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.

References and Notes

(1) Presented in part before the 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977.
(2) National Science Foundation Postdoctoral Fellow, 1976–1977; Miller Fellow, 1977–1978. Department of Chemistry, University of California.
(3) Department of Chemistry, William Marsh Rice University.
(4) L. Troost and P. Hautefeuilie, *Bull Soc. Chim. Fr.*, **16**, 240 (1871).
(5) See, for example, J. L. Margrave and P. W. Wilson, *Acc. Chem. Res.*, **4**, 145 (1971); D. L. Perry and J. L. Margrave, *J. Chem. Educ.*, **53**, 696 (1976).
(6) V. M. Rao, R. F. Curl, P. L. Timms, and J. L. Margrave, *J. Chem. Phys.*, **43**, 2557 (1965).
(7) H. P. Hopkins, J. C. Thompson, and J. L. Margrave, *J. Am. Chem. Soc.*, **90**, 901 (1968).
(8) P. L. Timms, D. D. Stump, R. A. Kent, and J. L. Margrave, *J. Am. Chem. Soc.*, **88**, 940 (1966).
(9) C. S. Liu, J. L. Margrave, J. C. Thompson, and P. L. Timms, *Can. J. Chem.*, **50**, 459 (1972).
(10) K. G. Sharp and J. L. Margrave, *Inorg. Chem.*, **8**, 2655 (1969).
(11) D. Solan and P. L. Timms, *Inorg. Chem.*, **7**, 2157 (1968).
(12) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *J. Inorg. Nucl. Chem.*, **32**, 1817 (1970).
(13) O. F. Zeck, Y. Y. Su, and Y. N. Tang, *J. Chem. Soc., Chem. Commun.*, 156 (1975).
(14) O. F. Zeck, Y. Y. Su, G. P. Gennaro, and Y. N. Tang, *J. Am. Chem. Soc.*, **98**, 3474 (1976).
(15) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave *J. Am. Chem. Soc.*, **87**, 2824 (1965).
(16) K. G. Sharp and J. L. Margrave, *J. Inorg. Nucl. Chem.*, **33**, 2813 (1971).
(17) P. L. Timms, T. C. Ehlert, J. L. Margrave, F. E. Brinckman, T. C. Farrar, and T. D. Coyle, *J. Am. Chem. Soc.*, **87**, 3819 (1965).
(18) Reactions of silicon difluoride with organic reagents offer attractive routes to a wide variety of silicon-containing materials. Alkynes and alkyl-substituted alkynes such as 1-butyne, 2-butyne, and 3,3-dimethyl-1-butyne combine with SiF_2, for example, in ratios of 1:2 and 2:2 to yield derivatives of disilacylobutene in the 1:2 case [C. S. Liu, J. L. Margrave, and J. C. Thompson, *Can. J. Chem.*, **50**, 456 (1972)]; the 2:2 compounds, however, have been shown to have an open chain structure resulting from migration of either α (to C≡C—CH) or acetylenic hydrogen or are derivatives of disilacyclohexadiene. Also see ref 5.
(19) J. L. Margrave and D. L. Perry, *Inorg. Chem.*, **16**, 1820 (1977).
(20) L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Acc. Chem. Res.*, **8**, 18 (1975). Also see ref 19.
(21) See, for example, ref 7 and notes therein.
(22) J. W. Hastie, R. H. Hauge, and J. L. Margrave, *High Temp. Sci.*, **1**, 76 (1969).
(23) J. W. Hastie, R. H. Hauge, and J. L. Margrave, *J. Am. Chem. Soc.*, **91**, 2536 (1969).
(24) M. J. Linevsky, *J. Chem. Phys.*, **34**, 587 (1961).
(25) R. H. Hauge and J. L. Margrave, Abstracts, 29th Southwest Regional Meeting of the American Chemical Society, El Paso, Tex., 1973, No. 247.
(26) D. E. Milligan, M. E. Jacox, and W. A. Guillory, *J. Chem. Phys.*, **49** 5330 (1968).
(27) M. V. Merritt and Richard W. Fessenden, *J. Chem. Phys.*, **56**, 2353 (1972).
(28) (a) S. S. Wise, W. N. Hubbard, H. M. Feder, and J. L. Margrave, *J. Phys. Chem.*, **66**, 381 (1962); **67**, 815 (1963); (b) T. C. Ehlert and J. L. Margrave, *J. Chem. Phys.*, **41**, 1066 (1964).
(29) C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, *Phys. Rev.*, **112**, 1169 (1958).

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

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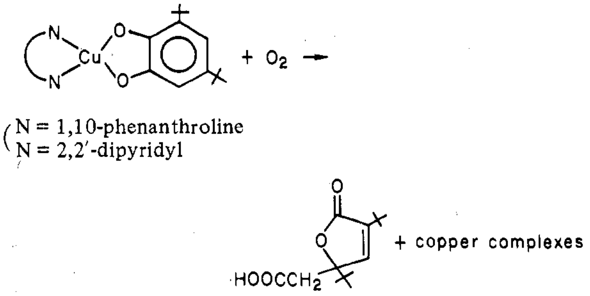
There are several reactions described in the literature in which a metal complex reacts with an alkyl halide resulting in removal of a halogen. These reactions fall into two distinct classes. The first of these involves nucleophilic attack on the alkyl halide by a low-valent metal.[2] A second type of 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·, 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



(1)

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.

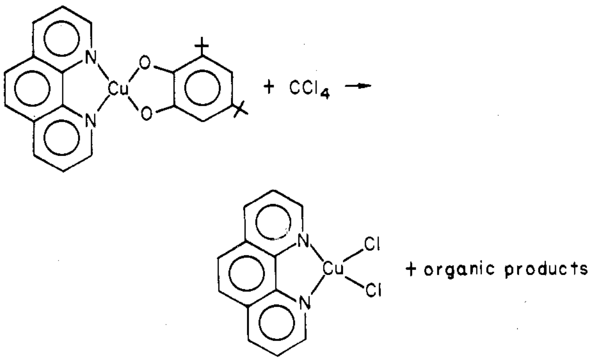
Experimental Section

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

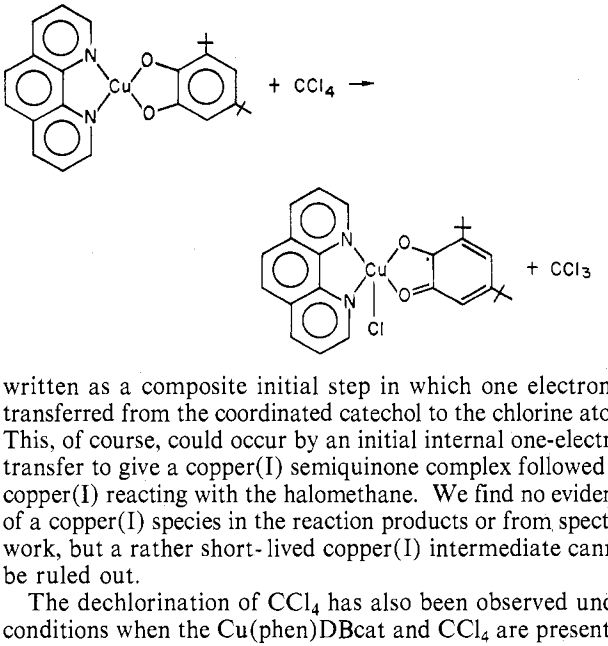


(2)

formed in quantitative yield and no other copper-containing compound has been detected.[9] Thus the reaction is quite clean with respect to the inorganic product formed. It is qualitatively observed that the reaction is accelerated by the presence of O_2 but even after rigorous deoxygenation by a series of freeze-thaw cycles Cu(phen)Cl_2 is readily formed. This reaction is different from halogen atom abstraction reactions previously reported in that the copper retains the same oxidation state while oxidation takes place on the catecholato ligand.

A similar reaction occurs with other halomethanes. The qualitative rates of the formation of Cu(phen)Cl_2 for a series of chloromethanes follows the order $CCl_4 > CHCl_3 > CH_2Cl_2$. In comparing the rates for CCl_4 and CBr_4 it is observed that CBr_4 reacts more rapidly forming Cu(phen)Br_2. These relative rates qualitatively parallel the relative rates for halogen *atom* abstraction. Therefore, it appears as if the reaction is initiated by halogen atom abstraction facilitated by a one-electron transfer from Cu(phen)DBcat to the halomethane.

Normally copper(II) could not be expected to carry out this type of dehalogenation. However, the catecholato ligand can readily undergo a one-electron oxidation to a coordinated semiquinone as we have previously demonstrated in a cobalt system.[12] We have also observed that facile one-electron oxidation of the starting material can be accomplished either by electrochemical means or with chemical oxidants.[13] Therefore we envision the initial step in the dehalogenation reaction as shown in eq 3.[14] The scheme shown in eq 3 is written as a composite initial step in which one electron is transferred from the coordinated catechol to the chlorine atom. This, of course, could occur by an initial internal one-electron transfer to give a copper(I) semiquinone complex followed by copper(I) reacting with the halomethane. We find no evidence of a copper(I) species in the reaction products or from spectral work, but a rather short-lived copper(I) intermediate cannot be ruled out.



(3)

The dechlorination of CCl_4 has also been observed under conditions when the Cu(phen)DBcat and CCl_4 are present in an inert solvent such as heptane in stoichiometric amounts, i.e., mole ratio 2:1, respectively. In this case Cu(phen)Cl_2 is still the predominant product but is not obtained in analytical purity. However, this indicates that all the chlorine atoms can be removed from the CCl_4 molecule. The presence of the orthocarbonate and carbonate[9] in the organic reaction products also reflects complete removal of chlorine atoms.

There is little work previously reported which is analogous to that presented here. Chan et al.[5a] have reported a reaction between cuprous phenoxides and CCl_4 to give orthocarbonates in varying yields which depend upon the particular phenoxide employed. These workers report quantitative recovery of the copper in the form of cuprous chloride. The phenoxide ligand is not redox active as is the coordinated catechol in the system discussed here. However, the apparent similarity between Chan's system and that reported here deserves mention.

In summary this appears to be a rather efficient, well-defined reaction in which halogen abstraction is facilitated by a redox-active ligand. The resulting copper(II) halide complex is obtained in quantitative yields. Further experiments are under way to learn if this system is capable of removing halogen atoms from rather unreactive halogenated organic compounds.

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References and Notes

(1) On sabbatical leave from Ithaca College, Ithaca, N.Y.
(2) (a) L. Vaska, *Acc. Chem. Res.*, **1**, 335 (1968); (b) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967); (c) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *ibid.*, **46**, 3879 (1968); (d) P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, 6 (1968).
(3) (a) C. E. Castro and W. C. Kay, *J. Am. Chem. Soc.*, **88**, 4447 (1966); (b) F. A. L. Anet, *Can. J. Chem.*, **37**, 58 (1959); (c) H. Lux, D. Sarre, and I. Schaffelhofer, *Ber. Dtsch. Chem. Ges.*, **97**, 2301 (1964); (d) T. Kiba and K. Terada, *Nippon Kagaku Zasshi*, **75**, 196 (1954).
(4) (a) J. Halpern, *Ann. N.Y. Acad. Sci.*, **239**, 2 (1974), and references cited therein; (b) *Acc. Chem. Res.*, **3**, 386 (1970).
(5) (a) T. H. Chan, J. F. Harrod, and P. van Gheluwe, *Tetrahedron Lett.*, 4409 (1974); (b) M. Asscher and D. Vofsi, *J. Chem. Soc. B*, 947 (1968).
(6) D. G. Brown, L. Beckmann, C. H. Ashby, G. C. Vogel, and J. T. Reinprecht, *Tetrahedron Lett.*, 1363 (1977).
(7) D. G. Brown, J. T. Reinprecht and G. C. Vogel, *Inorg. Nucl. Chem. Lett.*, **12**, 399 (1976).
(8) C. M. Harris, T. N. Lockyer, and H. Hanneke, *Nature (London)*, **192**, 424 (1961).
(9) Approximately 65–70% of the organic products is the red crystalline solid 3,5-di-*tert*-butyl-*o*-benzoquinone (I). Other minor (5–10%) organic products that have been identified are 2,4-di-*tert*-butyl-6-trichloromethyl-6-hydroxylcyclohexa-2,4-dienone (II), bis(3,5-di-*tert*-butylcatechyl) orthocarbonate (III), and 3,5-di-*tert*-butyl-*o*-phenylene carbonate (IV). Characterization of I: mp 114–115 °C (lit. 113–114 °C);[10] infrared spectrum was identical with that previously reported.[11] Characterization of II: mp 95–96.5 °C; IR (CCl_4) 3485, 2980, 1680 cm^{-1}; NMR (CCl_4) δ 1.17 (s, 9 H), 1.22 (s, 9 H), 4.34 (s, 1 H, exchangeable with deuterium), 6.11 (d, $J = 3$ Hz, 1 H), 6.75 (d, $J = 3$ Hz, 1 H); mass spectral intensities of isotope peaks show that 3 Cl are present; m/e (abundance) 338 (15, M), 323 (12, M – 15), 382 (11, M – 56), 221 (100, M – 117). Characterization of III: mp 249–250 °C; IR (CCl_4) 2980, 1190 cm^{-1}. Anal. Calcd: C, 76.95; H, 8.90. Found: C, 77.00; H, 8.78; m/e (abundance) 452 (100, M), 437 (24, M – 15). Characterization of IV (tentative): IR (CCl_4) 2980, 1870, 1845 cm^{-1} (see ref 15); m/e (abundance) 248 (25, M), 233 (48, M – 15), 74 (100, M – 174).
(10) W. Flaig, T. Ploetz, and Biergans, *Ann. Chem.*, **597**, 196 (1955).
(11) K. Ley and E. Muller, *Ber. Dtsch. Chem. Ges.*, **89**, 1402 (1956).
(12) P. A. Wicklund, L. S. Beckmann, and D. G. Brown, *Inorg. Chem.*, **15**, 1996 (1976).
(13) The complex Cu(phen)(DBcat) has been studied qualitatively by cyclic voltammetry and appears to undergo a one-electron oxidation at approximately +0.2 V vs. SCE. However, this is not reversible apparently due to subsequent reactions. In addition, we have carried out redox titrations using a variety of chemical oxidants which also indicate that the complex undergoes a one-electron oxidation. It has not been possible to isolate the oxidation product.
(14) Control experiments in which the potassium salt of 3,5-di-*tert*-butylcatechol was allowed to react as the CCl_4 showed no similar reaction. The metal center is obviously necessary to bring about chlorine abstraction.
(15) M. Avram and G. C. Mateescu, *J. Chem. Soc.*, 618 (1957).