to −196 °C. The remaining solid in the reaction vessel was pumped on until constant weight was achieved. In some cases the weight of the solid product was slightly larger than theoretically possible. This was due to a small amount of $S_2O_6F_2$ being absorbed by the Teflon stirring bar. The effect seemed to be more pronounced when the solvent C_7F_{16} was used.

Preparation of $VO(SO_3F)_3$. To 0.205 mmol of $V(CO)_6$, 5.66 mmol of $S_2O_6F_2$ was added at −196 °C. After 3 h at 50 °C the reaction was complete and a viscous red liquid that was sparingly soluble in excess $S_2O_6F_2$ was produced. An infrared spectrum of the volatile materials at −78 °C showed CO_2, CO, and $S_2O_5F_2$ to be present. Prolonged pumping on the residue at room temperature yielded 0.202 mmol of solid $VO(SO_3F)_3$ in 98.5% yield.

To 0.955 mmol of $V(CO)_6$, 1.2 mmol of dry degassed C_7F_{16} and 16.71 mmol of $S_2O_6F_2$ were added. After 3 h at 60 °C a viscous red liquid, insoluble in C_7F_{16}, was formed. Infrared spectra of the volatile materials at room temperature showed $S_2O_5F_2$, CO_2, C_7F_{16}, and $S_2O_6F_2$ to be present. Prolonged pumping on the residue at room temperature yielded 0.927 mmol of solid $VO(SO_3F)_3$ in 97% yield. The solid melts at 102–104 °C and decomposes to a yellow solid at 190 °C. Its infrared spectrum showed the following bands (cm^{-1}): 1410 (m, sh), 1350 (s, sh), 1285 (s, vbr), 1240 (s, sh), 1160 (s, br), 950 (m–s, sh), 890 (m, sh), 815 (m), 720 (m, br), 620 (m, vbr), 570 (m), 560 (m), 495 (m, sh), 450 (m–w, br), 380 (w, br).

The x-ray powder spectrum showed the solid to be amorphous.

Anal. Calcd for $VO(SO_3F)_3$: V, 13.99; S, 26.4; F, 15.7. Found: V, 14.04; S, 24.6; F, 16.0.

Preparation of $Cr(SO_3F)_3$. To 1.98 mmol of $Cr(CO)_6$, 19.55 mmol of $S_2O_6F_2$ was added. The mixture was warmed to room temperature and then heated to 60 °C for 20 days. A pale green solid that was insoluble in $S_2O_6F_2$ was formed. An infrared spectrum of the volatile material at −10 °C showed CO_2, $S_2O_5F_2$, and $S_2O_6F_2$ to be present. A pale green solid residue (2.06 mmol) of $Cr(SO_3F)_3$ was recovered in essentially 100% yield.

The infrared and electronic spectra of $Cr(SO_3F)_3$ prepared from $S_2O_6F_2$ and $Cr(CO)_6$ were found to agree with those of $Cr(SO_3F)_3$ prepared from CrF_5 and SO_3.[11] Further studies were not made.

Preparation of $FeO(SO_3F)$. To 2.89 mmol of $Fe(CO)_5$, 19.55 mmol of $S_2O_6F_2$ was added. A vigorous reaction occurred on warming to room temperature producing a brown solid. The reaction was complete after 1 h at room temperature. An infrared spectrum of the volatile material at room temperature showed CO, CO_2, $S_2O_5F_2$, and $S_2O_6F_2$ to be present. A tan solid product (2.94 mmol) of $FeO(SO_3F)$ was formed in 100% yield. $FeO(SO_3F)$ decomposed at 260 °C; UV (Me_2SO), 335 nm (s). Its infrared spectrum showed the following bands (cm^{-1}): 1440 (vw), 1355 (s), 1110 (s, vbr), 1000 (s, sh), 835 (s), 740 (w, sh), 660 (w, sh), 620 (s, sh), 570 (s), 550 (s), 420 (m), 320 (m).

The x-ray powder spectrum gave the following *d* values with their respective intensities: 9.12 (s), 4.70 (m), 4.03 (m), 3.73 (m), 3.28 (m), 3.21 (m) 10^{-1} nm.

Anal. Calcd for $FeO(SO_3F)$: Fe, 32.7; S, 18.7; F, 11.1. Found: Fe, 32.2; S, 18.3; F, 11.6.

Preparation of $Fe(CO)_4(SO_3F)_2$. To 1.84 mmol of $Fe(CO)_5$, 48.8 mmol of dry degassed C_7F_{16} and 22.4 mmol of $S_2O_6F_2$ were added. On warming to room temperature a reaction occurred and a bright yellow solid precipitated. After 2 h in the dark at room temperature, the reaction was complete. Removal of all volatile materials left behind 1.94 mmol of yellow solid, $Fe(CO)_4(SO_3F)_2$, in essentially 100% yield. The solid did not melt below 100 °C, but at 100 °C decomposed to $Fe(SO_3F)_2$ and CO. Its infrared spectrum showed the following bands (cm^{-1}): 2218 (m), 2200 (s), 2175 (s), 2140 (s), 1410 (s), 1340 (s), 1245 (s, sh), 1200 (s), 1150 (s, sh), 1040 (s), 920 (m, br), 785 (s), 615 (s–m), 600 (s), 580 (s), 520 (m), 430 (m, br), 400 (m).

A freshly prepared sample (0.576 mmol) of $Fe(CO)_4(SO_3F)_2$ was decomposed at 100 °C for 1 h. It produced 2.36 mmol of CO gas (mol wt: found, 27; theoretical, 28; the infrared spectrum agreed with the literature) and 0.562 mmol of the white solid, $Fe(SO_3F)_2$. The infrared spectrum of the white solid was identical with that of $Fe(SO_3F)_2$.

Anal. Calcd for $Fe(SO_3F)_2$: Fe, 22.0; S, 25.2; F, 14.9. Found: Fe, 22.2; S, 25.3; F, 14.5.

Preparation of $Mn(SO_3F)_4$. To 0.446 mmol of $Mn_2(CO)_{10}$, 16.29 mmol of $S_2O_6F_2$ was added. After 1 day at room temperature the reaction was complete. An infrared examination of the volatile materials at −78 °C showed CO, CO_2, $S_2O_5F_2$, and a small amount of SO_2F_2 to be present. A gray-brown solid product (0.850 mmol) of $Mn(SO_3F)_4$ was formed in 96% yield.

To 0.368 mmol of $Mn_2(CO)_{10}$, 37.3 mmol of dry-degassed C_7F_{16} and 20.0 mmol of $S_2O_6F_2$ were added. After 3 h, the reaction was complete. The infrared spectrum of the volatile material at room temperature showed CO_2, $S_2O_5F_2$, C_7F_{16}, and $S_2O_6F_2$ to be present. A gray-brown solid product (0.738 mmol), $Mn(SO_3F)_4$, was formed in essentially 100% yield. $Mn(SO_3F)_4$ decomposes without melting at 105 °C; UV (Me_2SO), 510 nm (ϵ 1.2×10^3) and 320 nm (ϵ 3.6×10^3). Its infrared spectrum showed the following bands (cm^{-1}): 1430 (m), 1370 (s), 1240 (s), 1180 (s), 1100 (s, sh), 1055 (s), 905 (m), 835 (m–s), 750 (m, sh), 640 (m), 575 (m), 555 (m), 435 (m, br), 350 (m).

The x-ray powder spectrum showed the solid to be amorphous.

Anal. Calcd for $Mn(SO_3F)_4$: Mn, 12.17; S, 28.3; F, 16.8. Found: Mn, 12.96; S, 27.2; F, 16.0.

Preparation of $Co(SO_3F)_2$. To 0.739 mmol of $Co_2(CO)_8$, 11.5 mmol of $S_2O_6F_2$ was added. On warming, the reaction began and was complete within 6 h at room temperature. An infrared spectrum of the volatile materials at −78 °C showed CO, CO_2, and $S_2O_5F_2$ to be present. A purple solid product (1.42 mmol) was obtained in 96% yield.

The use of the solvent C_7F_{16} did not change the reaction. To 0.310 mmol of $Co_2(CO)_8$, 26.5 mmol of dry-degassed C_7F_{16} and 6.22 mmol of $S_2O_6F_2$ were added. After 1 h at room temperature the reaction was complete and 0.640 mmol of the purple solid product $Co(SO_3F)_2$ was formed in essentially 100% yield. $Co(SO_3F)_2$ decomposed to a brown solid at 110 °C: UV (Me_2SO), 690 (ϵ 40.1), 535 (ϵ 239), 420 (ϵ 20.0), 260 nm (ϵ 466).

The x-ray powder spectrum showed the solid to be amorphous.

Anal. Calcd for $Co(SO_3F)_2$: Co, 22.8; S, 24.9; F, 14.7. Found: Co, 23.1; S, 25.1; F, 13.8.

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Registry No. $VO(SO_3F)_3$, 65776-46-7; $Cr(SO_3F)_3$, 55136-41-9; $FeO(SO_3F)$, 65776-54-7; $Fe(CO)_4(SO_3F)_2$, 65776-53-6; $Fe(SO_3F)_2$, 14928-65-5; $Mn(SO_3F)_4$, 65776-45-6; $Co(SO_3F)_2$, 15059-58-2; $V(CO)_6$, 14024-00-1; $Cr(CO)_6$, 13007-92-6; $Fe(CO)_5$, 13463-40-6; $Mn_2(CO)_{10}$, 10170-69-1; $Co_2(CO)_8$, 12553-61-6; $S_2O_6F_2$, 13709-32-5.

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Matrix-Isolation Infrared and Electron Paramagnetic Resonance Spectroscopic Studies of the Reaction of Lithium with Silicon Tetrafluoride

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Since Troost[4] first predicted the existence of SiF_2 in 1871, there has been extensive research into the chemistry of this

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highly reactive carbene analogue.[5] Silicon difluoride, a bent molecule (C_{2v} point group) having a bond angle of 100° 59′[6] and possessing a singlet ground electronic state,[7] has been shown to react with aromatic compounds such as benzene and toluene[8] and alkynes[9] by a presumed mechanism involving a dimerized silicon difluoride diradical. Alternately, a number of reactions such as SiF_2 with H_2S,[10] GeH_4,[11] and CF_3I[12] seem to proceed through the diamagnetic monomer to undergo what essentially is an insertion of the SiF_2 molecule into A–B bonds. Additional experimental evidence[13,14] utilizing nuclear recoil methods employing the transmutation $^{31}P(n,p)^{31}Si$ in which energetic ^{31}Si abstracts fluorine atoms from PF_3 yielding $^{31}SiF_2$ suggests the existence of both the singlet- and triplet-state molecules. When reacted with 1,3-butadiene, singlet silicon difluoride yields difluorosilacyclopent-3-ene-^{31}*Si*, but the triplet-state compound affords this product only in the presence of paramagnetic, gaseous reactants such as nitrogen oxides or oxygen. Singlet silicon difluoride, produced by the thermal reduction of SiF_4 with silicon,[15] has also been shown to react with a wide assortment of other compounds, including thionyl fluoride[16] and boron trifluoride.[17] Silicon difluoride reactions also serve as convenient preparative routes[18] to a large number of organosilicon derivatives. Such a high degree of reactivity coupled with the potential for preparing the much discussed multiply bonded silicon species[19,20] currently in the research literature necessitates even a more thorough understanding of this carbene analogue.

To date, however, the exact hybridization, bonding, and electronic character of silicon difluoride and the supposed diradical intermediate have not been totally elucidated. Rao et al.[6] found the bond length (1.591 Å) to be anomalously long and suggested that the bonding might possibly involve p^2 hybridization of the silicon orbitals with the p orbitals of the fluorine atoms directed along the bonds. The two nonbonding electrons on the silicon atom were thought to be in orbitals having either pure s or sp character with the possibility of silicon d orbital participation not being precluded. Another report[21] centered around the matrix-isolated electron paramagnetic resonance spectrum of SiF_2 in which a broad EPR spectrum was obtained only at high matrix concentrations of the molecule; unfortunately, no fine structure was observed, and the *g* factor for the broad spectrum was 2.003 ± 0.002, almost identical with that of a free electron.

This paper represents a new synthesis of diamagnetic silicon difluoride via the lithium atom abstraction technique in an argon matrix. In addition, a paramagnetic species is also produced which can be ascribed either to the silicon difluoride diradical or, alternately, to the silicon difluoride anion, SiF_2^-. These experimental spectroscopic data, when coupled with molecular orbital calculations, are potentially the basis for directly elucidating the hybridization of either the diradical or anionic SiF_2 species.

Experimental Section

The matrix-isolation infrared apparatus has been described previously.[22]

A schematic representation of the matrix-isolation electron paramagnetic resonance apparatus is shown in Figure 1. Basically, the experimental matrix equipment consisted of three major sections: (a) a movable vacuum cryostat to which the matrix substrate was attached, (b) a furnace chamber, and (c) a gas handling system. The vacuum cryostat consisted of a rotatable flange and a movable stainless steel rod, allowing positioning of the sapphire rod cryotip with respect to the incoming chemical reagents and matrix gases. The sapphire trapping surface was secured to the stainless steel rod using an indium metal seal; this cryotip, which was cooled by liquid helium, was lowered into the EPR cavity after the trapping period in order to record the spectrum. The electron paramagnetic resonance spectrometer used was a Varian Fieldial Mark II model.

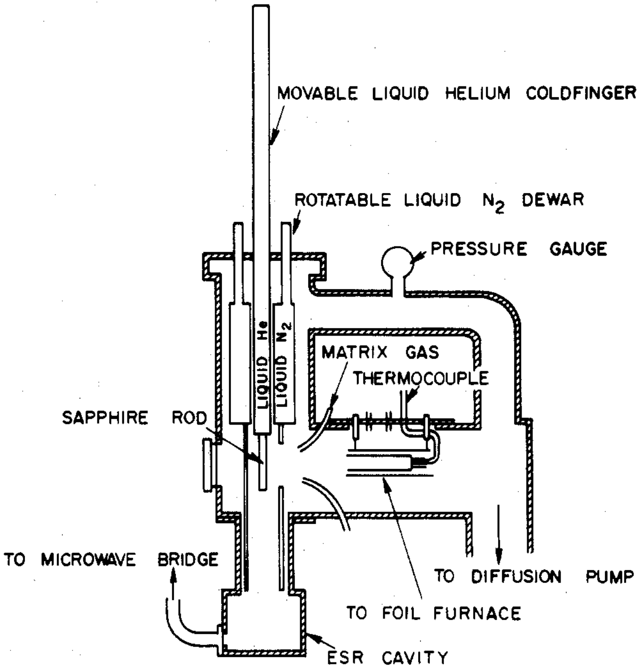

Figure 1. Matrix-isolation electron paramagnetic resonance apparatus.

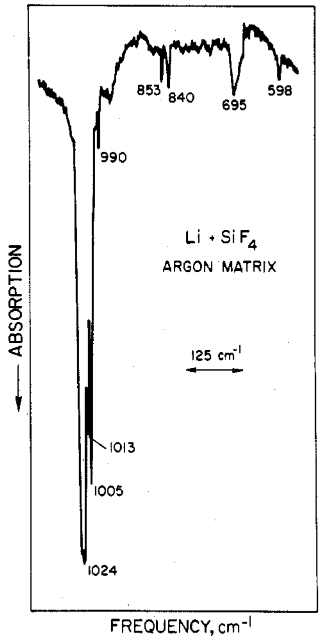

Figure 2. Argon matrix isolated infrared spectrum of the reaction between lithium atoms and silicon tetafluoride.

The furnace utilized in the present study was made of tantalum foil and resistively heated. Made from 0.001 in. thick tantalum foil, the furnace consisted of a 2.5 in. long tube (0.5-in. diameter) which was strapped on both ends with 0.020-in. tantalum strips to water-cooled copper electrodes. A 0–120-V autotransformer was connected to the 20–1 stepdown 1-kW transformer which was used to power the furnace. A recrystallized alumina tube lined the furnace to insulate the cell from the tantalum foil. The sample cells used in conjunction with the furnace were open-ended stainless steel cells with temperature monitoring being effected via a chromel–alumel thermocouple junction positioned $^1/_{16}$ in. deep into the back of the cell.

Both silicon tetrafluoride and argon were of high purity obtained from Matheson and were used without further purification. Lithium metal was purchased from Alfa Inorganics/Ventron and distilled before use in the present work. In order to ensure the reproducibility of all data taken, multiple spectra for multiple trappings were taken; in addition, both EPR and infrared blanks were run for both lithium and silicon difluoride to preclude the possibility of any reagent contaminants contributing to the spectra.

Discussion

In a typical experiment, lithium metal was vaporized at 435 °C and cocondensed with silicon tetrafluoride in an argon matrix for a typical trapping period of 1 h ($Ar:SiF_4 \approx 100:1$). The matrix-isolated infrared spectrum after the reaction is shown in Figure 2. The two bands located at 853 and 840 cm^{-1} could be unequivocally assigned as the ν_3 and ν_1 modes, respectively, of neutral SiF_2, since the values were identical with those previously reported for the infrared spectrum of the matrix-isolated molecule in argon.[23] There was some slight band structure between these two peaks which was attributable to either the $(SiF_2)_2$ dimer[23] or lithium fluoride[24] formed in the lithium atom abstraction process. The absorption band at 598 cm^{-1} could be tentatively ascribed to the SiF_2^- anion, since this band appeared in the spectrum of the $Na^+SiF_2^-$ charge-transfer complex formed in the reaction of sodium metal atoms with silicon difluoride in an argon matrix.[25] It must be emphasized that such an assignment was only tentative, since the other infrared band of the SiF_2^- anion was obscured in our spectrum (this peak is present at 530 cm^{-1} in the sodium complex, a region which consisted of a broadened, intense absorption band in all spectra observed in this investigation); however, the strongly corroborative EPR data discussed below supported such a conclusion.

The most predominant bands were observed at 1024, 1005, and 1013 cm^{-1} and could be attributed to unreacted SiF_4[23] and matrix splittings associated with this molecule in the argon matrix. The peaks at 990 and 695 cm^{-1} could similarly be assigned either to SiF_4 or alternately to Si_2F_6, Si_3F_8, or Si_4F_{10} (most likely Si_2F_6), since this band occurs in the infrared spectra of these compounds[15] as an active mode of the terminal–SiF_3 functional group. This same band was also found in the infrared spectrum of $C_6F_5SiF_3$ which is formed in the reaction between silicon difluoride and perfluorobenzene.[8] Assignments attributing these bands to such compounds are reasonable, since their formulation is known to occur when mixtures of SiF_4 and SiF_2 are cocondensed at low temperatures[15] and the mixture is allowed to warm to room temperature. Most certainly, reactions of the type $SiF_4(s) + SiF_2(s) = Si_2F_6(s)$ followed by addition of SiF_2 molecules to form compounds of the variety Si_nF_{2n+2} (Si_2F_6, Si_3F_8, etc.) are operative in the SiF_2/SiF_4 reaction system. An alternate route for the formation of Si_2F_6 would be the dimerization of the trifluorosilyl radical, $\cdot SiF_3$, produced by lithium abstraction of one of the fluorine atoms from the original SiF_4. Such a process is unlikely, however, since the Si–F bond is strong, and at no time during this study was any evidence obtained for the existence of the $\cdot SiF_3$ radical which has been previously studied in argon matrices utilizing both infrared[26] and EPR[27] spectroscopy. The total absence of this species in the present experimental system was somewhat surprising in light of the high Si–F bond energy of SiF_4 [$D(Si{-}F)_{av} = 142 \pm 2$ kcal],[28] but any $\cdot SiF_3$ formed must be reacting to form Si_2F_6 or with further lithium (always kept in excess is these experiments) to form SiF_2 or SiF_2^-. Furthermore, the infrared spectrum always indicated a decrease in the neutral, molecular SiF_2 with an attendant increase in the perfluorosilanes such as Si_2F_6 or Si_3F_8 when the concentration of SiF_4 was increased in the experiment. Since the infrared data indicated that SiF_2 and SiF_2^- were being formed and isolated in the cocondensation reaction, it was convenient to search for radical species using electron paramagnetic resonance (EPR) spectroscopy, assuming radical recombination does not occur to any significant extent. Figure 3 illustrates the EPR spectrum obtained from the cocondensation reaction of lithium atoms and silicon tetrafluoride. In order to make the results of the infrared and EPR experiments comparable, trapping times and other experimental conditions commensurate with those mentioned in the infrared discussion were used.

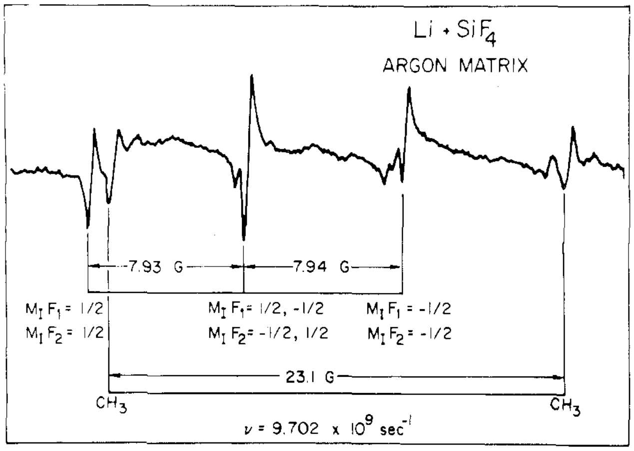

Figure 3. Argon matrix isolated electron paramagnetic resonance spectrum of the reaction between lithium atoms and silicon tetrafluoride.

Figure 3 depicts two lines (labeled CH_3) with a hyperfine splitting of 23.1 G. These two lines correspond to the inside two lines of the quartet resulting from a $\cdot CH_3$ radical (introduced into our system as a pumping oil hydrocarbon contaminant which was pyrolyzed on passing through the furnace and subsequently trapped in the matrix). The EPR spectrum of the methyl radical in an argon matrix has been studied previously,[29] and such lines served quite conveniently as internal calibrants. In addition, Figure 3 shows three other lines with a hyperfine splitting of 7.94 G and a g value of 2.0046 (very similar to that reported by Thompson et al.[21]). The lines show an intensity ratio of 1:2:1 and, on the basis of the atoms and molecules involved in the cocondensation reaction, would seem to be attributable to the coupling of two ^{19}F ($I = {}^1/_2$, natural abundance 100%) nuclei. The g value is very close to the value for a free electron, thus indicating an absence of any significant spin–orbit coupling. Thus the data indicate the presence of a silicon species involving two equivalent fluorine atoms; in addition, the g value suggests that the species is either a radical or a negatively charged molecule. As is the case with the ^{13}C of the methyl radical, the ^{29}Si is too low in abundance to be observed in the matrix EPR experiment.

The fluorine atom has an unusually large nuclear moment (2.6288 μ_B), and a previous study on the $\cdot SiF_3$ radical by Merritt and Fessenden,[27] where they reported a hyperfine constant of 136.6 for fluorine, shows that the hyperfine splitting resulting from a fluorine atom can be quite large. Although the hyperfine constant reported here might seem anomalously low in comparison, the magnitude might be appropriate if it is assumed that spin polarization is the cause of the observed hyperfine structure.

On the basis of this analysis, the observed EPR spectrum should be assigned to either the SiF_2^- anion or an SiF_2 diradical species. Due to the limitations of both the infrared and electron paramagnetic resonance techniques, unfortunately, the spectra cannot be unequivocally assigned to either chemical form. Because of the relatively low intensity of the EPR lines observed in this reaction, it would appear that this reaction results in no major formation of this radical or anion and surprisingly no trifluorosilyl radicals; alternatively, radical recombination might cause the absence of this radical species. Indeed, the infrared results indicate that an SiF_3 group is present in the form of a functional group, indicating the former presence of an SiF_3 radical which has been lost through radical recombination to form higher silanes such as Si_2F_6.

In order to obtain a more thorough understanding of the electronic nature of the radical or anionic species which is characterized by the EPR and infrared spectra observed in this study, ab initio SCF–MO calculations are currently being conducted with these two paramagenetic molecules as models. Such knowledge of the silicon difluoride system will further elucidate the mechanisms for the reactions of this reactive carbene analogue with both organic and inorganic reactants which lead to a wide and unique range of both simple inorganic silicon derivatives and more complex organosilicon derivatives.

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Registry No. SiF_4, 7783-61-1; Li, 7439-93-2; SiF_2, 13966-66-0.

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An Efficient Halogen Atom Abstraction Reaction Facilitated by a Redox-Active Ligand

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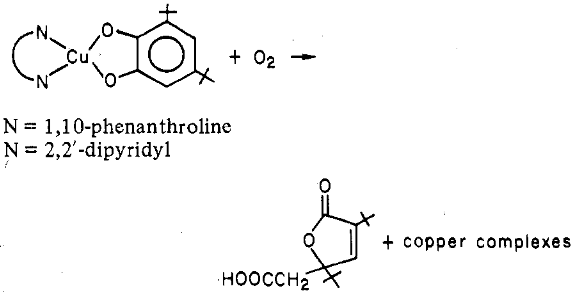
There are several reactions described in the literature in which a metal complex reacts with an alkyl halide resulting in removal of a halogen. These reactions fall into two distinct classes. The first of these involves nucleophilic attack on the alkyl halide by a low-valent metal.[2] A second type of reaction in which a metal removes a halogen involves a one-electron transfer from the metal to the alkyl halide in the transition state $[L_nM^{\delta+}\cdots X^{\delta-}\cdots R]$ followed by cleavage of the R–X bond.[3a,4a] This type of reaction results in a free radical, $R\cdot$, and a net formal increase of +1 in the metal oxidation state. The metal centers which have been most commonly studied in this type of reaction are chromium(II),[3] low-spin cobalt(II),[4] and copper(I).[5] In each case the metal attains a more stable higher oxidation state. The system described below carries out efficient halogen atom abstraction with no overall change in metal oxidation state but is instead facilitated by the presence of redox-active ligand.

As an extension of our work on oxygen-dependent ring cleavage in copper–catecholato complexes (eq 1)[6] we have begun an investigation of the solvent dependence of this reaction. We have discovered a striking side reaction which occurs in halogenated solvents which will be reported here.



(1)

Experimental Section

The (3,5-di-*tert*-butylcatecholato)diiminecopper(II) complexes[7] and the dihalo(diimine)copper(II) complexes[8] were prepared by methods previously reported. Mallinckrodt analytical reagent grade and Matheson Coleman and Bell spectroquality halomethanes were dried for at least 24 h over Linde 4A molecular sieves before use.

Results and Discussion

When either (3,5-di-*tert*-butylcatecholato)-1,10-phenanthrolinecopper(II), Cu(phen)DBcat, or (3,5-di-*tert*-butylcatecholato)-2,2′-dipyridylcopper(II), Cu(bpy)DBcat, is allowed to contact a halomethane solvent, a reaction occurs immediately which has been found to involve halogen abstractions from the halomethane. This reaction is unique from other transition-metal-assisted halogen abstractions described in the literature in that the metal ion does not undergo a net change in oxidation state. Instead, the ability of the coordinated catechol dianion to undergo facile one-electron oxidation is the interesting feature of this system. In addition, the reaction gives only one inorganic product, dihalo(diimine)copper(II).

In a typical experiment 3 g of Cu(phen)DBcat is suspended in 300 mL of CCl_4 and the mixture stirred at room temperature for an hour. A dark green solid forms immediately which transforms to a light green solid. Upon analysis this light green solid is found to be dichloro(1,10-phenanthroline)copper(II), $Cu(phen)Cl_2$ (eq 2). This compound is

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