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Organosulfur Derivatives of the Metal Carbonyls. XIII. Some Trifluoromethylthio Derivatives of Metal Carbonyls and Cyclopentadienyls[1,2]

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Reaction of $Mn(CO)_5Br$ with CF_3SAg in CH_2Cl_2 solution gives yellow crystalline $[CF_3SMn(CO)_4]_2$. However, reaction of $Re(CO)_5Br$ with CF_3SAg under similar conditions gives not only white $[CF_3SRe(CO)_4]_2$ but also white $CF_3SRe(CO)_5$; the latter compound is converted to $[CF_3SRe(CO)_4]_2$ upon boiling in cyclohexane. Reaction of $C_5H_5Fe(CO)_2I$ with CF_3SAg in acetone solution gives red-brown liquid $CF_3SFe(CO)_2C_5H_5$. Reaction of the π-allyl derivative $C_3H_5Fe(CO)_3I$ with CF_3SAg in CH_2Cl_2 solution gives red liquid $CF_3SFe(CO)_3C_3H_5$. Reaction of $C_5H_5Cr(NO)_2Cl$ with CF_3SAg in acetone solution gives yellow-brown crystalline $CF_3SCr(NO)_2C_5H_5$. Reaction of $(C_5H_5)_2TiCl_2$ with CF_3SAg does not give a CF_3S–Ti derivative. Instead a novel shift of fluorine from carbon to titanium occurs resulting in the formation of yellow $(C_5H_5)_2TiF_2$. The infrared, nmr, and mass spectra of the new compounds are discussed.

Numerous metal carbonyl and cyclopentadienyl derivatives containing the CH_3S group have been obtained. Most of these compounds have bridging CH_3S groups, *e.g.*, $[CH_3SMn(CO)_4]_2$,[5] $[CH_3SFe(CO)_3]_2$,[6] $[C_5H_5Mo(CO)_2SCH_3]_2$,[5] $[C_5H_5Fe(CO)SCH_3]_2$,[7] $[C_5H_5CoSCH_3]_2$,[7] and $[C_5H_5NiSCH_3]_2$.[8] However, the derivatives $C_5H_5Fe(CO)_2SCH_3$[9] and $(C_5H_5)_2Ti(SCH_3)_2$[10] with terminal CH_3S groups are also known.

The object of the work described in this paper was the preparation of analogous compounds containing CF_3S groups rather than CH_3S groups. The electronegativity of the fluorine atoms in the CF_3S groups would be expected to decrease drastically the basicity of the lone pairs on the sulfur atom thereby decreasing the tendency for CF_3S groups to act as bridges between two metal atoms. For this reason, compounds with terminal CF_3S groups were expected to be more prevalent than compounds with terminal CH_3S groups. The effect of substitution of hydrogen with fluorine in decreasing the basicity of potentially bridging groups has already been observed[11] in a comparative study of metal carbonyl derivatives containing $(CH_3)_2As$ and $(CF_3)_2As$[12] groups.

Known CF_3S derivatives are very limited in scope. The iron compound $[C_3F_7Fe(CO)_3SCF_3]_2$ was reported in 1963.[13] The manganese compound $[CF_3SMn(CO)_4]_2$ is mentioned only briefly without giving the detailed preparation.[14] The related selenium compounds $[CF_3SeMn(CO)_4]_2$,[15] $C_5H_5Fe(CO)_2SeCF_3$,[16] and $[CF_3SeFe(CO)_3]_2$[16] have been prepared.

Most RS derivatives of metal carbonyls are prepared by reactions of the corresponding mercaptan (RSH) or disulfide (RSSR) with an appropriate metal carbonyl derivative or other complex. However, the CF_3S derivative $[C_3F_7Fe(CO)_3SCF_3]_2$ was prepared by reaction of the silver derivative CF_3SAg with the halide $C_3F_7Fe(CO)_4I$.[13] Since CF_3SAg is readily available from carbon disulfide and silver(I) fluoride,[17] extension of this preparative method to other metal halide derivatives appeared to be an attractive route to new CF_3S derivatives. This paper describes the preparation of a variety of new CF_3S derivatives from the silver salt CF_3SAg and the properties of the resulting new compounds.

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Fluorine-19 nmr spectra were taken at 56.4 Mc. on a Perkin-Elmer Model R-20 spectrometer in dichloromethane solution with an internal $CFCl_3$ standard. Chemical shifts are reported in the scale of Filipovich and Tiers[18] ($\phi(CFCl_3) = 0.0$; $1\phi = 1$ ppm). Melting points were taken in capillaries and are uncorrected. A nitrogen atmosphere was routinely provided for the following operations: (a) carrying out reactions; (b) admitting to evacuated vessels.

The silver derivative CF_3SAg was prepared from silver(I) fluoride (Harshaw Chemical Co.) and carbon disulfide according to the published procedure.[17] The metal halides $M(CO)_5Br$ (M = Mn or Re),[19,20] $C_5H_5Fe(CO)_2I$,[21] $C_3H_5Fe(CO)_3I$,[22] and $C_5H_5Cr(NO)_2Cl$[23] were prepared by published procedures. The $(C_5H_5)_2TiCl_2$ was purchased from Arapahoe Chemicals Division of Syntex Corp., Boulder, Colo.

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(2) Portions of this work were presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

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TABLE I

INFRARED SPECTRA OF CF_3S DERIVATIVES[a]

Compound	Solvent	ν(CO), cm⁻¹	ν(CF), cm⁻¹
$[CF_3SMn(CO)_4]_2$	Cyclohexane	2097 vs, 2040 vs, 2028 vs, 2006 vs	1147 m, 1133 s, 1089 s
$[CF_3SRe(CO)_4]_2$	Cyclohexane	2110 vs, 2030 vs, 2018 vs, 1995 vs	1150 m, 1132 s, 1086 s
$CF_3SRe(CO)_5$	Cyclohexane	2145 vw, 2042 vs, 1998 s	1128 m, 1080 s
$CF_3SFe(CO)_2C_5H_5$	Cyclohexane	2044 vs, 2000 vs	1109 s, 1083 vs
$CF_3SFe(CO)_3C_3H_5$	Cyclohexane	2080 s, 2035 vs, 2010 vs	1113 m, 1080 s
$CF_3SCr(NO)_2C_5H_5$	Pentane	1830 vs,[b] 1729 vs[b]	1112 vs, 1085 vs

[a] These spectra were taken in the indicated solvents and recorded on a Perkin-Elmer Model 621 or 237 spectrometer with grating optics. [b] ν(NO) frequency.

Reaction of $Mn(CO)_5Br$ with CF_3SAg.—A mixture of 7.14 g (25.9 mmol) of $Mn(CO)_5Br$, 6.69 g (32 mmol) of CF_3SAg, and ~100 ml of dichloromethane was stirred for 2 hr at room temperature. The reaction mixture was then filtered. After addition of a few milliliters of hexane, solvent was removed from the filtrate at ~25° (40 mm) to give 6.26 g (89% yield) of yellow $[CF_3SMn(CO)_4]_2$. The analytical sample, mp 99°, was purified by sublimation at 70° (0.1 mm). *Anal.* Calcd for $C_{10}F_6Mn_2O_8S_2$: C, 22.4; Mn, 20.6; S, 12.0. Found: C, 22.6; Mn, 21.1; S, 11.9. Fluorine-19 nmr spectrum (CH_2Cl_2 solution): ϕ 34.2 (singlet).

Reaction of $Re(CO)_5Br$ with CF_3SAg.—A mixture of 1.035 g (2.54 mmol) of $Re(CO)_5Br$, 0.70 g (3.35 mmol) of CF_3SAg, and ~100 ml of dichloromethane was stirred for 2 hr at room temperature. Silver halide was then removed from the reaction mixture by filtration. A few milliliters of hexane was added to the filtrate and solvent was then removed at ~25° (40 mm). Sublimation of the white solid residue at 45° (25 mm) gave 0.239 g (22% yield) of white crystalline $CF_3SRe(CO)_5$, mp 78°. After removal of the $CF_3SRe(CO)_5$, further sublimation at 70° (0.1 mm) gave 0.533 g (53% yield) of white crystalline $[CF_3SRe(CO)_4]_2$, mp 129°. The purity of the rhenium complexes could be checked by their infrared spectra (Table I). If necessary, the fractional sublimation process described above could be repeated. *Anal.* Calcd for $C_6F_3O_5ReS$ $[CF_3SRe(CO)_5]$: C, 16.9; F, 13.3; O, 18.7; Re, 43.6; S, 7.5; mol wt, 427. Found: C, 16.8; F, 13.0; O, 18.7;[24] Re, 45.1; S, 8.9; mol wt, 438 (ebulliometric in benzene). Fluorine-19 nmr spectrum (CH_2Cl_2 solution): ϕ 26.7 (singlet). *Anal.* Calcd for $C_{10}F_6O_8Re_2S_2$ $[[CF_3SRe(CO)_4]_2]$: C, 15.0; F, 14.3; Re, 46.6; S, 8.0. Found: C, 15.3; F, 14.1; Re, 46.9; S, 8.1. Fluorine-19 nmr spectrum (CH_2Cl_2 solution): ϕ 38.8 (singlet).

Decarbonylation of $CF_3SRe(CO)_5$.—A solution of ~0.3 g of $CF_3SRe(CO)_5$ in ~50 ml of cyclohexane was boiled under reflux for 6 hr. The infrared spectrum of the resulting solution indicated conversion to $[CF_3SRe(CO)_4]_2$. A sample of pure $[CF_3SRe(CO)_4]_2$, mp 129°, was isolated from this solution by evaporation under reduced pressure followed by sublimation at 70° (0.1 mm).

Reaction of $C_5H_5Fe(CO)_2I$ with CF_3SAg.—A mixture of 4.066 g (13.1 mmol) of $C_5H_5Fe(CO)_2I$, 3.016 g (14.8 mmol) of CF_3SAg, and ~100 ml of acetone was stirred at room temperature for 24 hr. The reaction mixture was then filtered. A few milliliters each of hexane and cyclohexane were added to the filtrate. Solvent was then removed completely at ~25° (40 mm). The residue was extracted with 100 ml of cyclohexane in two portions and solvent removed from the filtered extract at ~25° (40 mm). The wet solid residue was then similarly extracted with methanol and solvent was removed from the filtered extract at ~25° (40 mm). The residue was then sublimed at ~50° (0.1 mm) onto a probe cooled to −78°. The red-brown solid which collected on the probe melted below room temperature to give 1.75 g (48% yield) of red-brown air-sensitive liquid $CF_3SFe(CO)_2C_5H_5$, fp ~15°. This product was not obtained when the reaction was carried out in dichloromethane rather than acetone solution. *Anal.* Calcd for $C_8H_5F_3FeO_2S$: C, 34.5; H, 1.8; F, 20.5; Fe, 20.1; S, 11.5. Found: C, 34.2; H, 1.9; F, 18.1; Fe, 18.9; S, 10.5. Fluorine-19 nmr spectrum (CH_2Cl_2 solution): ϕ 26.1 (singlet).

Reaction of $C_3H_5Fe(CO)_3I$ with CF_3SAg.—A mixture of 1.006 g (3.2 mmol) of $C_3H_5Fe(CO)_3I$, 0.750 g (3.6 mmol) of CF_3SAg, and ~100 ml of dichloromethane was stirred for 24 hr at room temperature. The reaction mixture was then filtered, and the solvent was removed partially at ~25° (40 mm). A few milliliters of hexane was added and slow evaporation of solvent continued at −78° (0.1 mm). The residual orange-red solid melted to a red liquid upon warming to room temperature to give 0.437 g (48% yield) of $CF_3SFe(CO)_3C_3H_5$. Upon prolonged standing of this liquid at room temperature it decomposed to form a brown solid exhibiting ν(CO) frequencies at 2028 and 1985 cm⁻¹. *Anal.* Calcd for $C_7H_5F_3Fe_2O_3S$: C, 29.8; H, 1.8; F, 20.2; Fe, 19.9; S, 11.3. Found: C, 30.0; H, 2.1; F, 19.8; Fe, 19.9; S, 10.9.

Reaction of $C_5H_5Cr(NO)_2Cl$ with CF_3SAg.—A mixture of 2.162 g (10.3 mmol) of $C_5H_5Cr(NO)_2Cl$, 2.22 g (10.6 mmol) of CF_3SAg, and ~100 ml of acetone was stirred for 6 hr at room temperature. The reaction mixture was filtered. Pentane was added to the filtrate and solvent was removed at ~25° (40 mm). The residue was purified by a Soxhlet extraction with pentane for 1 day. From the extract separated 1.95 g (70% yield) of yellow-brown crystalline $CF_3SCr(NO)_2C_5H_5$, mp 92–93°. *Anal.* Calcd for $C_6H_5CrF_3N_2O_2S$: C, 25.9; H, 1.8; Cr, 18.7; F, 20.5; N, 10.1; S, 11.5. Found: C, 26.4; H, 2.0; Cr, 18.4; F, 20.0; N, 9.7; S, 10.9. Fluorine-19 nmr spectrum (CH_2Cl_2 solution): ϕ 26.0 (singlet).

Reaction of $(C_5H_5)_2TiCl_2$ with CF_3SAg.—A mixture of 2.193 g (8.8 mmol) of $(C_5H_5)_2TiCl_2$, 4.2 g (20 mmol) of CF_3SAg, and ~100 ml of acetone or dichloromethane was stirred for 4 hr. The reaction mixture was then filtered. Hexane was added to the filtrate and solvent was removed at ~25° (40 mm) until separation of the yellow solid appeared to be complete. This yellow solid was filtered and then sublimed at ~110° (0.5 mm) to give 0.335 g (18% yield) of fluffy light yellow $(C_5H_5)_2TiF_2$, mp 238° dec. *Anal.* Calcd for $C_{10}H_{10}TiF_2$: C, 55.6; H, 4.6; F, 17.6; Ti, 22.2. Found: C, 55.5; H, 4.7; F, 17.5; Ti, 22.1. Infrared spectrum (KBr pellet): ν(CH) frequency at 3092 (w) cm⁻¹; other bands at 1449 (m), 1359 (w), 1257 (m), 1080 (s), 1010 (s), 950 (w), 867 (m), 810 (s), and 728 (w) cm⁻¹. Proton nmr spectrum ($CDCl_3$ solution): τ 3.57 (triplet, $J = 2$ cps). Fluorine-19 nmr spectrum (CH_2Cl_2 solution): ϕ −73.3 (singlet).

Reaction of $(C_5H_5)_2TiCl_2$ with AgF.—A mixture of 2.571 g (10.33 mmol) of $(C_5H_5)_2TiCl_2$, 2.646 g (20.83 mmol) of silver(I) fluoride, and ~100 ml of acetone was stirred for 24 hr at room temperature. The reaction mixture was then filtered and solvent removed at ~25° (40 mm). The resulting orange-yellow solid was sublimed at 110° (0.5 mm) to give 0.886 g (40% yield) of fluffy yellow $(C_5H_5)_2TiF_2$. The infrared spectrum of material prepared by this method was identical with that prepared from $(C_5H_5)_2TiCl_2$ and CF_3SAg.

Mass Spectra.—The following mass spectra were taken on a Perkin-Elmer Hitachi RMU-6 mass spectrometer at 70 eV with the inlet temperature around 150°. The relative abundances of the ions are indicated in parentheses.

A. $CF_3SRe(CO)_5$: $CF_3SRe(CO)_5^+$ (44), $CF_3SRe(CO)_4^+$ (44), $CF_3SRe(CO)_3^+$ (9), $CF_3SRe(CO)_2^+$ (16), $Re(CO)_5^+$ (25), $CF_3SRe(CO)^+$ (45), $Re(CO)_3S^+$ (11), $Re(CO)_4^+$ (9), $Re(CO)_3F^+$

(24) We are indebted to the Microanalytical Department of the University of Massachusetts Chemistry Department, Amherst, Mass., for carrying out this oxygen determination in the presence of fluorine and carbon.

(100), CF_3SRe^+ (63), $Re(CO)_2S^+$ (23), $Re(CO)_3^+$ (23), $Re(CO)_2F^+$ (28), $ReCOS^+$ (34), ReF_3^+ (26), $Re(CO)_2^+$ (11), $ReSF^+$ (18), $ReCOF^+$ (11), $ReCS^+$ (7), ReF_2^+ (3), ReS^+ (61), ReF^+ (5), ReO^+ (2), ReC^+ (9), Re^+ (42), CSF_2^+ (26), CF_3^+ (6), CFS^+ (34), COS^+? (10), CF_2^+ (6).

B. $[CF_3SMn(CO)_4]_2$: $(CF_3S)_2Mn_2(CO)_6^+$ (5), $(CF_3S)_2Mn_2(CO)_5^+$ (26), $(CF_3S)_2Mn_2(CO)_4^+$ (13), $(CF_3S)_2Mn_2(CO)_3^+$ (1), $(CF_3S)_2Mn_2CO^+$ (17), $(CF_3S)_2Mn_2^+$ (12), $CF_3SMn_2(CO)_2F^+$ (4), $CF_3SMn_2COF_2^+$ (0.6), $CF_3SMn_2COS^+$ (2), $Mn_2(CO)_4F_2^+$ (2), $CF_3SMn_2COF^+$ (4), $CF_3SMn_2F_2^+$ (11), $CF_3SMn_2S^+$ (4), $Mn_2(CO)_3F_2^+$ (11), $CF_3SMn_2F^+$ (35), $Mn_2S_2COF^+$ (2), $CF_3SMn_2^+$ (2), $Mn_2(CO)_2F_2^+$ (2), $Mn_2S_2CO^+$ (0.3), $Mn_2S_2F^+$ (3), Mn_2SCOF^+ (0.6), $Mn_2F_4^+$ (1), $Mn_2SF_2^+$ (7), $Mn_2COF_2^+$ (3), $Mn_2S_2^+$ (5), $Mn_2F_3^+$ (49), Mn_2SF^+ (25), CF_3SMn^+ (8), $Mn_2F_2^+$ (100), Mn_2S^+ (6), CF_2SMn^+ (6), Mn_2F^+ (7), $MnCFS^+$ (80), Mn_2^+ (4), MnS^+ (16), CSF_2^+ (off scale), CS_2^+? (16), MnF^+ (22), CFS^+ (23), Mn^+ (11), CF_2^+ (13).

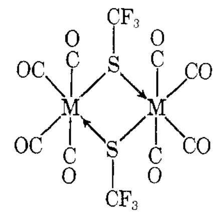
C. $C_5H_5Cr(NO)_2SCF_3$: $C_5H_5Cr(NO)_2SCF_3^+$ (92), $C_5H_5CrNOSCF_3^+$ (26), $C_5H_5CrSCF_3^+$ (100), $(C_5H_5)_2Cr^+$ (20), $C_5H_5Cr(NO)_2^+$ (48), $C_5H_5CrNOF^+$ (22), $C_5H_5CrS^+$ (~100), $C_5H_5CrNO^+$ (25), $C_5H_5CrF^+$ (>120), $C_5H_5Cr^+$ (73), CS_2F^+? (20), $C_3H_3Cr^+$ (16), $C_3H_2Cr^+$ (17), CSF_2^+ (~140), CS_2^+? (43), CrF^+ (48), $C_5H_6^+$ (~85), $C_5H_5^+$ (~85).

D. $(C_5H_5)_2TiF_2$: $(C_5H_5)_2TiF_2^+$ (34), $(C_5H_5)_2TiF^+$ (10), $C_5H_5TiF_2^+$ (100), $C_5H_5TiF^+$ (22).

Discussion

Recently various metal carbonyl perfluorocarboxylates were prepared by reactions of metal carbonyl halides with silver perfluorocarboxylates,[25] a class of silver derivatives soluble in organic solvents.[26] The solubility of trifluoromethylthiosilver, CF_3SAg, in polar organic solvents such as acetone[17] suggested a similar method for the preparation of trifluoromethylthio derivatives of metal carbonyls. This led to the investigation of the reactions between a variety of metal carbonyl halides and trifluoromethylthiosilver. In the initial studies dichloromethane was employed as a solvent. However the silver derivative CF_3SAg is much more soluble in acetone than in dichloromethane which made acetone the solvent of choice for reactions with less reactive metal halide complexes such as $C_5H_5Fe(CO)_2I$.

Reactions of the bromides $M(CO)_5Br$ (M = Mn or Re) with CF_3SAg in dichloromethane solution at room temperature gave the binuclear derivatives $[CF_3SM(CO)_4]_2$ (I, M = Mn or Re) as the major products. The infrared spectra exhibited the expected four ν(CO) frequencies like the analogous binuclear halides $[M(CO)_4Br]_2$ and other *cis*-$M(CO)_4X_2$ derivatives.[27] The reaction of the rhenium derivative $Re(CO)_5Br$ with CF_3SAg also gave some of the mononuclear derivative $CF_3SRe(CO)_5$ (II) which could be decarbonylated to the binuclear derivative $[CF_3SRe(CO)_4]_2$ (I, M = Re) by boiling in cyclohexane solution. The behavior of the trifluoromethylthiorhenium derivatives $CF_3SRe(CO)_5$ and $[CF_3SRe(CO)_4]_2$ prepared in this work is thus similar to that of the pentafluorophenylthio derivatives $C_6F_5SRe(CO)_5$ and $[C_6F_5SRe(CO)_4]_2$ prepared from $HRe(CO)_5$ and pentafluorothiophenol.[28] Furthermore, the isolation of $CF_3SRe(CO)_5$ (II) but not the manganese analog $CF_3SMn(CO)_5$ from reactions carried out at room temperature is a further indication of the stability of rhenium–carbon bonds relative to analogous manganese–carbon bonds also demonstrated by observations such as the higher decarbonylation temperatures of $R_fCORe(CO)_5$ derivatives relative to analogous $R_fCOMn(CO)_5$ derivatives.[29]



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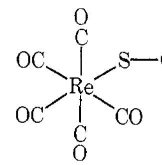
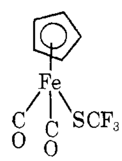


II

The substituted metal carbonyl halides $C_5H_5Fe(CO)_2I$ and $C_3H_5Fe(CO)_3I$ have stronger metal–carbonyl bonds than the $M(CO)_5X$ halides. They gave only the mononuclear derivatives $CF_3SFe(CO)_2C_5H_5$ (III) and $CF_3SFe(CO)_3C_3H_5$ (IV), respectively, upon reaction with CF_3SAg at room temperature. The π-allyl derivative IV, however, was unstable upon prolonged standing at room temperature decomposing to a brown solid exhibiting two ν(CO) frequencies; analyses on this brown solid indicated it to be a mixture. The nitrosyl derivative $C_5H_5Cr(NO)_2Cl$ also reacted with CF_3SAg to give a mononuclear derivative $CF_3SCr(NO)_2C_5H_5$ (V); no evidence for a binuclear derivative of the type $[C_5H_5CrNOSR]_2$ was found although other reactions of cyclopentadienylchromium nitrosyl systems yield such binuclear derivatives.[30]

Several alkylthio derivatives of titanium of the type $(C_5H_5)_2Ti(SR)_2$ (R = methyl, ethyl, phenyl, etc.) are known.[10] In an attempt to prepare an analogous trifluoromethylthio derivative, the reaction between $(C_5H_5)_2TiCl_2$ and CF_3SAg was investigated. The only titanium complex isolated from the reaction mixture was the fluoride $(C_5H_5)_2TiF_2$ (VI), previously obtained by Birmingham and Wilkinson[31] from $(C_5H_5)_2TiBr_2$ and hydrofluoric acid. The reaction between $(C_5H_5)_2TiCl_2$ and CF_3SAg thus results in a shift of fluorine from carbon to titanium apparently because of the great thermodynamic stability of bonds between the electronegative fluorine atom and the relatively electropositive +4 titanium atom. Attempts to effect the reverse shift of fluorine from titanium to carbon by heating $(C_5H_5)_2TiF_2$ (VI) with hexafluoropropene under a



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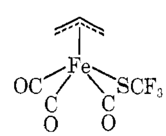

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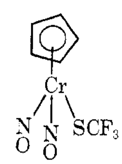
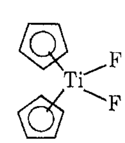


V



VI

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variety of conditions hoping to prepare $(C_5H_5)_2Ti[CF(CF_3)_2]F$ or $(C_5H_5)_2Ti[CF(CF_3)_2]_2$ have been uniformly unsuccessful apparently because of this stability of titanium–fluorine bonds.

Some spectroscopic properties of $(C_5H_5)_2TiF_2$ were investigated. The π-cyclopentadienyl resonance in the proton nmr spectrum of $(C_5H_5)_2TiF_2$ is split into a triplet (J = 2 cps) owing to interaction of these protons with the two equivalent fluorine atoms. This appears to be the first example of the splitting of a π-cyclopentadienyl resonance by coupling with fluorine atoms; similar splitting of π-cyclopentadienyl nmr resonances by coupling with phosphorus, rhodium, or platinum atoms is well known. The mass spectrum of $(C_5H_5)_2TiF_2$ exhibits the molecular ion which may undergo loss of either C_5H_5 or F. The ratio $[C_5H_5TiF_2^+]/[(C_5H_5)_2TiF^+]$ is 10 indicating that the π-cyclopentadienyl ring is lost much more easily than the fluorine atom. This indicates further the unusual stability of the titanium–fluorine bond especially since in most cyclopentadienyl derivatives except those of nickel, palladium, and platinum the ligands other than the π-C_5H_5 ring are lost much more easily than the π-cyclopentadienyl ring.[32]

All of the new trifluoromethylthio derivatives exhibit characteristic ν(CF) frequencies in the 1150–1080-cm^{-1} region of their infrared spectra (Table I). The mononuclear trifluoromethylthio derivatives exhibited the expected two ν(CF) frequencies at 1118 ± 10 and 1083 ± 3 cm^{-1}. However, the binuclear trifluoromethylthio derivatives $[CF_3SM(CO)_4]_2$ (I, M = Mn or Re) exhibit three ν(CF) frequencies indicating appreciable coupling between the vibrations of the two CF_3 groups. The ^{19}F nmr spectra of the mononuclear CF_3S derivatives ($CF_3SRe(CO)_5$, $CF_3SFe(CO)_2C_5H_5$, and $CF_3SCr(NO)_2C_5H_5$) exhibit the expected CF_3 singlet around ϕ 26. However, in the case of the binuclear CF_3S derivatives $[CF_3SM(CO)_4]_2$ (I) the chemical shifts of the CF_3 singlet are somewhat higher occurring in the range ϕ 34–39.

The mass spectra of the compounds $[CF_3SM(CO)_4]_2$ (I, M = Mn or Re), $CF_3SRe(CO)_5$ (II), and $CF_3SCr(NO)_2C_5H_5$ (V) were obtained. However, uncertainties in the m/e values of some of the higher m/e ions prevented a detailed analysis of the $[CF_3SRe(CO)_4]_2$ mass spectrum. Nevertheless, from the available data certain characteristic features of the mass spectra of CF_3S derivatives could be elucidated. These features are best illustrated in the mass spectrum of $CF_3SRe(CO)_5$ (II). This mass spectrum exhibits the molecular ion which undergoes successive loss of carbonyl groups in the usual manner[33] to give the family of ions $CF_3SRe(CO)_n^+$ (n = 5, 4, 3, 2, 1, and 0). The families of carbonyl ions listed below are also observed thereby indicating the occurrence of certain relatively favorable processes which can compete with the loss of carbonyl groups.

(1) $Re(CO)_n^+$ (n = 5, 4, 3, 2, and 0).—The presence of these ions indicates that complete cleavage of the rhenium–sulfur bond can compete with loss of the carbonyl groups. This is consistent with previous data[34] on the mass spectrum of the derivative $CH_3SFe(CO)_2C_5H_5$ with a terminal methylthio group.

(2) $Re(CO)_nS^+$ (n = 3, 2, 1, and 0).—The presence of these ions indicates that cleavage of the trifluoromethyl–sulfur bond can also compete with loss of the carbonyl groups. Processes of this type are rarely encountered in the mass spectra of methylthio derivatives before all carbonyl groups are lost.[34,35] However, the substitution of hydrogen atoms with fluorine atoms in going from a methyl group to a trifluoromethyl group is well known to increase the electronegativity of the carbon atom which in this case would decrease the electronegativity difference between carbon and sulfur and hence weaken the carbon–sulfur bond in the CF_3S group relative to the CH_3S group.

(3) $Re(CO)_nF^+$ (n = 3, 2, 1, and 0).—The presence of these ions indicates the ease of a fluorine shift from carbon to the metal atom similar to the formation of $(C_5H_5)_2TiF_2$ from $(C_5H_5)_2TiCl_2$ and CF_3SAg discussed above. In going from an M–SCF_3^+ ion to an M–F^+ ion a neutral CSF_2 fragment is eliminated; ionization of this fragment would lead to CSF_2^+ which is the strongest ion in the mass spectra of $[CF_3SMn(CO)_4]_2$ and $CF_3SCr(NO)_2C_5H_5$.

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