TABLE III
SPECTROSCOPIC PARAMETERS FOR COMPLEXES CONTAINING THE $Cr^{III}S_6$ CHROMOPHORE[a]

	Dq, cm^{-1}	B, cm^{-1}	β_{35}	$\epsilon_m(\nu_1)$	$\epsilon_m(\nu_2)$	$\nu_2 - \nu_1$, cm^{-1}
$Cr(R\text{-dtp})_3$	1445	418–434	0.45–0.48	~350	~255	4540–4600
$Cr(dtc)_3$[b]	1550	457	0.50	380	360	4860
$Cr(S_2CNH_2)_3$[b]	1550	426	0.46	310	310	4500
$Cr(xan)_3$[b]	1612	403	0.44	...	...	4380
$KCa(Cr(S_2C_2O_2)_3)\cdot 6H_2O$[c]	1700	454	0.50	435	1028	4900
$((C_3H_7)_4N)_3(Cr(i\text{-mnt})_3)$[d]	1515	487	0.53	360	500	5100
$Cr(MTU)_6(ClO_4)_3$[e]	1450	423	0.46	...	...	4500
$Cr(DMTU)_6(ClO_4)_3$[e]	1400	487	0.53	...	...	4200

[a] Dq and B for all compounds were calculated using strong octahedral field matrices: R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, 6, 1338 (1967).   [b] dtc = diethyldithiocarbamate, xan = ethylxanthate.   Spectral data were taken from ref 7.   [c] R. L. Carlin and F. Canziani, *J. Chem. Phys.*, 40, 371 (1964).   [d] *i*-mnt = $S_2C_2(CN)_2{}^{2-}$: J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, 88, 3913 (1966); D. Coucouvanis, *Progr. Inorg. Chem.*, in press.   [e] MTU = N-methylthiourea; DMTU = N,N'-dimethylthiourea: P. Askalani and R. A. Bailey, *Can. J. Chem.*, 47, 2275 (1969).

ulated. Table III compares the spectroscopic properties of a number of compounds containing the Cr^{III}-S_6 chromophore. It should be noted that the octahedral polymers $Cr(SR)_3$ (R = methyl, ethyl, phenyl, benzyl) reported by Brown and coworkers[18] are not included in Table III; reasonable values of B could not be calculated using the reported spectra.

Table II shows that there is essentially no substituent effect on the spectroscopic properties of the complexes. This demonstrates that the properties of the complexes are predominantly determined by the CrS_2P chelate rings. The Dq value for dithiophosphate ligands places them below water ($Dq = 1740$ cm^{-1}) in the spectrochemical series for chromium(III). This result is not in conflict with the inference of strong metal–ligand covalency from esr data if it is noted that the electronic spectra of complexes are a function of Dq *and* Racah interelectronic repulsion parameters and not just Dq alone. The large values of the oscillator strengths of the electronic transitions, indicative of extensive metal–ligand delocalization, must be interpreted with some caution. Although the transition energies can be treated reasonably well in terms of an O_h model, the band intensities of chromium(III) complexes are a rather sensitive function of molecular geometry. On going from complexes conforming fairly well to octahedral geometry to those with D_3 symmetry, which is expected for $Cr(R\text{-dtp})_3$ complexes, the oscillator strengths increase two- to fivefold due to loss of the center of inversion. The oscillator strengths of $Cr(R\text{-dtp})_3$ complexes attain their magnitudes through operation of both symmetry and covalency effects, the latter probably being the more significant as low nephelauxetic parameters and esr data would suggest.

Table III shows that there is a great similarity in the spectroscopic properties of complexes containing the $Cr^{III}S_6$ chromophore although the Dq values range from 1400 to 1700 cm^{-1}. The β_{35} values are indicative of strong covalency in the metal–ligand σ bonds.[8] The nephelauxetic parameters, β_{55}, obtained from a consideration of low-energy quartet–doublet transitions[8] are also consistent with appreciable Cr–S π bonding in complexes containing $Cr^{III}S_6$ chromophores.

(18) D. A. Brown, W. K. Glass, and B. Kumar, *J. Chem. Soc., A*, 1510 (1969).

In the 400–200-cm^{-1} region of the infrared spectra the $Cr(R\text{-dtp})$ complexes exhibit a strong band near 318 cm^{-1} and two bands of medium to weak intensity near 356 and 397 cm^{-1}. These bands are in the region 440–200 cm^{-1} assigned to predominantly metal–sulfur stretching frequencies of sulfur-donor chelates[19] and are independent of the alkyl substituents in the Cr-$(R\text{-dtp})_3$ compounds. The observed bands are tentatively identified with chromium(III)–sulfur stretching frequencies until more extensive studies of the infrared and Raman spectra of these and complexes with other metal ions are completed.

(19) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold (Publishers) Ltd., London, 1967, p 319.

The Reaction of Silicon Tetrachloride and Silane with Small Carbon Molecules

BY JEHUDA BINENBOYM AND RILEY SCHAEFFER

The reactions of small carbon molecules generated in a carbon arc with various organic substances have been intensively studied by Skell and coworkers.[1-6] It has also been shown that carbon vapor reacts with

(1) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, 88, 3749 (1966).
(2) P. S. Skell and R. R. Engel, *ibid.*, 88, 4883 (1966).
(3) P. S. Skell and R. R. Engel, *ibid.*, 89, 2912 (1967).
(4) P. S. Skell and R. F. Harris, *ibid.*, 87, 5807 (1965).
(5) P. S. Skell, J. H. Plonka, and R. R. Engel, *ibid.*, 89, 1748 (1967).
(6) P. S. Skell and R. F. Harris, *ibid.*, 91, 4440 (1969).

inorganic boron compounds.[7,8] We report here the reaction of carbon with silicon tetrachloride to produce trichlorosilylchloroacetylene ($Cl_3SiC\equiv CCl$) (an apparent insertion of C_2 species into an Si—Cl bond) and the reaction of carbon with silane to produce methylsilane, acetylene, diacetylene, benzene, and disilane.

Experimental Section

Silicon tetrachloride was of commercial grade, purified by low-temperature fractionation. Silane was prepared by the reduction of silicon tetrachloride with lithium aluminum hydride and purified by distillation from a bulb at —160°.[9] The carbon electrodes used were of spectroscopic grade. The apparatus and the procedure were essentially those described by Skell, *et al.*;[1,10] a brass reactor was used and a 75-A dc source powered the carbon arc. The volatile products were isolated and purified by conventional high-vacuum techniques. Silicon tetrachloride was in general injected continuously while the arc was on. Cycling the arc on and off and injection of $SiCl_4$ when the arc was off did not affect the yield or the nature of the products. Multiple runs were carried out using approximately 5-g samples of $SiCl_4$; loss of weight of the carbon electrodes was about 0.6 g per run. About 0.1 g of a volatile product was obtained per run. An unknown fraction of the carbon sputtered to the walls in a form which was probably unreactive making meaningful yield calculations impossible.

In the case of silane a buildup of pressure in the cell was observed; the arc and the silane addition were then interrupted until the pressure dropped in the reactor. About 30-mm samples of SiH_4 were used and 0.3 g of carbon evaporated per run. Yields of product were very low and products of several arc runs were generally combined to obtain sufficient quantity for separation.

Infrared spectra were obtained with a Perkin-Elmer 621 grating spectrometer. Raman spectra were obtained with a Cary 81 spectrometer with a Spectra Physics Model 125 He–Ne laser source. Mass spectra were obtained with an AEI MS9 mass spectrometer.

Results and Discussion

Low temperature fractionation isolated a product which passed a —63° trap slowly but was retained at —78°. The product is a colorless, moisture-sensitive liquid with a vapor pressure given by log P_{mm} = $8.882 - (2272.6/T)$. Vapor pressure measurements: 22°, 14.0 mm, 15.2 mm (calcd); 19°, 12.0 mm 12.7 mm (calcd); 0°, 4 mm, 3.7 mm (calcd); —10°, 2.0 mm, 1.7 mm (calcd); —20°, 0.75 mm, 0.80 mm (calcd). The normal boiling point from the equation is 105.5° and the heat of vaporization is 10.04 kcal/mol.

The partial mass spectrum of the product is recorded in Table I where only ions containing ^{12}C, ^{28}Si, and/or ^{35}Cl are recorded. The measured relative intensities of the other peaks in the mass envelopes are in agreement with the calculated intensities based on the isotopic abundances of the atoms in C_2SiCl_4. Exact mass measurements on the parent peak yielded m/e 191.-8533; (calcd for $C_2SiCl_4{}^+$: 191.8523).

The intensity of peaks attributed to $SiCl_4{}^+$, $SiCl_3{}^+$, and $SiCl^+$ varied somewhat depending on sample

(7) S. R. Prince and R. Schaeffer, *Chem. Commun.*, 451 (1968).

(8) (a) J. E. Dobson, P. M. Tucker, R. Schaeffer, and F. G. A. Stone, *ibid.*, 452 (1968); (b) J. E. Dobson, P. M. Tucker, F. G. A. Stone, and R. Schaeffer, *J. Chem. Soc., A*, 1882 (1969).

(9) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

(10) P. S. Skell, L. D. Westcott, J-P. Golstein, and R. R. Engel, *ibid.*, **87**, 2829 (1965).

TABLE I
PARTIAL MASS SPECTRUM OF $Cl_3SiC\equiv CCl$

m/e	Rel abund	Ion	m/e	Rel abund	Ion
192	39.6	$C_2SiCl_4{}^+$	98	7.9	$SiCl_2{}^+$
168	16.6	$SiCl_4{}^+$	87	18.2	C_2SiCl^+
157	100	$C_2SiCl_3{}^+$	63	49	$SiCl^+$
133	42.8	$SiCl_3{}^+$	52	7.9	C_2Si^+
122	7.9	$C_2SiCl_2{}^+$	47	14.2	CCl^+

purification. However, the variation was not consistent with contamination with $SiCl_4$. Traces of higher molecular weight impurities were evident in all mass spectra and could not be removed by trap-to-trap or low-temperature column separation. The linearity of the vapor pressure curve and the independence of vapor pressure on gas-phase volume suggest that any impurity is present in only minor degree.

The infrared spectrum of gas-phase samples and the Raman spectrum of liquid-phase samples were measured. Infrared spectrum: 2710 (vw), 2520 (vw), 2160 (vs), 950 (s), 780 (m), 635 (vs), 605 (vs), 550 (vs), 510 (s), 480 (vvw), 435 (w), 380 (m), 325 (vw), 250 cm^{-1} (m).[11] Raman spectrum: 2905 (vw), 2162 (s, p), 950 (vw), 780 (vvw), 600 (m, d), 550 (s, p), 520 (m, p), 450 (w), 425 (m, p), 408 (s, p), 380 (vs, p), 335 (w), 300 (vvw), 288 (w, d), 262 (m, d), 222 (vw), 195 (vs, d), 170 cm^{-1} (vs, d).[11]

A tentative assignment of the main bands can be made as follows: $C\equiv C$ str, 2160 cm^{-1}; $\equiv C$—Cl str, 950 cm^{-1}; $SiCl_3$ sym str, 550 cm^{-1}; $SiCl_3$ unsym str, 605 cm^{-1}; $\equiv C$—Si str, 380 cm^{-1}; $C\equiv C$—Si bend, 262 cm^{-1}.

The $\equiv C$—Cl stretch band at 950 cm^{-1} is unusually high but seems reasonable if compared to the $\equiv C$—Cl stretch band at 905 cm^{-1} in $(CH_3)_3SiC\equiv CCl$ reported by Steingross and Zeil.[12] The $\equiv C$—Si stretch vibration in $(CH_3)_3SiC\equiv CCl$ is given at 383 cm^{-1}.[12]

The data of the mass spectral, infrared, and Raman analyses of the product support the Cl_3Si—$C\equiv C$—Cl structure. This structure is further confirmed by reaction of the product with bromine to produce a colorless liquid with negligible vapor pressure at room temperature. The infrared spectrum of this liquid was measured: 1520 (s), 1480 (vw), 945 (s), 935 (s), 830 (m), 815 (m), 675 (w), 660 (w), 600 (vs), 500 (s), 485 (s), 335 (w), 325 (w), 285 (m), 250 cm^{-1} (vw).[11]

The spectrum of the new compound lacks the band at 2160 cm^{-1} assigned to the $C\equiv C$ stretch and has instead a strong band at 1520 cm^{-1} attributed to a $C=C$ stretch. The mass spectrum of this compound supports the suggested composition since it contains ions corresponding to

$$\underset{\displaystyle SiCl_3\overset{\displaystyle Br\ \ Br}{\underset{|\quad |}{C}=CCl}}{}$$
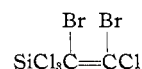
The small amounts of this compound available prevented more detailed characterization of it including exact mass measurements.

(11) Abbreviations: v, very; s, strong; w, weak; m, medium; p, polarized; d, depolarized.

(12) W. Steingross and W. Zeil, *J. Organometal. Chem.* (Amsterdam), **6**, 109 (1966).

The identified products from the experiments with SiH$_4$ were shown by ir, mass spectral, and vpc analyses to be methylsilane, acetylene, diacetylene, benzene, and disilane. The high volatility of SiH$_4$ and the observed pressure increase during this experiment raise some questions as to the nature of the reaction. In ordinary studies the pressure in the cell remains sufficiently low so that the mean free path exceeds substantially the distance from the entry port to the wall. Gas-phase reaction or reactions on the hot electrodes are thereby largely eliminated in normal work. The possibility of such effects cannot be eliminated in the silane case. Thus, acetylene, diacetylene, and benzene may arise from the secondary reaction of hydrogen with the hot carbon electrodes. The low thermal stability of silanes strongly suggests, however, that they are not formed in such secondary processes.

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Substitution Reactions of Copper(II) Chelates with Sodium Maleonitriledithiolate

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Maleonitriledithiolate (mnt^{2-}) is the best known of a series of 1,2-dithiolate ligands that form a wide variety of interesting and unusual metal complexes.[1] Little or nothing has been reported concerning the kinetics and mechanisms of substitution reactions involving these ligands. For this reason we investigated the reactions of several copper(II) chelates with mnt^{2-} as the nucleophile.

Experimental Section

The Na$_2$mnt was prepared as previously described[2] and was checked for purity by spectrophotometric titration with a standard nickel(II) perchlorate solution. G. F. Smith and Co. copper(II) perchlorate was standardized *via* EDTA titration. Fisher Certified reagent grade Na$_2$EDTA·2H$_2$O was used. The disodium salts of nitrilotriacetic acid (NTA) and iminodiacetic acid (IDA) were purchased from Eastman Kodak. The Na$_2$-NTA was crystallized twice from 50:50 ethanol–water. Spectra were recorded on a Cary 14 spectrophotometer. The reactions were followed at 470 nm in aqueous solution at 25 ± 0.1° on a commercially available[3] stopped-flow apparatus. The ionic strength was adjusted to 0.2 M with sodium perchlorate. The total copper concentration was 5×10^{-5} M and the Na$_2$mnt concentration was $(5-45) \times 10^{-4}$ M, thus maintaining pseudo-first-order conditions. The EDTA, NTA, and IDA complexes of copper were prepared *in situ* by combining equimolar quantities of copper perchlorate and ligand, except that a 1:2 molar ratio was used for Cu(IDA)$_2{}^{2-}$. The pH of the copper(II)–EDTA and –NTA solutions was adjusted to 7.5, thus ensuring the absence of protonated and/or hydroxy forms.[4,5] The fully deprotonated

(1) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).
(2) A. Davison and R. H. Holm, *Inorg. Syn.*, **10**, 8 (1967).
(3) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).
(4) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 331 (1948).
(5) T. R. Bhat and M. Krishnamurthy, *J. Inorg. Nucl. Chem.*, **25**, 1147 (1963).

form of IDA, *i.e.*, Na$_2$IDA, was used so that no pH adjustment was necessary. The pH of the Na$_2$mnt solutions was about 8.

Results and Discussion

The product spectrum for the reaction CuL^{z-} + 2mnt^{2-} → Cu(mnt)$_2{}^{2-}$ + L$^{(z+2)-}$ was identical with the spectrum of a Cu(mnt)$_2{}^{2-}$ solution prepared from a copper perchlorate solution. For reaction 1 the form of the pseudo first-order rate constant, k_{obsd}, is given

$$Cu(EDTA)^{2-} + 2mnt^{2-} \longrightarrow Cu(mnt)_2{}^{2-} + EDTA \quad (1)$$

in eq 2. With NTA as the leaving group (eq 3)
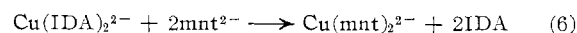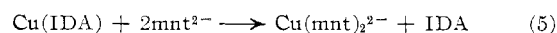
$$k_{obsd}(sec^{-1}) = 5.2 + 7.6 \times 10^3[mnt^{2-}] \quad (2)$$

the results are given in eq 4. For reactions 1 and 3

$$Cu(NTA)^- + 2mnt^{2-} \longrightarrow Cu(mnt)_2{}^{2-} + NTA \quad (3)$$
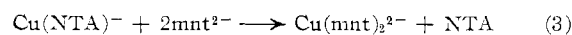
$$k_{obsd}(sec^{-1}) = 0.88 + 1.6 \times 10^3[mnt^{2-}] \quad (4)$$

excellent first-order kinetics were followed. The reactions with IDA as given in reactions 5 and 6 were

$$Cu(IDA) + 2mnt^{2-} \longrightarrow Cu(mnt)_2{}^{2-} + IDA \quad (5)$$

$$Cu(IDA)_2{}^{2-} + 2mnt^{2-} \longrightarrow Cu(mnt)_2{}^{2-} + 2IDA \quad (6)$$

too rapid to observe. This means that k_{obsd} must have been greater than 100 sec^{-1} for reactions 5 and 6. Figure 1 shows the experimental results.
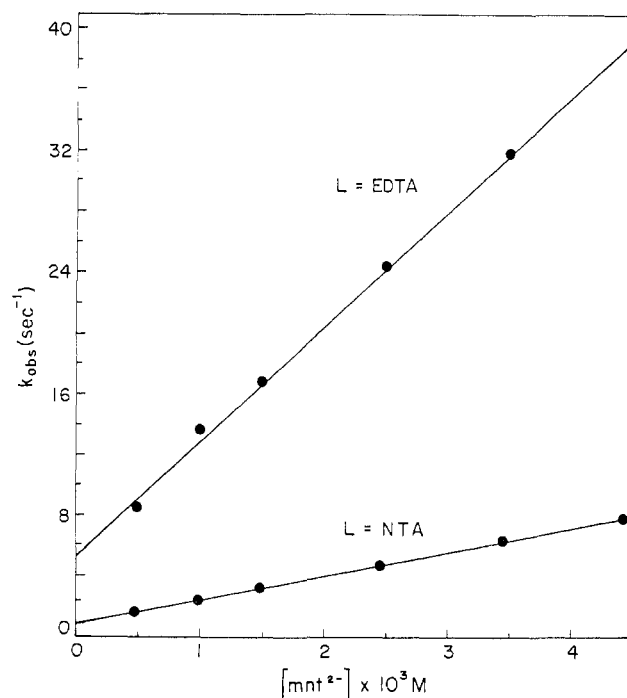

Figure 1.—The dependence of k_{obsd} on mnt^{2-} concentration for the reactions Cu(L)$^{z-}$ + 2mnt^{2-} → Cu(mnt)$_2{}^{2-}$ + L' (z = 1 or 2).

The mechanism proposed to account for the observed kinetics with Cu(EDTA)$^{2-}$ is shown in Figure 2. A similar mechanism is expected for the NTA and IDA complexes. It is expected that the copper–oxygen bonds would be broken in preference to the copper–nitrogen bonds as the first mnt^{2-} group is added.[6] It is generally found, however, that cleavage of the cop-

(6) D. W. Margerum, D. L. Janes, and H. M. Rosen, *J. Am. Chem. Soc.*, **87**, 4463 (1965).