J. Am. Chem. Soc. **1987**, *109*, 4855–4860

Synthesis of Trifluorosilyl Organometallic Complexes from Trifluorosilyl Radicals and Metal Atoms

T. R. Bierschenk, M. A. Guerra, T. J. Juhlke, S. B. Larson, and R. J. Lagow*

Contribution from the Department of Chemistry, University of Texas, Austin, Texas 78712.

Received September 17, 1986

Abstract: Trifluorosilyl radicals generated in a radio frequency glow discharge of hexafluorodisilane were reacted with metal atoms to give the first homoleptic trifluorosilyl metal compounds. Bis(trifluorosilyl)tellurium, tris(trifluorosilyl)bismuth, tris(trifluorosilyl)antimony, and bis(trifluorosilyl)mercury were formed in moderate yields by cocondensation of tellurium, bismuth, antimony, and mercury with trifluorosilyl radicals ($^{\bullet}SiF_3$) on a cryogenic surface. In a similar manner trifluorosilyl complexes containing additional ligands were also prepared. For example, we have successfully prepared bis(trifluorosilyl)tris(trimethylphosphine)nickel, (η^6-toluene)bis(trifluorosilyl)nickel, bis(trifluorosilyl)bis(trimethylphosphine)palladium, bis(trifluorosilyl)cadmium–glyme, and bis(trifluorosilyl)zinc–2-pyridine.

Despite the extensive study of fluorocarbon-substituted metal compounds in recent years, very few compounds exist in which the SiF_3 ligand is bonded to an element other than carbon. The lack of known compounds is presumably due to the lack of a suitable synthetic technique for preparing the compounds. The first metal trifluorosilyl complex $F_3SiCo(CO)_4$ was prepared by using a method analogous to that used by Chalk and Harrod for preparing $R_3SiCo(CO)_4$ complexes (R organic groups).[1] The reaction of trifluorosilane with the binuclear metal carbonyl $Co_2(CO)_8$ gave $F_3SiCo(CO)_4$ in 84% yield.[2] Similar reactions at 160 °C with $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$ yielded $F_3SiMn(CO)_5$, $F_3SiRe(CO)_5$, and $F_3SiFe(\pi\text{-}C_5H_5)(CO)_2$.[3] It was later noticed that the compounds could be made equally as well by using iodotrifluorosilane in place of the trifluorosilane, but the products were more difficult to separate.[3] The scarcity of known trifluorosilyl compounds is not too surprising when one considers the forcing reaction conditions necessary (160 °C). Recently Sharp has reported the synthesis of $P(SiF_3)_3$ by using a novel approach.[4] The compound was prepared from $^{\bullet}SiF_3$ radicals generated by mercury-sensitized photolysis of Si_2F_6 in the presence of PF_3.

We have found that the metal vapor/plasma technique which we have been developing in our laboratory over the past several years[5] can be used to prepare a wide variety of new trifluorosilyl-substituted compounds. Metal vapors, usually generated by resistively heating a metal in a vacuum, are allowed to react with extremely reactive trifluorosilyl radicals on a liquid-nitrogen-cooled surface. The $^{\bullet}SiF_3$ radicals are generated in a hexafluorodisilane plasma. Hexafluorodisilane is an excellent precursor for the synthesis of trifluorosilyl compounds because the silicon–fluorine bond energy of about 140 kcal/mol is considerably greater than the silicon–silicon bond dissociation energy of about 50 kcal/mol.[6,7] The large difference in bond energies leads primarily to $^{\bullet}SiF_3$ formation while byproducts such as $^{\bullet}Si_2F_5$, $:SiF_2$, and SiF_4 do not appear to be produced in the plasma to any great extent.

Although it is not known at this time what utility such compounds will have, they are interesting from a structural point of view. It is well-known that many silyl compounds have structures different from their carbon analogues. For example $(SiH_3)_3N$ is planar whereas $(CH_3)_3N$ is pyramidal.[8] These differences are usually attributed to $(p \rightarrow d)$-π-bonding effects for the silicon analogue.[8] It has been suggested that an analogous $(d \rightarrow d)$-π interaction may be operative for metal trifluorosilyl complexes.[1,9] Preliminary vibrational studies using $F_3SiCo(CO)_4$ suggest that there may be significant $(d \rightarrow d)$-π double-bond character in the silicon–cobalt bond.[10] Additional studies using photoelectron spectroscopy should prove advantageous.

Experimental Section

Materials, Analysis, and Physical Measurements. All of the metals used were purchased from Alfa Products and were Puratronic grade. Hexafluorodisilane was prepared by using a slight modification of the method reported by Booth and Stillwell.[11] Hexachlorodisilane was fluorinated with SbF_3 in a closed system with $SbCl_5$ being used as a catalyst. Hexachlorodisilane was prepared by chlorinating calcium–silicide ($CaSi_2$) at 150 °C.[12] The tungsten baskets used to resistively heat the metals were acquired from R.D. Mathis Co., Long Beach, CA. The X-ray crystallographic data was collected on a Syntex $P2_1$ automated diffractometer equipped with a low-temperature inert-gas delivery system which held the crystal at −100 °C with cold, dry nitrogen during the course of the experiment. Mo Kα radiation of 0.71069 Å was used. The crystal was mounted on a glass fiber with an epoxy adhesive. Fluorine and hydrogen NMR spectra were recorded on a Varian EM 390 spectrometer operating at 90 MHz for proton and 84.87 MHz for fluorine. Low-temperature ^{19}F NMR spectra were run on a Bruker WH-90 spectrometer with a deuteriated solvent being used for the lock signal. IR spectra were taken on a Beckman IR-20A. The mass spectra were taken on a Bell and Howell Model 21-490 low-resolution spectrometer operating at 70 eV with a source temperature of 240 °C. Elemental analysis was obtained from Schwarzkopf Microanalytical Laboratories in Woodside, NY.

All of the metal atom reactions described gave rise to products which were very air-sensitive. For this reason, all vacuum line manipulations were executed with the careful exclusion of air and moisture. When a nonvolatile product was obtained, the compound was separated and purified in an inert-atmosphere box.

Apparatus. Two basic reactor designs were used in preparing the compounds described in this paper. The first reactor (Figure 1) is a modification of the one described in an initial publication and is used primarily for preparing metal complexes of easily vaporized metals.[5] It consists of a Pyrex cold finger (A) attached to a reactor base (B) with a glass O-ring connector (C). The base was made of brass with water-cooled electrical feedthroughs (D) which were used to resistively heat a tungsten basket or crucible heater (E). The feedthrough was electrically insulated from the base with high density polyethylene and an O-ring which also forms the vacuum seal. For best results, the feedthrough should be made from stainless steel with all of the connections being

---

[1] Clark, A. J.; Harrod, J. F. *J. Am. Chem Soc.* **1965**, *87*, 1133.

[2] Hagen, A. P.; MacDiarmid, A. G. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 345.

[3] Schruke, R. R.; West, B. O. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 141.

[4] Sharp, K. G. *J. Chem. Soc., Chem. Commun.* **1977**, 564.

[5] (a) Juhlke, T. J.; Bierschenk, T. R.; Lagow, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 3229. (b) Firsich, D. W.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1283. (c) Bierschenk, T. R.; Juhlke, T. J.; Lagow, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 7340. (d) Guerra, M. A.; Bierschenk, T. R.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1550. (e) Guerra, M. A.; Bierschenk, T. R.; Lagow, R. J. *J. Organomet. Chem.* **1986**, *307*, C58.

[6] McDonald, J. P.; Williams, C. H.; Thompson, J. C.; Margrave, J. L. *Mass Spectrom. Inorg. Chem.* **1968**, *72*, 261.

[7] Ehlert, T. C.; Margrave, J. L. *Chem. Phys.* **1964**, *41*, 1066.

[8] (a) Ebsworth, E. A. V. *Int. Ser. Monogr. Inorg. Chem.* **1963**, *4*, 101. (b) Ebsworth, E. A. V. *J. Chem. Soc., Chem. Commun.* **1966**, 350.

[9] Aylett, B. J.; Campbell, J. M. *J. Chem. Soc., Chem. Commun.* **1965**, 217.

[10] Hagen, A. P.; MacDiarmid, A. G. *Inorg. Chem.* **1967**, *6*, 686.

[11] Booth, H. S.; Stillwell, W. D. *J. Am Chem. Soc.* **1934**, *56*, 1531.

[12] Schumb, W. C.; Gamble, L. *Inorg. Synth.* **1939**, *1*, 42.

0002-7863/87/1509-4855$01.50/0

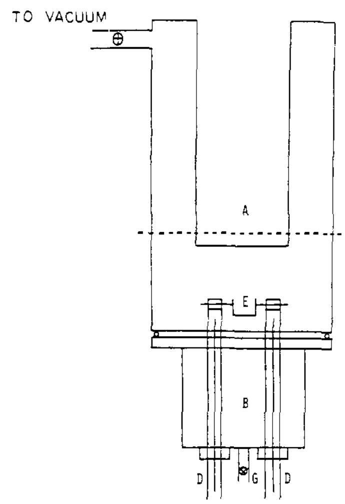

Figure 1. Metal atom reactor used for the reaction of main-group metals and trifluorosilyl radicals.

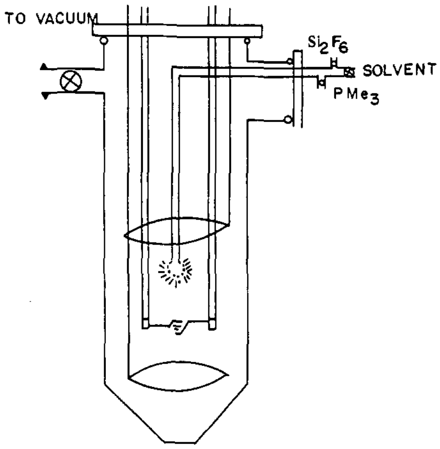

Figure 2. Metal atom reactor used for the reaction of transition metals with trifluorosilyl radicals.

heli-arced. The plasma was formed by attaching the ground to the reactor base and the high voltage lead of the radio frequency generator to a band (F) on the reactor top. This allowed the radio frequency power to be capacitively coupled to the reactor. Hexafluorodisilane entered through an inlet (G). Mercury, tellurium, and antimony were vaporized from a quartz crucible wrapped with tungsten wire while bismuth was evaporated from a tungsten basket which was coated with aluminum oxide.

The second reactor (Figure 2) was similar in design to reactors which are commercially available and was used primarily for preparing transition-metal complexes. The increased distance between the metal vapor source and the walls minimized the heating of the matrix by radiation being emitted by the vaporizing metal. Additionally, the design of the reactor made the addition of other ligands easier by providing a surface upon which the matrix could melt and be allowed to stand. The reactor consisted of a Pyrex glass bottom which was submerged in liquid nitrogen. A Plexiglas top plate was attached to the reactor bottom using a 100-mm O-ring connector. The plasma gas was capacitively coupled to the radio frequency power supply with internal $^1/_4$-in. stainless-steel electrodes, which were placed inside of Pyrex tubes for protection from the plasma. These electrodes were fed through the Plexiglas top of the reactor by using a Cajon O-seal joint. The high current electrical feedthroughs for resistively heating the tungsten basket were water-cooled. The feedthroughs were placed inside of Pyrex tubing to electrically insulate them from the internal electrodes which were used to capacitively couple the plasma gas to the radio frequency generator. A side arm containing a 30-mm O-ring connector sealed to a $^1/_2$-in. Plexiglas plate with an O-ring provided an inlet for the hexafluorodisilane, the solvent, and trimethylphosphine. Cadmium, cobalt, nickel, palladium, and zinc metals were placed directly in the tungsten basket.

General Procedure. The metal was preweighed and loaded in a crucible or an aluminum oxide coated tungsten basket. The reactor was assembled and evacuated overnight. Hexafluorodisilane was introduced by placing about 40 g in a 25-mm glass tube placed in a frozen chlorobenzene slush. This allowed the disilane to slowly vaporize into the reactor at a rate of about 10 g/h. About 1 g of metal was vaporized over the course of a typical 2–3-h reaction. If a volatile metal product was formed, it was separated from the unreacted hexafluorodisilane and metal by condensing the product in a dry ice/acetone-cooled vacuum distillation trap. The contents of the −78 °C trap, the product plus minor amounts of plasma catenation products, were further fractionated by vacuum distillation through a low-temperature thermal gradient sublimation apparatus. All nonvolative products were manipulated in an inert-atmosphere box.

Synthesis of Bis(trifluorosilyl)mercury. Bis(trifluorosilyl)mercury was prepared by the codeposition of mercury vapor with trifluorosilyl radicals produced from hexafluorodisilane in a glow discharge. Approximately 1.5 g of mercury was placed in a quartz crucible, and the reactor (Figure 1) was evacuated to about 10^{-3} torr. The cold finger was cooled with liquid nitrogen, and the hexafluorodisilane was allowed to flow into the reactor. The mercury was evaporated at a rate sufficient to allow complete evaporation over a 3-h period. Upon completion of the reaction, the volatile products were pumped from the reactor into a vacuum trap which was held at −196 °C. Bis(trifluorosilyl)mercury as well as unreacted mercury remained behind in the reactor and was removed in an inert-atmosphere box. The crude product was dissolved in toluene, which had been dried over CaH_2 and filtered through a fine porosity filter frit. The filtrate was brought to dryness and sublimed twice at 50 °C onto a 0 °C cold finger to give 700 mg of $Hg(SiF_3)_2$ (22% yield) on the basis of metal evaporated: mp 205 °C; IR (KBr disk) 880 (vs), 825 (s), 305 (w) cm^{-1}; ^{19}F NMR (in acetonitrile, in ppm relative to external CF_3COOH) δ +29 (s, $J(^{199}Hg\text{-}F)$ = 1160 Hz); MS, Hg^+ (21%), SiF_2Hg^+ (14%), $Si_2F_5Hg^+$ (0.4%), SiF_6Hg^+ (0.8%).

Synthesis of Tris(trifluorosilyl)bismuth. Approximately 1.5 g of bismuth was placed in an aluminum oxide coated tungsten basket. The metal was slowly evaporated over a 3-h period and condensed with trifluorosilyl radicals in the reactor shown in Figure 1. When the reaction was completed, the cold finger was quickly warmed and the volatiles were pumped into a liquid-nitrogen-cooled trap. The liquid nitrogen level on the trap was kept as low as possible so that the compound coould be condensed out as near to the bottom of the trap as possible. This was done because $Bi(SiF_3)_3$ is thermally very unstable, and the bottom of the trap generally stays cooler than the top during a routine vacuum distillation. Also, it was observed that a substantial amount of the bismuth product decomposed in the reactor if the cold finger was warmed too slowly following a reaction. When the cold finger was allowed to warm quickly, the Si_2F_6 could "blow" some of the bismuth product over before the cold finger was warm enough for the $Bi(SiF_3)_3$ to have sufficient vapor pressure to volatilize.

The trap containing the unreacted Si_2F_6 and the $Bi(SiF_3)_3$ was warmed to −63 °C, and the products were vacuum distilled (the unreacted Si_2F_6 stops in a −131 °C trap, while the bismuth product and plasma catenation products stop in a −78 °C trap). After approximately 1 h, the −63 °C slush was removed and the remaining products were pumped from the trap.

The products stopping in the −78 °C trap were vacuum-distilled on a Dobson low-temperature distillation apparatus. The Dobson column was cooled to −150 °C, and the products were condensed inside of the column. The column was slowly warmed, and the products were separated into three basic bands. The top band consisted of very small, wet crystals, the second band, the $Bi(SiF_3)_3$, gave very large crystals (1–3 mm), and the third band, the least volatile compound, consisted of very small opaque crystals. The column was slowly warmed and the $Bi(SiF_3)_3$ (630 mg) was collected in a trap on the vacuum line (21% yield based on metal vaporized: ^{19}F NMR (CD_2Cl_2 at −30 °C, in ppm relative to external $CFCl_3$) δ +90.4 (s); MS, Bi^+ (77%), SiF_2Bi^+ (22.4%), $(SiF_3)_2Bi^+$ (0.1%).

Synthesis of $Te(SiF_3)_2$. Approximately 1.5 g of tellurium was placed in a quartz crucible which was heated by a tungsten crucible heater. The reactor was assembled and evacuated to less than 10^{-3} torr. The metal was evaporated at a rate sufficient to allow complete vaporization over a 3-h period and was condensed with the $^{\bullet}SiF_3$ radicals formed in the plasma. Upon completion of the reaction, the volatiles were pumped from the reactor and condensed in the bottom of a −196 °C trap. The products were vacuum-distilled to obtain a crude product ($Te(SiF_3)_2$ stops in a −78 °C trap while Si_2F_6 stops in a −131 °C slush). The contents of the −78 °C trap were passed through a −45 °C trap resulting in 773 mg of a dark yellow liquid bis(trifluorosilyl)tellurium (25% yield) being retained in the trap: ^{19}F NMR (neat at −45 °C, in ppm relative to external $CFCl_3$) δ +102 (s, $J_{F\text{-}Te}$ = 210 Hz); MS, SiF_3^+ (100%), Te^+ (7.0%), SiF_2Te^+ (4.5%), SiF_3Te^+ (1.4%), SiF_5Te^+ (0.4%), $Si_2F_6Te^+$ (0.22%).

Synthesis of $Sb(SiF_3)_3$. Tris(trifluorosilyl)antimony was prepared by slowly vaporizing 0.5 g of antimony from an aluminum oxide coated tungsten basket while hexafluorodisilane was slowly vaporized from a −45

°C slush during a 3-h reaction. The volatile products were vacuum-distilled from the reactor and separated from the unreacted hexafluorodisilane by vacuum distillation through a −78 and −131 °C traps. (The $Sb(SiF_3)_3$ as well as plasma catenation products stopped in the −78 °C trap while the hexafluorodisilane stopped in a −131 °C trap). Trap to trap separation of the stop −78 °C fraction using −45 and −63 °C traps gave $Sb(SiF_3)_3$ in about 90% purity in the −63 °C trap. Attempts to further purify the compound using gas chromatography were unsuccessful. Three columns were tried and in each case the compound decomposed on the column (30% SE 30 on Chromosorb P, 10% Fluorosilicone on Chromosorb P, and 15% Dinonyl Phthalate on Chromosorb P). The compound, 480 mg (31% yield based on metal vaporized), was obtained in about 99% purity (NMR) by distillation on a Dobson low-temperature column: IR (gas phase) 1215 (w), 1030 (vs), 1005 (s), 995 (s), 892 (w), 882 (m), 860 (w), 823 (m) cm^{-1}; ^{19}F NMR (neat at 25 °C, in ppm relative to external $CFCl_3$) δ +95.3 (s); MS, SiF_3^+ (100%), Sb^+ (82%), SiF_3Sb^+ (26%), $Si_2F_6Sb^+$ (4.5%), $Si_3F_8Sb^+$ (1.3%), $Si_3F_9Sb^+$ (0.6%).

Synthesis of (η^6-Toluene)Ni(SiF_3)$_2$. (η^6-Toluene)bis(trifluorosilyl)nickel was prepared by slowly vaporizing 0.5 g of nickel from a tungsten basket while 5 g of toluene and 15 g of Si_2F_6 were simultaneously deposited on the liquid-nitrogen-cooled walls of the reactor (Figure 2). Upon completion of the 3-h reaction, the matrix was warmed and a reaction took place which gave a dark solution in the bottom of the reactor. The volatiles were vacuum-distilled from the reactor to leave a dark solid which was extracted in the drybox to give 520 mg of a green solid, (η^6-toluene)bis(trifluorosilyl)nickel (19% yield based on nickel vaporized). The compound was obtained in 99% purity, according to ^{19}F and ^1H NMR, after crystallization in toluene: IR (KBr disk) 3400 (s), 2960 (w), 1620 (m), 1500 (w), 1445 (w), 1130 (s), 780 (m), 730 (s) cm^{-1}; ^{19}F NMR (in $CDCl_3$, in ppm relative to external $CFCl_3$) δ +91 (s); ^1H NMR (in $CDCl_3$, in ppm relative to Me_4Si) 6.9 (m), 2.5 (s); MS, P−F (2.0%).

Synthesis of (SiF_3)$_2$Ni(PMe_3)$_3$. Bis(trifluorosilyl)tris(trimethylphosphine)nickel was prepared by slowly cocondensing 0.5 g of nickel with 15 g of Si_2F_6 on a −196 °C surface during a 3-h reaction in the reactor shown in Figure 2. The Si_2F_6 was vacuum-distilled from the reactor at −78 °C leaving behind the unstable nickel trifluorosilyl complex $Ni(SiF_3)_2$ to which 1 mL of trimethylphosphine and 10 mL of dichloromethane are added. The phosphine-containing solution was allowed to warm to room temperature with continuous stirring to give 225 mg of a dark orange solid, $(SiF_3)_2Ni(PMe_3)_3$ (5.7% yield). The compound was obtained in greater than 99% purity by extraction with methylene chloride followed by a thermal gradient sublimation.

An alternate route to $(SiF_3)_2Ni(PMe_3)_3$ has been found which takes advantage of the unusually high lability of the arene ring of (η^6-toluene)bis(trifluorosilyl)nickel. The reaction of the nickel arene complex with an excess of trimethylphosphine at 0 °C gives $(SiF_3)_2Ni(PMe_3)_3$ in quantitative yield after a few minutes. The compound has identical properties as the authentic sample prepared using metal vapor chemistry: IR (KBr disk) 2980 (m), 2958 (m), 1440 (m), 1417 (m), 1290 (s), 1260 (s), 1100 (s), 1025 (s), 90 (vs), 865 (m), 825 (vs), 774 (vs), 715 (w), 668 (m) cm^{-1}; ^{19}F NMR (in $CDCl_3$ at 30 °C, in ppm relative to $CFCl_3$) δ +89.0 (q, J_{P-F} = 5.8 Hz); $^{31}P\{^1H\}$ NMR (in $CDCl_3$ at 25 °C, in ppm relative to H_3PO_4) δ 20.8 (septet, J_{P-F} = 5.8 Hz); ^1H NMR (in $CDCl_3$ at 25 °C, in ppm relative to Me_4Si) δ 1.4 (s); MS, $(SiF_3)_2Ni(PMe_3)_3^+$ (0.7%), $(P-F)^+$ (3.1%).

Synthesis of (SiF_3)$_2$Pd(PMe_3)$_2$. Bis(trifluorosilyl)bis(trimethylphosphine)palladium was prepared by using the reactor shown in Figure 2 by slowly reacting 0.1 g of palladium with 20 g of Si_2F_6 on a liquid-nitrogen-cooled surface in a 3-h codeposition reaction. Upon completion of the reaction, the Si_2F_6 was slowly pumped from the reactor at −45 °C to leave a dark red, unstable compound which is believed to be $Pd(SiF_3)_2$. If the compound is stirred with an excess of trimethylphosphine along with 10 cm^3 of toluene prior to warming to room temperature, the stable yellow compound $(SiF_3)_2Pd(PMe_3)_2$ can be isolated (8% yield based on metal vaporized): ^{19}F NMR (in CD_2Cl_2 at 25 °C, in ppm relative to $CFCl_3$) δ 96.7 (s); ^{19}F NMR (in CD_2Cl_2 at −30 °C) δ 96.7 (t, J_{P-F} = 17 Hz).

Synthesis of (SiF_3)$_2$Cd·glyme. Bis(trifluorosilyl)cadmium−glyme was prepared by cocondensing 99.4 mg of cadmium vapor with plasma-generated $^{\bullet}SiF_3$ radicals in a 2-h reaction (using the reactor shown in Figure 2). Following the reaction, the reactor was warmed to −40 °C to pump off the excess Si_2F_6. Ether (10 mL) and 1 mL of dimethoxyethane were then condensed into the reactor at −196 °C. The contents of the reactor were allowed to melt giving rise to the title compound. The crude product mixture was removed from the reactor in a drybox and extracted with ether to give bis(trifluorosilyl)cadmium−glyme which was further purified by crystallization in hexane (36 mg, 10.9% yield) to give a white solid: IR (KBr disk) 2920 (m), 1400 (m), 1250 (m), 1120 (m), 1070 (vs), 1005 (s), 785 (m) cm^{-1}; ^{19}F NMR (in CD_2Cl_2 at 25 °C, in ppm relative to external $CFCl_3$) δ +98.7 (s, J_{Cd-F} = 581/556 Hz); ^1H NMR (in CD_2Cl_2 at 25 °C, in ppm relative to external Me_4Si) δ 3.7, 3.5; MS, SiF_3^+ (100%), $Cd(SiF_3)^+$ (9%), Cd·glyme$^+$ (1%), Cd^+ (15%). Anal. Calcd for $C_4H_{10}Si_2F_6Cd$: C, 12.9; H, 2.7; F, 30.6. Found: C, 12.6; H, 2.5; F, 30.1.

With use of a slight modification of the procedure outlined above, unsolvated bis(trifluorosilyl)cadmium can be obtained. Following the removal of the unreacted Si_2F_6 at −45 °C, 10 mL of methylene chloride can be condensed onto the reactor walls at −196 °C. When the methylene chloride is melted a solution containing the unsolvated cadmium compound is obtained. Bis(trifluorosilyl)cadmium has a half-life of approximately 24 h at +25 °C: IR (KBr disk) 1250 (m), 1070 (vs), 1005 (s), 785 (m) cm^{-1}; ^{19}F NMR (in CD_2Cl_2 at −78 °C, in ppm relative to external $CFCl_3$) δ 102.3 (s, J_{Cd-F} = 601/564 Hz); MS, SiF_3^+ (100%), Cd^+ (58%), $CdSiF_3^+$ (75%), $Cd(SiF_3)SiF_2^+$ (2%), $Cd(SiF_3)_2^+$ (1.4%).

Synthesis of (SiF_3)$_2$Zn−2-pyridine. Bis(trifluorosilyl)zinc−2-pyridine was prepared by resistively heating and vaporizing 214 mg of zinc metal in the presence of $^{\bullet}SiF_3$ radicals generated in a Si_2F_6 glow discharge. Following the 2-h reaction, the frozen matrix was dropped into the bottom of the reactor shown in Figure 2 by warming the cold finger. The unreacted Si_2F_6 was vacuum distilled from the reactor at −40 °C leaving behind a residue containing the product. The addition of methylene chloride (−40 °C) followed by rapid stirring resulted in the dissolution of the product into the methylene chloride. The solution can either be transferred from the reactor via a cannula into a chilled container to give unsolvated bis(trifluorosilyl)zinc or 1 mL of pyridine can be condensed into the reactor to give bis(trifluorosilyl)zinc−2-pyridine upon warming to room temperature. The compound is recovered in high purity by extraction of the nonvolatile product with methylene chloride in a drybox: IR (KBr disk) 2970 (w), 1330 (s), 1220 (s), 1020 (m), 990 (m), 790 (w) cm^{-1}; ^{19}F NMR (in CD_2Cl_2 at 25 °C, in ppm relative to external $CFCl_3$) δ +99.3; ^1H NMR (in CD_2Cl_2 at 25 °C, in ppm relative to external Me_4Si) δ 8.3 (ortho), 7.2 (meta), 7.6 (para). Anal. Calcd for $C_{10}H_{10}N_2Si_2F_6Zn$: C, 30.5; H, 2.6; F, 290.0. Found: C, 30.9; H, 2.7; F, 28.3.

Results and Discussion

Bis(trifluorosilyl)mercury is a colorless, crystalline solid soluble in most common solvents. It easily hydrolyzes but can be kept for long periods of time in an inert atmosphere. The compound, when reacted with fluorine in a passivated Kel-F and stainless-steel system, gave silicon tetrafluoride (identified by infrared and mass spectra) after the reaction products were pumped through a −196 °C trap to remove the unreacted fluorine.

Preliminary X-ray crystallographic data suggests that $Hg(SiF_3)_2$ crystallizes in the space group $P42_12$ with two molecules per unit cell. The lattice constants were a = 6.3939 Å, b = 6.3939 Å, and c = 7.6982 Å, while $\alpha = \beta = \lambda = 90°$. The crystal was grown in a thermal gradient sublimer with one end heated to +35 °C while the other end was cooled to about −20 °C. Using these conditions the crystal grew in about 12 h. The crystal was mounted on a glass fiber with an epoxy resin and placed in a −100 °C nitrogen stream for data collection.

Tris(trifluorosilyl)bismuth is a colorless compound soluble in nonpolar organic solvents. Based on its ^{19}F NMR spectrum, the compound was obtained in greater than 95% purity with some volatile decomposition products such as SiF_4 also being present. However, if a −45 °C slush was placed around the NMR tube after the product was condensed into the tube, the volatile decomposition products could be pumped away leaving behind $Bi(SiF_3)_3$ having a purity of about 99%. When the sample is warmed to +15 °C, the fluorine resonance for the SiF_3 ligand slowly disappeared, suggesting that decomposition was occurring.

The mass spectrum could not be recorded by using a normal inlet on a mass spectrometer cooled to room temperature. A direct inlet was tried in order to minimize the degree of decomposition. This too was unsuccessful because the SiF_4 formed in the decomposition reaction was the only gas-phase species observed. The mass spectrum was easily recorded by placing a −30 °C slush around the tube containing the compound which allowed it to slowly vaporize (and decompose). The more volatile decomposition products as well as the majority of the $Bi(SiF_3)_3$ was quickly condensed in a second tube held at −196 °C. A metering valve between the two tubes allowed some of the gaseous products to enter into the mass spectrometer. The distance between the −30 and −196 °C traps was under 12 in., and large tubing (16 mm)

Table I. Crystallographic Summary for $Ni(SiF_3)_2(P(CH_3)_3)_3$

A. Crystal Data (−110 °C)[a]	
a, Å	12.780 (7)
V, Å^3	2087.5 (19)
d_{calcd} g cm^{-3} (−110 °C)	1.394
empirical formula	$Ni(SiF_3)_2(P(CH_3)_3)_3$
fw	438.09
cryst system	cubic
space group	$P2_13$
Z	4
F(000), electrons	944
B. Data Collection (−110 °C)[b]	
radiatn λ, Å	Mo Kα, 0.71069
mode	Ω scan
scan range	symmetrically over 1.5° about K$\alpha_{1,2}$ maximum
bkgd	offset 1.0 and −1.0° in Ω from K$\alpha_{1,2}$ maximum
scan rate, deg min^{-1}	2.5–6.0
exposure time, h	36.3
stability analysis	
computed a	0.002573
computed b	−0.000108
max correctn (on I)	5.1%
2θ range, deg	4.0–60.0
range in hkl	
min	0,0,1
max	12,17,17
total reflectns measd	1695 (1144 unique)
data cryst dimensns, mm	0.25 × 0.24 × 0.24 × 0.21 (square bipyramid)
data cryst volume, mm^3	0.0106
data cryst faces	$111; \bar{1}\bar{1}\bar{1}; 11\bar{1}; 1\bar{1}\bar{1}; \bar{1}11; 1\bar{1}1; \bar{1}1\bar{1}$
abs coeff μ(Mo Kα), cm^{-1}	13.089
tranmissn factor range	0.765–0.793
C. Structure Refinement[c]	
ignorance factor p	0.04
reflctns used, $F \rightarrow 4\sigma_F$	745
no. of variables	76
goodness of fit, S	1.865
R_1, R_2	0.0841, 0.0682
R_1 for all data	0.1336
max shift/esd	0.0055
max peak in diff map, e Å^{-3}	1.54 (0.92 Å from Ni)
min density in diff map, e Å^{-3}	−1.16

[a] Unit-cell parameters were obtained by least-squares refinement of the setting angles of 30 reflections with $22.17° < 2\theta < 29.18°$. [b] Syntex $P2_1$ autodiffractometer with a graphite monochromator and a Syntex LT-1 inert-gas (N_2) low-temperature delivery system. Data reduction was carried out as described in: Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 381. Crystal and instrument stability were monitored by remeasurement of four check reflections after every 96 reflections. These data were analyzed as detailed in: Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1511. [c] Relevant expressions are as follows, where in this footnote F_o and F_c represent respectively the observed and calculated structure factor amplitudes. Function minimized as $\sum w(F_o - F_c)^2$, where $w = \sigma_F^{-2}$. $R_1 = \sum \mathrm{abs}(F_o - F_c)/\sum F_o$. $R_2 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$.

was used to ensure a rapid transfer. With use of this technique a representative sample of the gas phase could be observed instead of the more volatile products. The gaseous sample was metered directly into the cool ionization region of the mass spectrometer (60 °C). The identity of the parent ion was confirmed by high-resolution mass spectroscopy.

Bis(trifluorosilyl)tellurium is an unstable, volatile liquid soluble in most organic solvents but reacts vigorously with water, oxygen, alcohols, and other polar organic solvents. The compound is sufficiently stable to be vaporized at −30 °C in vacuo with minimal decomposition. Similarly, tris(trifluorosilyl)antimony is a colorless liquid having a melting point of about −40 °C and is soluble in nonpolar solvents such as toluene. Although the compound is stable at room temperature for extended periods of time, it begins to decompose at 50 °C. The pure compound is very air-sensitive and ignites instantly when in contact with moist air.

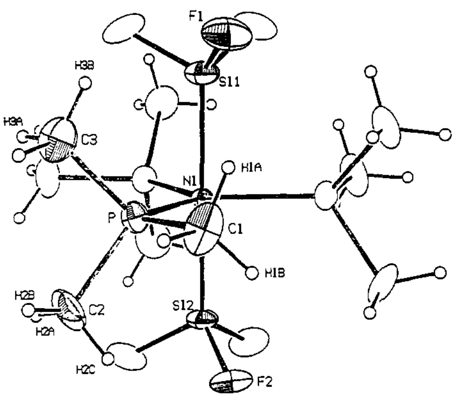

Figure 3. The molecular structure of $(SiF_3)_2Ni(PMe_3)_3$.

Table II. Bond Lengths (Å) and Bond Angles (deg) in $Ni(SiF_3)_2(P(CH_3)_3)_3$

1	2	3	1–2	1–2–3
P	Ni	Si1	2.204 (3)	89.45 (14)
P	Ni	Si2		90.55 (13)
P	Ni	P*1[a]		119.99 (14)
P	Ni	P*2		119.99 (14)
Si1	Ni	Si2	2.182 (4)	180.0 (2)
C1	P	C2	1.83 (2)	101.1 (7)
C1	P	C3		102.8 (7)
C1	P	Ni		112.2 (5)
C2	P	C3	1.82 (2)	96.7 (8)
C2	P	Ni		120.5 (6)
C3	P	Ni	1.818 (12)	120.4 (5)
F1	Si1	Ni	1.596 (9)	117.6 (4)
F1	Si1	F1*1		100.3 (5)
F1	Si1	F1*2		100.3 (5)
F2	Si2	Ni	1.580 (8)	117.6 (4)
F2	Si2	F2*1		100.3 (4)
F2	Si2	F2*2		100.3 (4)
H1A	C1	P		100.8 (14)
H1B	C1	P		120.9 (15)
H1C	C1	P		106.0 (14)
H2A	C2	P		112.5 (14)
H2B	C2	P		110.8 (15)
H2C	C2	P		104.9 (14)
H3A	C3	P		104.1 (12)
H3B	C3	P		109.9 (12)
H3C	C3	P		114.1 (13)

[a] Atoms marked *1 and *2 are related to unmarked atoms with same label by z, x, y and y, z, x, respectively.

(η^6-Toluene)bis(trifluorosilyl)nickel is a yellow solid which decomposes prior to melting at about 50 °C. The compound is soluble in benzene, toluene, chloroform, and methylene chloride. It has relatively good short term stability at ambient temperature but decomposes in air to give a white solid. Attempts to sublime the compound were unsuccessful and resulted in decomposition. The product when heated to 50 °C gives a nickel mirror as well as toluene and Si_2F_6. (η^6-Toluene)bis(trifluorosilyl)nickel has recently been reported.[13]

Bis(trifluorosilyl)tris(trimetylphosphine)nickel is an orange solid which is relatively stable in air for short periods of time; however, the compound is routinely handled in an inert-atmosphere box. The compound sublimes in a vacuum (10^{-4}), with some decomposition, when heated at 120 °C. The compound decomposed rapidly, without melting, at 160 °C.

The NMR findings suggest that the compound has trigonal-bipyramidal symmetry with the SiF_3 ligands occupying axial positions. This assumption is further supported by X-ray crystallographic data collected on a single crystal prepared by vacuum sublimation (see Figure 3). The data suggests that the complex

---

[13] (a) Lin, S. T.; Groshens, T. J.; Klabunde, K. J. *Inorg. Chem.* **1984**, *23*, 1. (b) Lin, S. T.; Narske, R. N.; Klabunde, K. J *Organometallics* **1985**, *4*, 571.

Table III. Atomic Positions in Fractional Coordinates and U_{eq} for $Ni(SiF_3)_2(P(CH_3)_3)_3$

atom	*x*	*y*	*z*	U_{eq}, Å^2
Ni	−0.22212 (10)	−0.22212 (10)	−0.22212 (10)	0.0231 (3)
P	−0.2294 (3)	−0.3388 (2)	−0.0953 (2)	0.0373 (10)
Si1	−0.1235 (3)	−0.1235 (3)	−0.1235 (3)	0.0507 (11)
Si2	−0.3213 (3)	−0.3213 (3)	−0.3213 (3)	0.0429 (10)
F1	−0.0282 (6)	−0.1781 (7)	−0.0642 (7)	0.084 (4)
F2	−0.2886 (7)	−0.4397 (5)	−0.3347 (6)	0.073 (3)
C1	−0.1202 (12)	−0.4307 (12)	−0.1002 (12)	0.066 (6)
C2	−0.3398 (12)	−0.4280 (12)	−0.0854 (14)	0.070 (7)
C3	−0.2294 (13)	−0.2972 (11)	0.0407 (9)	0.067 (6)
H1A	−0.0603 (12)	−0.3832 (12)	−0.0835 (12)	0.08 (3)
H1B	−0.1043 (12)	−0.4708 (12)	−0.1655 (12)	0.08 (3)
H1C	−0.1313 (12)	−0.4806 (12)	−0.0410 (12)	0.08 (3)
H2A	−0.4086 (12)	−0.3912 (12)	−0.0914 (14)	0.04 (2)
H2B	−0.3373 (12)	−0.4680 (12)	−0.0182 (14)	0.04 (2)
H2C	−0.3312 (12)	−0.4774 (12)	−0.1455 (14)	0.04 (2)
H3A	−0.2901 (13)	−0.2481 (11)	0.0457 (9)	0.05 (2)
H3B	−0.1632 (13)	−0.2586 (11)	0.0567 (9)	0.05 (2)
H3C	−0.2387 (13)	−0.3555 (11)	0.0920 (9)	0.05 (2)

has D_{3h} symmetry. The trifluorosilyl groups occupy axial positions with average bond lengths of 2.182 Å while the trimethylphosphines are positioned in the equatorial plane with an average Ni–P bond length of 2.204 Å (see Tables I–III). Unlike other trigonal-bipyramidal complexes of nickel such as $(CH_3)_2Ni(PMe_3)_3$ and $(CF_3)_2Ni(PMe_3)_3$,[5b] the trifluorosilyl complex is not fluxional at ambient temperature as is evident by the phosphorus and fluorine NMR. This "freezing out" of the structure (at room temperature) with the SiF_3 ligands in the axial positions may result from the unusually high electronegativity of the SiF_3 moiety, or it may be due to a π-interaction involving the silicon d orbitals and the filled metal d orbitals of proper symmetry. If this interaction is maximized by placing the two SiF_3 ligands in axial positions, a sufficient kinetic barrier may be present to block the normal fluxional behavior exhibited by many trigonal-bipyramidal complexes.

Bis(trifluorosilyl)bis(trimethylphosphine)palladium (mp 186–188 °C) is a light yellow solid which is stable in air for short periods of time. It is soluble in most common organic solvents and can be sublimed in a vacuum. Although the compound appears to be fluxional in solution at room temperature, the trifluorosilyl ligands are trans to each other at −30 °C (D_{3h} symmetry).

Bis(trifluorosilyl)cadmium·glyme is a white solid with a melting point of 87 °C and is stable in air for short periods of time. Unsolvated bis(trifluorosilyl)cadmium has sufficiently stability to be characterized at room temperature. It has a slight vapor pressure at room temperature and reacts readily with oxygen and moisture.

Bis(trifluorosilyl)zinc, unlike its cadmium analogue, is too unstable to be fully characterized; however, its ^{19}F NMR can be recorded at −78 °C. A singlet is obtained at +122.9 ppm from external $CFCl_3$ when CD_2Cl_2 is used as a solvent. The addition of pyridine gives a stable compound bis(trifluorosilyl)zinc–2-pyridine which can be characterized. Bis(trifluorosilyl)zinc–2-pyridine (mp 86 °C) is a light brown, tacky solid that reacts with air and moisture. The compound undergoes decomposition before it can be sublimed.

NMR evidence was obtained which strongly suggests that an additional trifluorosilyl complex $(\eta^6\text{-toluene})Co(SiF_3)_2$ can be prepared in an identical fashion as the nickel compound. The yellow-green compound, having only 17 valence electrons, was paramagnetic and gave a broad singlet in the fluorine NMR at +90 ppm from $CFCl_3$. ^1H NMR of a dilute CD_2Cl_2 solution of the compound gave resonances at 2.5 and 6.9 ppm from Me_4Si presumably due to the toluene methyl and aromatic protons, respectively. The mass spectrum gave strong evidence supporting the compound's existence. A parent peak (1.5%), $P^+ - 2(SiF_3)$ (67.6%), $P^+ - (SiF_3)$ (100%), toluene$^+$ (70.3%), SiF_3^+ (54.9%), and Co^+ (46.8%) were observed. Infrared absorbances were seen at 3400 (s), 2960 (w), 1620 (m), 1500 (w), 1445 (w), 1130 (s), 780 (m), and 730 (s) cm^{-1}. The compound is quite reactive at room temperature, making it exceedingly difficult to purify and characterize. For example, the compound reacts with trimethylphosphine at room temperature to give a compound which is believed to be bis(trifluorosilyl)tris(trimethylphosphine)cobalt. All of the expected ion fragments were observed in the mass spectrum with the exception of the parent ion $(SiF_3)_2Co(PMe_3)_3^+$. A broad singlet was observed in the ^{19}F NMR at 91.0 ppm from $CFCl_3$ (paramagnetic). ^1H NMR showed a broad singlet at +1.2 ppm resulting from the trimethylphosphine groups. It should be noted that the nickel and cobalt compounds are extremely interesting from a structural point of view since (π-arene)ML_2 complexed are extremely rare.[14]

The successful synthesis of $Sb(SiF_3)_3$ and $Bi(SiF_3)_3$ in conjunction with K. G. Sharp's recent preparation of $P(SiF_3)_3$[4] completes the list of group V trifluorosilyl compounds with the exception of $As(SiF_3)_3$. Not even a trace of the compound was prepared when arsenic metal was cocondensed with trifluorosilyl radicals. This is not surprising since all of the group V metalloids vaporize as tetramers with phosphorus and arsenic forming the most stable oligomers. The heats of atomization have been reported for each of the elements which make it possible to estimate the bond dissociation energies for each tetramer (P, 71; As, 63; Sb, 52; and Bi, 34 kcal/mol).[15] The free electrons in a low power radio frequency plasma of Si_2F_6 have energies which are quenched (or restricted) by the Si–Si bond (50 kcal/mol[6,7]), so few electrons acquire enough energy to break the arsenic tetramer while the majority have sufficient energies to form both antimony and bismuth atoms. Presumably $As(SiF_3)_3$ could be prepared by reacting AsI_3 with a Si_2F_6 plasma in a fashion analogous to that used for preparing $M(CF_3)_n$-type compounds from metal halides.[16,17] Alternatively, the arsenic tetramer could be cleaved by using a laser or by vaporizing the metal from a double Knudsen cell.

Trifluoromethyl-containing metal compounds decompose by eliminating difluorocarbene to form metal fluorides. Preliminary experiments using $Hg(SiF_3)_2$, $Te(SiF_3)_2$, and $Bi(SiF_3)_3$ suggest that metal trifluorosilyl compounds cannot be used as a source of difluorosilane. For instance, as $Te(SiF_3)_2$ and $Bi(SiF_3)_3$ are slowly warmed to room temperature, SiF_4 is generated (identified by infrared and mass spectral analyses) instead of products more consistent with $:SiF_2$ formation. In addition, metallic mirrors are deposited by both compounds as they decompose with little or no evidence of metal fluoride formation. Similar results were reported by Hagen and MacDiarmid for the thermal decomposition reaction of $F_3SiCo(CO)_4$.[10] The primary decomposition products reported were elemental silicon and SiF_4 in a ratio consistent with the following reaction: $8F_3SiCo(CO)_4 \rightarrow Co_4(CO)_{12} + 2Co_2(CO)_8 + 2Si + 6SiF_4 + 4CO$.[10] Presumably the reaction is intramolecular and does not involve free $\cdot SiF_3$ radicals since Si_2F_6 is not generated.

The decomposition of $Hg(SiF_3)_2$ appears to be free radical in nature. After 3 days at 210 °C, a sample of $Hg(SiF_3)_2$ in benzene completely decomposed to give elemental mercury, Si_2F_6, and a minor product which had a ^{19}F NMR chemical shift similar to that reported for (trifluorosilyl)benzene (the identity of the compound was not confirmed). This suggests that bis(trifluorosilyl)mercury may be a useful reagent for preparing trifluorosilyl-containing metal complexes in much the same way as bis(trifluoromethyl)mercury can be used in exchange reactions to make a limited number of trifluoromethyl compounds. In fact, preliminary experiments have shown that it may be superior to its trifluoromethyl analogue in that it reacts readily with several

---

(14) (a) Radonovich, L. J.; Klabunde, K. J.; Behrens, C. B.; McCollov, D. P.; Anderson, B. B. *Inorg. Chem.* **1980**, *19*, 1221. (b) Radonovich, L. J.; Koch, F. J.; Albright, T. A. *Inorg. Chem.* **1980**, *19*, 3373.

(15) Carlson, P. D.; Kohl, F. J.; Manuel Uy, O. *Mass Spectrosc. Inorg. Chem.* **1972**, *72*, 245.

(16) Lagow, R. J.; Gerchman, L. L.; Jacob, R. A.; Morrison, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 518.

(17) (a) Jacob, R. A.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* **1973**, *4*, 104. (b) Morrison, J. A.; Lagow, R. J. *Inorg. Chem.* **1977**, *16*, 1823. (c) Eujen, R.; Lagow, R. J. *Inorg. Chem.* **1975**, *14*, 2138.

of the metal halides tried even at room temperature while $Hg(CF_3)_2$ usually requires elevated temperatures.

Bis(trifluorosilyl)mercury will undergo a ligand-exchange reaction at room temperature when reacted with group 4 and 5A metal halides such as germanium tetraiodide and arsenic triiodide.[18] The mercurial product is especially reactive toward low-valent, late-transition-metal complexes such as $PdBr_2(PMe_3)_2$ which will react rapidly at 0 °C to give $Pd(SiF_3)_2(PMe_3)_2$. This is especially exciting since the only other known route to a metal trifluorosilyl, besides the metal vapor technique, involves the reaction of SiF_3H or SiF_3I with a binuclear metal carbonyl. This reaction is extremely limited, requires high temperatures, and gives rise to a product containing only one trifluorosilyl group.[2,3]

Trifluorosilyl complexes prepared by using main-group metals were much less stable than their corresponding trifluoromethyl analogues. For example, $Te(CF_3)_2$ and $Bi(CF_3)_3$ are thermally quite stable at room temperature while $Te(SiF_3)_2$ and $Bi(SiF_3)_3$ decompose well below room temperature. In contrast, a very different trend may be observed for the transition metals since the silicon d orbitals can interact with filled metal d orbitals. For example, the trifluorosilyl nickel arene complex $(\eta^6\text{-toluene})Ni(SiF_3)_2$ is stable at room temperature while $(\eta^6\text{-toluene})Ni(CF_3)_2$ decomposes moderately fast at room temperature.[19] Unusually stable metal alkyls incorporating metals such as tungsten, tantalum, and uranium, just to mention a few, may result upon cocondensing these metals with trifluorosilyl radicals.

Acknowledgment. We are grateful for support of this work by the Air Force Office of Scientific Research (AFOSR-82-0197), the National Science Foundation (CHE-8521390), and the Robert A. Welch Foundation (F-700).

---

(18) Bierschenk, T. R.; Guerra, M. A.; Lagow, R. J., to be submitted for publication.

(19) Bierschenk, T. R.; Lagow, R. J., to be submitted for publication.

Syntheses, Kinetics, and Mechanism of Ligand Substitution Reactions of 17-Electron Cyclopentadienyl and Pentadienyl Vanadium Carbonyl Complexes

Ruth M. Kowaleski,[†] **Fred Basolo,***[†] **William C. Trogler,***[‡] **Robert W. Gedridge,**[§] **Timothy D. Newbound,**[§] **and Richard D. Ernst***[§]

Contribution from the Departments of Chemistry, Northwestern University, Evanston, Illinois 60201, University of California at San Diego, La Jolla, California 92093, and University of Utah, Salt Lake City, Utah 84112. *Received January 21, 1987*

Abstract: Reported are the syntheses of bis(η^5-pentadienyl)vanadium carbonyls and corresponding triethylphosphine compounds. The CO substitution lability in the complexes $(\eta^5\text{-L})_2VCO$ ($L = C_5H_5, C_5Me_5, C_5H_7, 2,4\text{-}C_7H_{11}$) was investigated. The exchange reaction of $(\eta^5\text{-}C_5H_5)_2V^{13}CO$ or of $(\eta^5\text{-}C_5Me_5)_2V^{13}CO$ with CO is first-order in both CO and metal complex: for $L = C_5Me_5$, kinetic parameters in toluene are $\Delta H_2^\ddagger = 8.9 \pm 0.7$ kcal/mol, $\Delta S_2^\ddagger = -21 \pm 3$ cal/(mol K), and k_2 (0.0 °C) = 12.7 (±0.1) $M^{-1}\ s^{-1}$. The rate of CO addition to the 15-electron complex Cp^*_2V is slower than the CO exchange rate for Cp^*_2VCO: $\Delta H^\ddagger = 6.3 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -37 \pm 4$ cal/(mol K), and k (0.0 °C, toluene) = $0.424 \pm 0.005\ M^{-1}\ s^{-1}$. The vanadium carbonyl complexes containing one or two pentadienyl ligands react 10^3–10^4 times slower than the bis(cyclopentadienyl) complexes, and the CO exchange rates depend only slightly on CO concentration. The electronic and steric features in these complexes, which allow for associative reactions for $(\eta^5\text{-}C_5H_5)_2VCO$ and $(\eta^5\text{-}C_5Me_5)_2VCO$ but prohibit this pathway for the pentadienyl complexes, are discussed.

The reactivity of 17-electron organometallic complexes is of interest in view of the role of metal radicals as intermediates in catalytic, photochemical, and electrochemical reactions.[1-3] Kinetic studies have established associative mechanisms for ligand substitution in the 17-electron complexes $V(CO)_6$,[4] $Mn(CO)_5$,[5] $Mn(CO)_3(PR_3)_2$,[6] $Re(CO)_5$,[7] $[Cp'Mn(CO)_2L]^+$,[8] and $[Fe(CO)_3(PR_3)_2]^+$,[9] and associative mechanisms have also been implicated for $CpMo(CO)_3$,[10] $CpW(CO)_3$,[11] $[(py)W(CO)_5]^+$,[12] and $[(\eta^6\text{-}C_6Me_6)W(CO)_3]^+$.[13] The rapid rates of associative ligand substitution in these complexes compared to analogous 18-electron complexes have been attributed to the lower energy barrier for formation of a 19-electron transition state or intermediate from a 17-electron species, compared to the higher energy barrier for formation of a 20-electron species.

Dissociative mechanisms for CO substitution in 17-electron complexes are far less common. A dissociative mechanism was originally proposed to account for the reactivity of $Mn(CO)_5$ and, in analogy, other species such as $Co(CO)_4$ involved in radical chain processes.[14,15] Subsequent quantitative evidence for associative CO substitution in $Mn(CO)_5$ has led to speculation that CO

[†] Northwestern University.

[‡] University of California at San Diego.

[§] University of Utah.

(1) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978.

(2) Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80–89.

(3) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345–399.

(4) (a) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71–76. (b) Richmond, T. G.; Shi, Q.-Z.; Trogler, W. C.; Basolo, F. *Ibid.* **1984**, *106*, 76–80.

(5) Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700–5703.

(6) McCullen, S. B.; Walker, H. W.; Brown, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4007–4008.

(7) Fox, A.; Malito, J.; Poë, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1052–1053.

(8) (a) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771–3784. (b) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *Ibid.* **1983**, *105*, 61–73.

(9) (a) Therien, M. J.; Ni, C.-L.; Anson, F. C.; Osteryoung, J. G.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 4037–3042. (b) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 3697–3702.

(10) (a) Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 4066–4067. (b) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *Ibid.* **1983**, *105*, 6032–6037.

0002-7863/87/1509-4860$01.50/0