about one-tenth the accumulation time required for undoped samples to produce ^{15}N spectra having comparable signal-to-noise ratios.

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Reactions of Main Group 4 Species with Organic Reagents. 1. Tin and Tin(II) Fluoride Reactions with Ethylene in Argon Matrices[2]

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During the last several years, much attention has been focused on the reactions of metal vapors with a wide array of chemical species. The integration of the high-temperature volatilization (and subsequent condensation) of the reactive metal vapors and coreactants with the technique of matrix isolation spectroscopy has provided a convenient means of investigating possibly reactive intermediates in hetero- and homogeneous catalysis which are often transient species and thus difficult to observe. This approach has permitted such systems as carbon monoxide on metal surfaces, metal atom–olefin interactions, and the catalytic oxidation of ethylene to ethylene oxide to be studied, with many of these systems being quite elegantly and extensively investigated by Ozin and his co-workers.[3] By trapping and thus stabilizing these intermediates, one may then study them by means of a variety of techniques such as infrared, Raman, and ultraviolet–visible spectroscopy in order to more fully elucidate their bonding and spectroscopic properties. Matrix isolation experiments also allow researchers to study the feasibility of new reaction systems advancing to macroscale or production scale syntheses which involve much more costly expenditures in both production equipment and materials.

Current interest in this laboratory in the utilization of matrix isolation spectroscopy to monitor and study chemical reactions
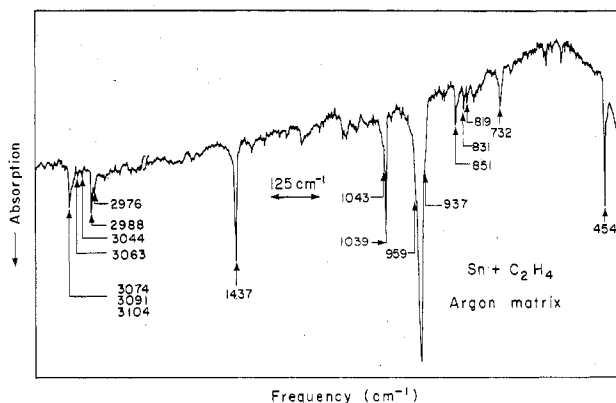

Figure 1. Infrared spectrum of the matrix-isolated product formed in the reaction of tin with ethylene.

lies in the continuation of ongoing research concerning the chemistry of main group 4 elements with added emphasis on the dipositive state, research which has already yielded a rich chemistry for divalent silicon.[4] Bassler et al., for example, first demonstrated the reactivity of certain fluorides (and trapping at rare-gas-matrix temperatures) by reporting the reactions of SiF$_2$ with small molecules such as CO and NO.[5] In addition, tin vapor has been found to react[6] with oxygen (which is isoelectronic with ethylene as reported in this study) to form molecular species of the types SnO$_2$ and Sn$_2$O$_2$. Both tin metal and tin(II) halides have also been shown to be quite important catalysts in several reactions of olefins,[7] ethylene being the simplest, prototypical example; the facile homogeneous hydrogenation of ethylene has been effected by use of Pt(II)/Sn(II) solutions containing tin–platinum clusters.[8]

The present report details the results of the matrix isolation infrared study of the reaction of tin and tin(II) fluoride with ethylene with the reaction products being trapped in argon matrices and represents the first evidence for a reaction chemistry involving the group 4A elements with olefins in the gas phase. Such data should be quite useful in providing initial insight into the use of tin and tin(II) species as catalysts in several industrially important reaction systems in which high-temperature complexes similar to the ones reported here quite likely exist and serve as reactive intermediates or metastable species for such catalytic processes; also, the initial data gathered here serve as the basis for further work relating to the vapor-phase synthesis of group 4A metal clusters with olefins as well as metal atom/organic reagent slurries which can serve as active, synthetic reagents themselves.

Experimental Section

The matrix isolation trapping apparatus used in this investigation has been described previously[9] with cooling of the copper deposition block being provided by an Air Products helium closed-cycle refrigeration system. Both tin metal and tin(II) fluoride were vaporized from a tantalum foil furnace at 1050 and 400 °C, respectively, and condensed into argon matrices; the furnace temperature was monitored by utilizing a standard Pt–Pt 10% Rh thermocouple. All spectra were recorded in the 400–4000-cm^{-1} range with a Beckman IR-9 spectrometer calibrated against water vapor. Trapping times for all cocondensation reactions reported here were 0.5 h unless otherwise stated.

Tin powder (Fisher), tin(II) fluoride (Alfa Ventron), and ethylene (Matheson. 99.99% purity) were used as received with no further purification. Impurities were monitored by running blank spectra of each reactant and, in the case of tin(II) fluoride and ethylene, by checking the spectra against published spectra.

Results and Discussion

Sn/C$_2$H$_4$ Reaction. Matrix isolation experiments in this laboratory have demonstrated the existence of a reaction when tin vapor and ethylene are cocondensed in an argon matrix,

Table I. Infrared Spectra of Sn/C_2H_4 and SnF_2/C_2H_4 Complexes

$Sn-C_2H_4$, cm^{-1}	assignment	$SnF_2-C_2H_4$, cm^{-1}	assignment
454	π-bonded complex	522	O_b, $(SnF_2)_x$
		537.5	ν_3, $SnF_2-C_2H_4$
		551.5	ν_1, $SnF_2-C_2H_4$
		570.5	ν_3, SnF_2
		580	O_a, $(SnF_2)_2$
		593	ν_1, SnF_2
732	π-bonded complex	680–690	SnF_4
819	π-bonded complex, CH_2 wag	821	π-bonded complex, CH_2 wag
831	ν_4, C_2H_4	831	ν_4, C_2H_4
851	π-bonded complex		
937	ν_7, C_2H_4, CH_2 wag	937	ν_7, C_2H_4, CH_2 wag
949	ν_7, C_2H_4, CH_2 wag	949	ν_7, C_2H_4, CH_2 wag
959	ν_7, C_2H_4, CH_2 wag	959	ν_7, C_2H_4, CH_2 wag
		994	$Sn_x-C_2H_4$ cluster
1039	π-bonded complex, CH_2 scissor	1024	$Sn_x-C_2H_4$ cluster
1043	π-bonded complex, CH_2 scissor	1040	π-bonded complex, CH_2 scissor
1437	C_2H_4, CH_2 scissor	1437	C_2H_4, CH_2 scissor
2976	C_2H_4, CH str	2976	C_2H_4, CH str
2988	C_2H_4, CH str	2988	C_2H_4, CH str
3044	π-bonded complex, CH str		
3063	π-bonded complex, CH str		
3074	C_2H_4, CH str	3074	C_2H_4, CH str
3091	C_2H_4, CH str	3091	C_2H_4, CH str
3104	C_2H_4, CH str	3104	C_2H_4, CH str

a typical infrared spectrum of this reaction product being shown in Figure 1. Utilizing a C_2H_4/Ar ratio of 1/100, one observes absorptions for the free ethylene isolated in the argon matrix as well as a series of new bands appearing at 819, 1039, 1043, 3044, and 3063 cm^{-1} which are clearly attributable to a complex formed between tin and ethylene. These bands compare favorably with those observed by Ozin and his co-workers[3] (see Table I for band assignments in this work) in similar metal–ethylene reactions trapped in rare-gas matrices, and thus they can be interpreted as resulting from a donor–acceptor complex in which tin is bonded to ethylene via the π system of the olefin.

In addition to these bands, new ones at 851, 732, and 454 cm^{-1} appear. The 851-cm^{-1} peak is a CH_2-wagging mode with a value very close to that found in the $Cu(C_2H_4)_2$ (862 cm^{-1})[10] and Zeise's salt (844 cm^{-1})—$K_2[Cl_3Pt(C_2H_4)]\cdot H_2O$—investigated by Chatt et al. and other workers.[11] The absorption at 732 cm^{-1} is almost identical in value to 730 cm^{-1} reported for Zeise's salt, this band being attributed to the torsional mode ν_4 in the coordinated ethylene.

The relatively intense, low-frequency band at 454 cm^{-1} is particularly noteworthy and can be tentatively assigned as a $\nu(Sn-C_2H_4)$ stretching mode involving a cyclic species in which tin may be pictured as approaching the ethylene molecule laterally and forming a three-membered tin–carbon–carbon ring system containing the doubly bonded olefin component which remains intact.[12] Such a complex has been postulated as a logical intermediate in oxidative-addition reactions of tin(II) halides with multiply bonded carbon–carbon systems to form organotin(IV) derivatives,[13] and the tin–carbon stretching frequencies of the final cyclic tin–olefin species in such reactions lie in the $\sim$400–450-cm^{-1} range; also, the metal–carbon frequencies in several metal–olefin complexes lie in the 400–500-cm^{-1} region.[14]

The absence of a noticeably strong $\nu(C≡C)$ stretching mode in the spectrum, an ethylene mode that should be infrared active upon coordination to tin, can be attributed to the low concentration of the complex relative to the whole trapped
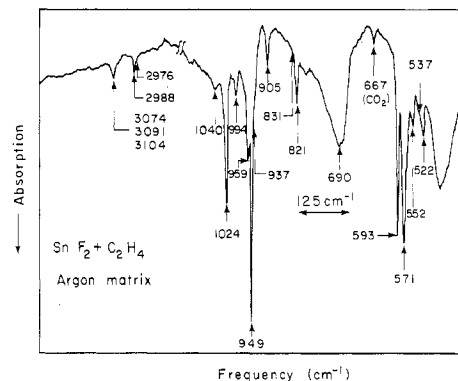

Figure 2. Infrared spectrum of the matrix-isolated product formed in the reaction of tin(II) fluoride with ethylene.

tin/ethylene mixture and to the inherent weakness of this mode in the complex; indeed, several attempts to increase the concentration of the tin–ethylene complex in the matrix by varying trapping conditions proved unsuccessful. This band most likely lies in one of the two sets of weak multiplets in the $\sim$1520–1550-cm^{-1} region (Figure 1), an assignment that would be in excellent agreement with those of Ozin et al. One should not forget, however, that the $\nu(C≡C)$ and $\delta(CH_2)$ modes are highly coupled[14,15] in both free ethylene and metal–ethylene complexes, with the band in the 1150–1350-cm^{-1} range assigned as the $\delta(CH_2)$ mode in various complexes[16] having significant $\nu(C≡C)$ character, even in the weakly perturbed silver–ethylene complex $[Ag(C_2H_4)]^+BF_4^-$.[14] A distinguishable multiplet with the maximum absorption at 1265 cm^{-1} appears in the spectrum of the tin–ethylene complex shown here. Annealing the matrix produced no noticeable formation of new products.

SnF_2/C_2H_4 Reaction. In the spectrum of the matrix-isolated products of the reaction between tin(II) fluoride and ethylene (Figure 2), several processes are evident, two of which concern the reaction of the SnF_2 exclusively without interaction with the ethylene. First, the bands at 522 and 580 cm^{-1} indicate the formation of polymerization products of the type $(SnF_2)_x$ which have been previously reported[17] in matrix isolation studies of tin(II) fluoride. Second, a broad, intense band envelope at 680–690 cm^{-1} represents the presence of SnF_4[17] and thus quite evident disproportionation of tin(II) fluoride to the tin(IV) species and elemental tin (which is observed as the residue in the furnace after each set of of experiments) during the volatization of the SnF_2 at 400 °C. As a result, many of the new bands present in the spectrum of the SnF_2/C_2H_4 reaction—specifically, those at 821 (819 cm^{-1} in the case of the tin system) and 1040 cm^{-1} (1039 and 1043 cm^{-1} with tin)—also appear in the spectrum of the Sn/C_2H_4 reaction discussed above. This is also true of the two bands at 994 and 1024 cm^{-1} which appear in the Sn/C_2H_4 system when a large excess of tin vapor is reacted with ethylene; consequently, they may tentatively be attributed to a species of the type $Sn_x-C_2H_4$ in which several tin atoms are clustered around a single ethylene molecule. Presumably, bands which represent coordinated SnF_4 modes in products (if any) between SnF_4 and ethylene are also present in this broad, unresolved absorption region. As with the Sn/C_2H_4 matrices, annealing failed to change the spectrum.

In addition to the bands above that are assignable to SnF_2 (both monomeric and polymeric) and SnF_4, one also observes the appearance of two additional bands at 551.5 and 537.5 cm^{-1}, bands which can be assigned as the shifted ν_1 and ν_3 vibrational modes of the bent (C_{2v} point group) SnF_2 molecule complexed to ethylene. Such a complex results from the π-electron donation from ethylene to the tin(II) species, thus causing a concomitant red shift in the tin–fluorine stretching

frequencies. The red shifts of 41.3 and 33 cm^{-1} for ν_1 and ν_3, respectively, are somewhat larger in magnitude than those reported by Perry et al.[18] for the similar SnF_2/C_6H_6 reaction system, with shifts of 29 and 19 cm^{-1} for these same two fundamental vibrational modes.

Work is currently underway to broaden the present research to include isotopic substitution (both ^2H and ^{13}C) and con-centration-dependency studies between ethylene and tin and tin(II) fluoride; in addition, the studies will be extended to include other main group 4 atoms and halides. Such inves-tigations should yield much additional knowledge concerning bonding between group 4A species and organic reactants, especially information related to acceptor–donor bond strengths involving bare metal atoms and metal halides with organic π-electron system donor ligands in reaction (and subsequent trapping) environments. These exclude solvent effects and tend to minimize intermolecular contact factors that would be encountered in conventional solid-state and solution chemistry, factors such as crystal-packing effects and hydrogen bonding which are eliminated when the reactants and the ensuing products are kept in very low concentrations in the frozen matrices.

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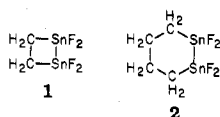
from bulk cocondensation of SnF$_2$ with ethylene (analogous to SiF$_2$ condensation products[4a]) can also be postulated; however, the data obtained in the present study should be considered as only *very tentative* for any

of these compounds. Consequently, all assignments in Table I refer to vibrational modes of the tin/tin(II) fluoride complexes of ethylene as resulting from a π-bonding interaction of the metal or metal fluoride species with the olefinic bond.

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Autocatalytic Chain Reaction in the Photochemical Decomposition of Tris(2,2'-bipyridyl)chromium(III) in Dimethylformamide[1]

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In an investigation of the excited-state properties of Cr-(bpy)$_3^{3+}$ (bpy = 2,2'-bipyridine) in DMF at room temperature, we have observed a chain reaction initiated by light leading to complete solvation of one bpy ligand. Previous work has demonstrated photoaquation of Cr(bpy)$_3^{3+}$ in alkaline solu-tion.[2] Also in aqueous solution, some photoreduction of Cr(bpy)$_3^{3+}$ by such weak donors as Ru(bpy)$_3^{2+}$ and Fe^{2+} occurs followed by immediate back electron transfer, con-stituting therefore quenching of the phosphorescent state of Cr(bpy)$_3^{3+}$.[3]

We report evidence here that the chain carrier is a chro-mium(II) complex with bpy and that the chain reaction occurs via electron transfer.

Experimental Section

Tris(2,2'-bipyridyl)chromium(III) perchlorate, [Cr(bpy)$_3$](ClO$_4$)$_3$, was synthesized by a modification of published methods.[4-6] Addition of Cr^{2+}(aq) to a nitrogen-saturated acidic aqueous suspension of excess bipyridine resulted in the immediate precipitation of purple-black microcrystals of [Cr(bpy)$_3$](ClO$_4$)$_2$ which were collected by filtration, washed with chloroform to remove excess ligand, and dried. This solid (which is stable in dry air[5]) was oxidized to Cr(bpy)$_3^{3+}$ by sprinkling it slowly (over the course of several hours) into 10 mL of 0.01 M HClO$_4$ which was continuously stirred and bubbled with oxygen or chlorine.[7] As the black solid dissolved and was oxidized, a yellow solution formed. The yellow [Cr(bpy)$_3$](ClO$_4$)$_3$ solid obtained on cooling was filtered and purified by recrystallization from dilute HClO$_4$.

This procedure gives a good yield and is superior to methods[4] in which the oxidizing agent is added slowly to a suspension of [Cr(bpy)$_3$]$^{2+}$. In acidic aqueous media, Cr(bpy)$_3^{3+}$ is inert, whereas Cr(bpy)$_3^{2+}$ is labile. Adding the reduced solid material slowly to an oxygen saturated acidic solution permits rapid oxidation to the Cr(III) form of the tris complex. Conversely, if the Cr(II) complex is allowed to equilibrate with an oxygen-free solution and then oxidized slowly, large amounts of pink crystals (presumably [Cr(bpy)$_2$(H$_2$O)$_2$](ClO$_4$)$_3$) are formed at the expense of the desired product.

Photolysis and emission measurements were carried out in DMF which was distilled daily at 25–30 °C under reduced nitrogen pressure. Sulfuric acid and copper sulfate were added to the still pot to prevent the formation of amine and formate impurities. Photolysis solutions were degassed for at least 1 h in a Zwickel flask with a stream of chromous-scrubbed, dried argon; a 3-mL aliquot was then transferred to a 1-cm spectrometer cell and sealed under 20 torr positive pressure of argon. The necessity for exhaustive degassing of the system cannot be overstressed. A He–Cd laser was used for irradiation at 325 or