), 6.62 (d, H^1 and H^8, J = 12.5 Hz),[3] which resembles closely the spectra of the corresponding Li^+ salt in THF and the silyl enol ether in $CDCl_3$.[4] This and the facile transformation ($\tau_{1/2}$ at 50 °C, 25 min) into the dihydroindene valence isomer[4] support the fulvenoid structure **1**. The spectrum at −52 °C (δ_{rel} 6.31–6.88 (m, H^2–H^7), 7.78 (br d, H^1 and H^8)) on the other hand, is essentially the same as the spectrum of the aromatic K^+ salt in THF.[4] Thus, at −52 °C the aromatic ion pair **2** is the preferred one. *Between 25 and −52 °C* (as, e.g., at −8 °C) one observes spectra with weighted average values. Therefore, one can estimate a rate constant $k \geqslant 330\ s^{-1}$ for the exchange $1 \rightleftharpoons 2$, corresponding to $\Delta G^{\ddagger}(-52\ °C) \leqslant 10.2$ kcal mol^{-1}.

The temperature dependence and the differences in the structures of the species **1** and **2** are in agreement with known properties of anion-Na^+ and solvent-Na^+ interactions.[1,2,5] At 25 °C, the enolate oxygen is closely bound to Na^+ to give **1**, most likely a contact ion pair.[2] It is only at lower temperatures that the donor abilities of the THF oxygen[6] enable it to compete successfully for a near-neighbor site[5] at Na^+ to form **2** ($\Delta H°$ = −6.9 kcal mol^{-1}; $\Delta S°$ = −30 eu), supposedly a solvent separated ion pair.[7] This is in accord with the ^{1}H NMR observation that only **2** is formed in 1,2-dimethoxyethane.

In summary, we have demonstrated that the concentration of the aromatic anion **2** can be a *function of temperature* owing to ion-pair effects. Furthermore, the system **1**–**2** is a very simple and sensitive probe for the study of solvent-M^+ interactions.

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(3) The data specified are for a 1.5 M solution. On lowering the concentration we found a steady downfield shift of the whole vinyl H absorption. In a 0.25 M sample H^1 and H^8, e.g., resonate at δ 6.82 at 25 °C. The line broading at −52 °C is not due to a viscosity effect as shown by the K^+ compound which at 25 °C displays signals of similar shape. The reason for the broading is not known.

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Facile Attachment of Transition Metal Complexes to Graphite Electrodes Coated with Polymeric Ligands. Observation and Control of Metal–Ligand Coordination among Reactants Confined to Electrode Surfaces

Sir:

Intense recent research on the modification of electrode surfaces by chemical treatments[1] has included several instances in which polymeric materials were attached to electrodes[2–5] or appear to be formed during the attachment procedures.[6,7] Electrochemical responses from attached polymers containing ferrocene centers[2,5–7] have been observed, but electrochemical monitoring of the binding of metal ions to an attached polymeric ligand has not previously been reported. We have found conditions under which polymers containing functional groups that are good ligands for metal ions can be quickly and strongly attached to graphite electrode surfaces. The resulting surfaces extract metal complexes from solution by coordination and the oxidation and reduction of the attached complex can be readilly observed and controlled electrochemically.

In this report we describe representative examples in which ruthenium complexes are attached to graphite electrodes coated with polyvinylpyridine (PVP) or polyacrylonitrile. The simplicity and speed of the polymer attachment and metalation procedures, the longevity of the resulting electroactive coatings, and the availability of a large variety of polymeric ligands indicate that the same general method may be used to prepare electrode surfaces that will accept almost any desired metal cation. The obvious potential that such electrode surfaces hold for exploitation in electrocatalytic cycles supplied much of the incentive for the present investigation.

Pyrolytic graphite disks with the graphite basal planes exposed were sealed into glass tubing with heat-shrinkable polyolefin tubing and electrical contact was made to the rear

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