[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

(Iso)cyanides of Silicon, Germanium and Tin as Ligands in Iron Carbonyl Complexes

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Trimethyl(iso)cyanosilane and trimethyl(iso)cyanogermane react with iron pentacarbonyl forming yellow, crystalline, sublimable and extremely air-sensitive $(CH_3)_3SiN{=}C{-}Fe(CO)_4$ and $(CH_3)_3GeN{=}C{-}Fe(CO)_4$ in good yield. The infrared spectra of these compounds are discussed. Trimethyltin (iso)cyanide also reacts with iron pentacarbonyl, but the analogous $(CH_3)_3SnN{=}C{-}Fe(CO)_4$ is formed only in very low yield, while anionic iron carbonyl species are formed in a side reaction.

Evidence has been presented that trimethyl(iso)cyanosilane[1] and its germanium analog[2] consist of equilibrium mixtures of the cyano and isocyano isomers [$(CH_3)_3M{-}C{\equiv}N$ and $(CH_3)_3M{-}N{=}C$, M = Si and Ge], with the former isomer predominating. We report here another reaction of these compounds which is indicative of the presence of the isocyanide isomer in these compounds. In addition, the analogous reaction of trimethyltin (iso)cyanide,[2] which exhibits properties of a highly polar cyanide, is described.

Organic isonitriles react with iron pentacarbonyl, displacing carbon monoxide to form either $RN{=}C{-}Fe(CO)_4$ or $(RN{=}C)_2Fe(CO)_3$, depending on reaction conditions.[3] The yellow-orange, crystalline monosubstituted products are typical covalent compounds, soluble in organic solvents, readily sublimable and air- and light-sensitive. On the other hand, the reaction of organic nitriles with iron pentacarbonyl does not proceed well, and iron tetracarbonyl, $[Fe(CO)_4]_3$, reacts more smoothly with benzo- and phenylacetonitrile.[4] In this case, red-colored, non-sublimable, *ionic* products of type $[Fe(N{\equiv}CC_6H_5)_n][Fe_3(CO)_{11}]$ and $[Fe(N{\equiv}CCH_2C_6H_5)_n][Fe_3(CO)_{11}]$ result. Thus the reaction with $Fe(CO)_5$ could possibly be used as a diagnostic test for the isocyanide structure in trimethyl(iso)cyanosilane and -germane and in trimethyltin (iso)cyanide.

We found that trimethyl(iso)cyanosilane and the corresponding germane react very readily with iron pentacarbonyl at 65–75°, liberating carbon monoxide and forming the compounds $(CH_3)_3SiN{=}C{-}Fe(CO)_4$ and $(CH_3)_3GeN{=}C{-}Fe(CO)_4$ in good yield.

$$(CH_3)_3M{-}N{=}C + Fe(CO)_5 \longrightarrow (CH_3)_3M{-}N{=}C{-}Fe(CO)_4 + CO \ (M = Si \text{ and } Ge)$$

Both compounds had properties characteristic of organic isonitrile-iron tetracarbonyl derivatives. Of special interest was the thermal stability of trimethylsilylisonitrile-iron tetracarbonyl and its germanium analog. Hieber and Pigenot[3] reported that methylisonitrile-iron tetracarbonyl decomposes above 75° with gas evolution. In contrast, in the absence of oxygen $(CH_3)_3SiN{=}C{-}Fe(CO)_4$ did not decompose until temperatures of 120–130° were reached. It must be emphasized that the reaction of these Group IV (iso)cyanides with iron carbonyl, a reaction characteristic of the isonitrile structure, does not differentiate between a 100% isocyano structure and a mixture of isocyano and normal cyano isomers in equilibrium but merely demonstrates the presence of the isocyano isomer.

The reaction of trimethyltin (iso)cyanide with iron pentacarbonyl was more complex. Work-up of the reaction mixture gave only very low yields of a sublimable product which analyzed correctly for $(CH_3)_3SnN{=}C{-}Fe(CO)_4$. and its infrared spectrum (Table I) was also consistent with this structure. The major part of the reaction product, a brown-red oil, was nonvolatile and showed chemical properties characteristic of anionic iron carbonyl species. Whether the iron carbonyl anions were formed in the primary reaction or in secondary decomposition reactions during subsequent operations could not be ascertained. Neither could the fate of the unaccounted for $(CH_3)_3SnCN$ be determined. In any case, trimethyltin (iso)cyanide stands apart from the carbon, silicon and germanium analogs in its behavior toward iron pentacarbonyl. All previous evidence[2] gave no indication of the presence of an isocyano isomer of trimethyltin (iso)cyanide, and we are led to the tentative conclusion that $(CH_3)_3Sn{-}N{=}C$ can be present only in very low equilibrium concentration and that the rate at which equilibrium is attained between the isocyano and cyano isomers is very slow in the tin compound, compared to the analogous silicon and germanium derivatives.

The infrared spectra of the silicon-, germanium- and tin-substituted isonitrile-iron tetracarbonyls resembled very closely those of organic isonitrile-iron tetracarbonyl compounds.[5] Table I lists the observed N=C and CO frequencies of three of the latter compounds and of our Group IV isonitrile-iron tetracarbonyl derivatives.

Table I

Infrared Spectra of Isonitrile-$Fe(CO)_4$ Compounds (in Chloroform Solution)

Compound	N=C (cm.$^{-1}$)	CO (cm.$^{-1}$)
$CH_3N{=}C{-}Fe(CO)_4$	2218	2072, 1996, 1967
$C_6H_5N{=}C{-}Fe(CO)_4$	2174	2067, 2003, 1973
$(CH_3)_3CN{=}C{-}Fe(CO)_4$	2186	2066, 1997, 1967
$(CH_3)_2SiN{=}C{-}Fe(CO)_4$	2132	2050, 1996, 1972
$(CH_3)_3GeN{=}C{-}Fe(CO)_4$	2135	2057, 1997, 1968
$(CH_3)_3SnN{=}C{-}Fe(CO)_4$	2142	2065, 2002, 1986

The infrared spectra in the pertinent region of trimethylsilyl- and trimethylgermylisonitrile-iron tetracarbonyl are shown in Fig. 1.

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(1) T. A. Bither, W. H. Knoth, Jr., R. V. Lindsey, Jr., and W. H. Sharkey, This Journal, **80**, 4151 (1958); and earlier references cited therein.

(2) D. Seyferth and N. Kahlen, unpublished.

(3) W. Hieber and D. von Pigenot, *Chem. Ber.*, **89**, 193 (1956).

(4) A. Lipp, Thesis, Technische Hochschule, München, 1959.

(5) We are indebted to Prof. F. A. Cotton and Dr. R. V. Parish for permission to quote their unpublished infrared data on organic isonitrile-iron tetracarbonyls.

The organic isonitrile-iron tetracarbonyls have been shown[5] to have a trigonal bipyramid structure, and the similarity of the spectra of the silicon, germanium and tin isonitrile-iron tetracarbonyl compounds suggests that these have the same structure. The lowered N=C stretching frequencies of the silicon, germanium and tin compounds in comparison to those of the methyl- and *tert*-butylisonitrile derivatives is reminiscent of the shift observed in the C=O stretching frequency when one goes from an organic ester to a trimethylsilvl ester of acetic acid[6] (*i.e.*, 1750–1735 cm.$^{-1}$ for normal saturated esters, 1715 cm.$^{-1}$ for $(CH_3)_3SiO_2CCH_3$). It is possible that this shift to lower frequencies of the N=C stretching frequency of the $RN{=}C{-}Fe(CO)_4$ compounds is due to increasing electron release in the series $R = CH_3 < (CH_3)_3C < (CH_3)_3Si \sim (CH_3)_3Ge \sim (CH_3)_3Sn$. Such a positive inductive effect would result in a strengthening of the $C_{isonitrile}$–Fe bond and possibly in enhancement of back donation from Fe to C_{CO} and would explain the higher thermal stability of the Group IV isonitrile-iron tetracarbonyls as compared to $CH_3N{=}C{-}Fe(CO)_4$. Alternatively, an interpretation of the shifts in the N=C stretching frequency in terms of back donation involving overlap of filled nitrogen p_π and vacant silicon d_π orbitals is possible, and such π-bonding also might result in increased thermal stability.

Experimental[7]

1. **Trimethylsilylisonitrile-iron Tetracarbonyl.**—Trimethyl(iso)cyanosilane[8] (1.5 g., 0.015 mole) was condensed in a Schlenk tube at −196° under nitrogen and 2.98 g. (0.015 mole) of iron pentacarbonyl was added. The tube was evacuated, sealed and heated for 22 hr. at 65°. It was then cooled to −196° and the liberated carbon monoxide pumped off. On warming to room temperature a light yellow solution remained. Removal of unreacted (iso)cyanide and iron carbonyl *in vacuo* gave 3.8 g. of bright yellow crystalline solid, a yield of 93%. The substance melted at 47–48° and was readily sublimed, forming long, light yellow needles at the cooled surface of the sublimation apparatus. It was extremely air-sensitive and immediately became brown in the presence of oxygen.

Anal. Calcd. for $C_8H_9O_4NSiFe$: C, 35.99; H, 3.40; N, 5.24; Si, 10.53; Fe, 20.92. Found: C, 36.04, 36.22; H, 3.50; 3.70; N, 5.50; Si, 10.45; Fe, 20.66, 21.22.

The compound is readily soluble in organic solvents such as ether, benzene and chloroform. The iodine–pyridine reagent liberated carbon monoxide vigorously.

The hydrolysis of $(CH_3)_3SiN{=}C{-}Fe(CO)_4$ was investigated briefly. One ml. of water was added to a solution of 1 g. of the compound in 15 ml. of carbon tetrachloride. After the mixture was stirred briefly, a red, non-crystalline solid precipitated. The mixture was filtered after it had been stirred for 4 hr. and the carbon tetrachloride layer was separated and dried. Its infrared spectrum showed the presence of hexamethyldisiloxane [$(CH_3)_3Si$ at 1255 and 841 cm.$^{-1}$, broad absorption 740–825 cm.$^{-1}$; Si–O–Si at 1055 cm.$^{-1}$: see ref. 9], as well as the presence of iron pentacarbonyl (strong bands at 2038 cm.$^{-1}$ and 2015 cm.$^{-1}$ identical with those in the spectrum of an authentic sample of $Fe(CO)_5$ in carbon tetrachloride). The red solid was not soluble in organic solvents and was not investigated further.

2. **Trimethylgermylisonitrile-iron Tetracarbonyl.**—In the manner described above 0.8 g. (5.57 mmoles) of $(CH_3)_3GeCN$[2] and 2.0 g. (10.4 mmoles) of iron pentacarbonyl were heated for 24 hr. at 70–75° in an evacuated Schlenk tube. The liberated carbon monoxide was pumped off and the excess iron pentacarbonyl distilled *in vacuo*, leaving 1.2 g. (69.4%) of light yellow solid, m.p. 69–70°. Sublimation at 45° and 0.5 mm. gave pure crystalline $(CH_3)_3GeN{=}C{-}Fe(CO)_4$.

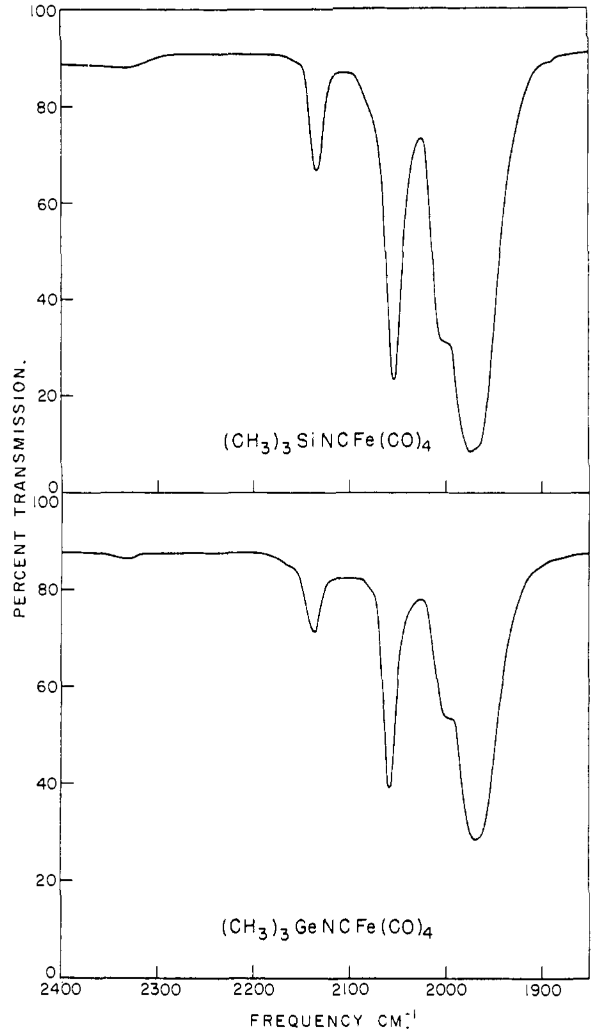

Fig. 1.—Infrared spectra of trimethylsilylisonitrile-iron tetracarbonyl and trimethylgermylisonitrile-iron tetracarbonyl (chloroform solution).

Anal. Calcd. for $C_8H_9O_4NGeFe$: C, 30.84; H, 2.91; N, 4.49; Ge, 23.30; Fe, 17.92. Found: C, 31.02; H, 3.11; N, 4.40; Ge, 23.18; Fe, 18.09.

The compound, like its silicon analog, is extremely sensitive to oxygen and is readily soluble in acetone, ether and chloroform, and sparingly soluble in petroleum ether.

3. **Trimethylstannylisonitrile-iron Tetracarbonyl.**—One g. (5 mmoles) of $(CH_3)_3SnCN$[2] was suspended in 4 cc. of toluene, and 2.3 g. (14 mmoles) of iron pentacarbonyl was added. The mixture was cooled to −196° and the Schlenk tube was evacuated. The reaction mixture was heated at 100–110° for 4 hr. A homogeneous solution formed and carbon monoxide was evolved vigorously. As the reaction progressed a small amount of light yellow solid deposited from solution. Cooling, removal of carbon monoxide, filtration and evaporation of the filtrate *in vacuo* left a brown-red, oxygen-sensitive oil. Sublimation (110–115° at 0.2 mm.) resulted in the collection of a small amount of light yellow, oily, amorphous solid on the cold finger cooled to −78°. The sublimate was extremely easily decomposed by oxygen, was very soluble in chloroform, ether and acetone, soluble in benzene and difficultly soluble in petroleum ether.

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(6) J. P. Freeman, THIS JOURNAL, **80**, 5954 (1958).

(7) Analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Melting points were determined in evacuated sealed tubes and are uncorrected. Infrared spectra were determined using a Perkin-Elmer model 21 spectrophotometer.

(8) J. J. McBride and H. C. Beachell, THIS JOURNAL, **74**, 5247 (1952).

(9) N. Wright and M. J. Hunter, *ibid.*, **69**, 803 (1947).

Anal. Calcd. for $C_8H_9O_4NSnFe$: C, 26.86; H, 2.54; N, 3.92; Sn, 33.18; Fe, 15.61. Found: C, 27.12; H, 2.56; N, 4.10; Sn, 33.33; Fe, 15.53.

A portion of the nonvolatile oil was dissolved in ether and treated with 9 *M* sulfuric acid. The characteristic odor of iron carbonyl hydride became noticeable. When a solution of $[Ni(o\text{-phen})_3]Cl_2$ was added to an acetone solution of the oil, a voluminous yellow precipitate was formed. These reactions are used as qualitative tests for the presence of anionic iron carbonyl species.[10]

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[10] W. Hieber and G. Brendel, *Z. anorg. u. allgem. Chem.*, **289**, 324 (1957).

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Stereochemistry of Complexes Based on Metal Tetrafluorides

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The general behavior of metal tetrafluorides toward a variety of organic donor molecules has been investigated. Most monofunctional donors formed octahedral complexes of the type $MF_4 \cdot 2$ donor, and in the case of the soluble TiF_4 and SnF_4 complexes, n.m.r. data showed them to have the donor atoms at positions *cis* to each other. Amides were found to complex through the carbonyl-oxygen atom. The tertiary amines were unpredictable in behavior forming either mono- or bis-amine complexes. The 1:1 amine complexes appear "polymeric" and are postulated to have octahedrally coördinated metal atoms through "fluorine bonding." Tendency to form 1:1 complexes is favored by the large steric requirements of tertiary amines and is enhanced if the metal fluoride is itself an associated compound. Silicon and germanium tetrafluorides appear to be much weaker acceptor molecules than TiF_4, SnF_4 and MoF_4, and in the case of the TiF_4 and SnF_4 complexes, rapid ($k \geqq 10^3$ sec.$^{-1}$) exchange of base occurs in solutions of the complexes in excess base at -25 to 25°.

Complexes of silicon tetrafluoride with certain organic donor molecules, *e.g.*, $N(CH_3)_3$, $HCON(CH_3)_2$ and complexes of titanium tetrafluoride with nitriles, ketones, alcohols and amines have been described. We have extended this chemistry with respect to the type of base and with respect to the fluoride. Fluorides investigated include TiF_4, ZrF_4, SiF_4, GeF_4, SnF_4, SF_4, TeF_4 and MoF_4. The major goals of this study were establishment of the general acceptor behavior of the metal tetrafluorides and determination of structure in these complexes.

Experimental

Reagents.—The tetrafluorides and tetrachlorides were obtained from commercial sources or were prepared by standard literature procedures. The gaseous tetrafluorides were purified by distillation; no purification procedure was used for the solid tetrafluorides.

Preparation of Complexes.—The SiF_4 and GeF_4 complexes were prepared by passing the gases into solutions of the base in ether, acetonitrile or benzene, and the complexes generally precipitated immediately from solution. The complexes were recrystallized from ether or acetonitrile. All of the complexes appeared to be decomposed rapidly by water or alcohols. Molecular weights in water decreased with time to fractional values in accord with observed changes, *e.g.*, silica precipitation or rapid decomposition.

ZrF_4 complexes were prepared by refluxing a slurry of the tetrafluoride in excess organic base and then filtration into a mixture of toluene and ether to precipitate the complex. No crystalline complexes were obtained by this approach with pyridine, acetone oxime and N,N,N',N'-tetramethylethylenediamine. Ethers, nitriles and sulfones did not react at 50–160° with ZrF_4.

Sulfur tetrafluoride reactions with a wide variety of organic bases were investigated in a vacuum train. The high solubility in these bases indicated complex formation, but the F^{19} spectra[1] of these SF_4 solutions gave no evidence of complex formation with the exception of $N(CH_3)_3$, $N(C_2H_5)_3$ and pyridine where, instead of the characteristic SF_4 resonance, a single F^{19} resonance was observed. Crude tensiometric studies indicated 1:1 proportion for the amine complexes in the case of pyridine and of triethylamine. The pyridine complex was significantly dissociated at 25°.

Two general methods for the preparation of TeF_4, MoF_4, TiF_4 and SnF_4 complexes were used: (1) Solution of MF_4 in tetrahydrofuran, dimethoxyethane or acetonitrile, filtration of the solution, and addition of the organic base or a solution of the base in an ether to the MF_4 solution. (2) Direct reaction of MF_4 and the base and isolation of the complex by concentration (solvent evaporation) to incipient crystallization or by vacuum removal of the excess base (a last resort that was necessary only for the TiF_4 complexes with ketones, alcohols and carboxylic acid). The relationship of the 1-propanol–TiF_4 system was established by tensiometric studies.

Pyridine–TiF_4 System.—The reaction of pyridine and titanium tetrafluoride was investigated in some detail. The only analytically pure product obtained, a 1:1 complex, was prepared by adding pyridine to a dilute solution of TiF_4 in dimethoxyethane. A precipitate formed immediately. The precipitate was filtered and washed at least six times with dimethoxyethane and with ether and then dried at ~30° for 12 hr. The 1:1 complex when extracted (very slow process—12 hr. for 0.6 g. to be extracted) with refluxing pyridine yielded a white solid (no melting point) that by analysis was neither $TiF_4 \cdot py$ nor $TiF_4 \cdot 2py$ but of a composition intermediate between these two. Further washing with ether and vacuum drying of this solid led to a reduction in amine content. A solid that gave analysis and behavior similar to the extracted solid was obtained by adding a dilute dimethoxyethane solution of TiF_4 to a solution of pyridine in dimethoxyethane keeping the pyridine in large excess. This behavior suggests either that the 1:1 complex strongly adsorbs pyridine or that the 2:1 complex is significantly dissociated at room temperature. The latter explanation is the more probable, since Emeleus and Rao[3] report that their $TiF_4 \cdot 2py$ preparation has a dissociation pressure of about 3 mm. at ~60°.

Miscellaneous Reactions.—Several base reactions deserve special comment. Trifluoroacetic acid proved to be the only "inert" solvent for TiF_4 in that TiF_4 could be recrystallized from the acid. 1,1,2,2-Tetrafluoroethanol dissolved TiF_4 without heat evolution but some slight irreversible reaction prevented complete recovery of TiF_4 from the solution. Tetramethylene sulfone also dissolved TiF_4 but no crystalline

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[1] E. L. Muetterties and W. D. Phillips, THIS JOURNAL, **81**, 1084 (1959).