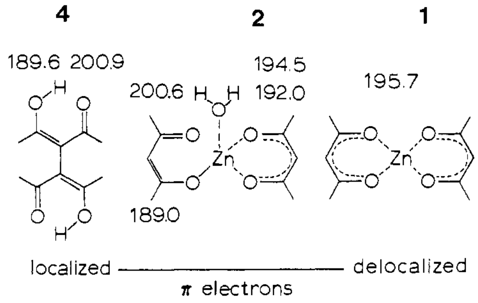

Figure 2. Schematic representations of the relations between the ^{13}C chemical shifts for the carbonyl carbon nuclei and the delocalization of the π electrons in compounds **1**, **2**, and **4**.

in the spectrum of **1** upon absorbing moisture from the air. Clearly, an additional coordination of a water molecule into the ZnO_4 structure in **1** perturbs the electronic energy levels of the oxygen atoms in the acac residues, leading to inequivalent ^{13}C chemical shifts in **2**. Thus, this inequivalence of the ^{13}C chemical shifts can be attributed to incomplete delocalization of the π electrons in the acac residues. The chemical shifts of the carbonyl carbon nuclei are, therefore, a more sensitive probe for studying delocalization of the π electrons in acac residues than the atomic coordinates from signal-crystal x-ray diffraction determinations; for in **2** the latter method predicts almost equivalent local structures for the four carbonyl groups.[5] Some lines with small intensities in the NMR spectra shown in Figure 1b,c, which cannot be assigned to either **1** or **2**, may be attributed to other modifications of the Zn-acac complex, such as **3**.

The chemical shifts of the four different carbonyl carbon nuclei in **2** can be assigned as follows. The close resemblance of the chemical shift values of 200.6 and 189.0 ppm in **2** to those of 200.9 and 189.6 ppm in 3,4-diacetyl-2,5-hexanedione (**4**)[15] lead us to conclude that those two carbon nuclei in **2** are in one acac residue in which the degree of delocalization of the π electrons is similar to that in the acac residue in **4**. This does, however, not mean that the π-electrons are completely localized in one of the two acac residues in **2**. On the contrary, in the interpretation of both the diffraction[16] and solid-state NMR[15] studies, it was postulated that delocalization of the π electrons occurs in **4**. The other two chemical shifts of similar value, namely 192.0 and 194.5 ppm, in **2** can be assigned to the other acac residue, the π electrons of which are *more* completely delocalized. Figure 2 summarizes these conclusions.

Another series of spectra (Figure 1a,e,f) show that **1** gradually transforms into **3** in vacuo; i.e., the most stable form of anhydrous Zn-acac is the trimer. There are six independent carbonyl carbon nuclei in a trimer (Figure 3), four of which are "chelating only" and two of which are "chelating and bridging". Thus, the six ^{13}C CP-MAS signals in Figure 1f can be assigned to the six *chemically inequivalent* carbonyl carbon nuclei in the molecule. Further, it is interesting to note that the CP-MAS spectrum of **3**, obtained by sublimation of **1** (Figure 1f), shows narrower lines than that of **3**, obtained by storing **1** in vacuo for 2 days (Figure 1e). The broader line width found in the latter trimeric complex may be due to crystal imperfections.

To investigate the possibility of an exchange of the four inequivalent carbonyl groups in **2** by alternation of the π bondings, two-dimensional exchange NMR experiments[17] were performed for the four ^{13}C resonances of the carbonyl carbon nuclei in **2**. However, no "cross peaks" could be observed in our experiments with mixing times up to 3 s at room temperature. This implies that the π electrons are *localized* in **2**.

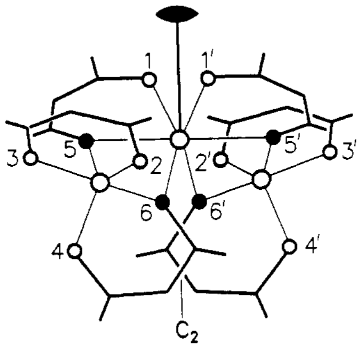

Figure 3. Schematic structure of **3**. The chelating-only oxygen atoms are denoted by the symbol ○, the chelating-bridging oxygen atoms by ●, and the zinc atoms by ◯. The thick lines represent the carbon skeleton, and the thin lines the oxygen-zinc coordination. C_2 and the solid ellipsoid indicate the twofold rotation axis within a molecule.

$Ce(acac)_2$ has been reported to exist in a white[18] and a reddish[19] modification, both of which do not contain any water molecules. A tetrahedral coordination of the carbonyl groups is therefore to be expected. CP-MAS ^{13}C NMR spectra should then help us further to substantiate or to reject our hypothesis concerning the delocalization of the π electrons in **1**. Both samples of white $Cd(acac)_2$ studied gave rise to the same spectrum; unfortunately, it was different from the one of monomeric $Zn(acac)_2$. The chemical shift values are summarized in Table I. This surprising result can be understood by recalling that the structure of the white $Cd(acac)_2$ seems to be identical with that of reddish $Cd(acac)_2$ determined by X-rays[20] and that the slight color of the reddish compound may be due to impurities, such as CdO. This structure consists of edge-sharing Cd,O-octahedra that form linear polymers. These chains contain four independent carbonyl carbon nuclei and one independent Cd nucleus. All the structural features can be explained convincingly by our observation of the four carbonyl lines in the ^{13}C spectrum, the one line in the ^{113}Cd spectrum, and its chemical shift value (−18 ppm), which is characteristic of an octahedral coordination around the Cd atom.[21]

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Solid-Propellant-Based Pure Fluorine Gas Generators

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The storage and handling of either cryogenic liquid fluorine or high-pressure gaseous fluorine frequently presents safety and logistics problems. These problems can be overcome by the use of solid-propellant fluorine gas generators. During the past 15 years numerous fluorine gas generators were developed that are based on NF_4^+ salts.[1] In these systems, a highly overoxidized

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grain, consisting mainly of an NF_4^+ salt and several percent of a fuel, such as powdered aluminum, is burned. The heat, Q, generated in the burning process dissociates the bulk of the NF_4^+ salt, as shown in (1). If the heat Q is high enough, some of the

$$NF_4MF_6 \xrightarrow{+Q} NF_3 + F_2 + MF_5 \qquad (1)$$

NF_3 is also dissociated as shown in (2). Although impressive

$$2NF_3 \xrightarrow{+Q} N_2 + 3F_2 \qquad (2)$$

fluorine yields were achieved with these generators, they suffer from the disadvantage of producing NF_3 and some N_2 as byproducts. Whereas in many cases these byproducts can be tolerated, there are certain applications that require pure F_2. Consequently, the development of solid-propellant systems capable of generating pure fluorine gas was highly desirable.

Experimental Section

Materials. BiF_5 and K_2NiF_6 (both from Ozark Mahoning Co.) were of high purity and were used without further purification. TiF_4 (Allied Chemical) was treated in a Monel cylinder for 2 days at 250 °C with F_2 at 70 atm to eliminate some impurities formed by hydrolysis during prolonged storage of the material. The syntheses of Cs_2CuF_6 and Cs_2MnF_6 have previously been described.[2] Prior to its use, CoF_3 (Ozark Mahoning Co.) was prefluorinated for 3 days with 8 atm of F_2 at 300 °C.

Apparatus and Procedure. All solid-propellant F_2 gas generation reactions were carried out in a well-passivated (with 2 atm of F_2 at 200 °C) stainless steel apparatus consisting of a 30-mL Hoke cylinder equipped with a cross fitting and a feed-through for a sheathed thermocouple that almost touched the bottom of the cylinder. A pressure transducer (Validyne DP-15) and a Hoke valve leading to a stainless steel vacuum line were connected to the two remaining sides of the cross. Weighed amounts of the transition-metal fluoride salt and the Lewis acid were thoroughly mixed in the dry-nitrogen atmosphere of a glovebox and loaded into the apparatus. The apparatus was then connected to the vacuum line, evacuated, and leak-checked. The bottom of the cylinder was rapidly heated by the hot air stream from a heat gun, and the pressure evolution and inside temperature of the reactor were followed on a strip chart recorder. The evolved fluorine was measured by standard PVT methods and analyzed for its purity by reacting it with mercury. The material balance was further cross-checked by weighing the reactor before the reaction and after removal of the evolved fluorine.

The CoF_3 decomposition experiments were carried out in either a Monel reactor with an Al_2O_3 boat as a sample container or a sapphire tube (Tyco). Pressure and temperature were monitored as described above. The reactors were heated by a fluidized-sand bath.

Results and Discussion

Generation of F_2 by Reversible Reactions. Since certain transition-metal fluorides, such as CoF_3, are known to decompose at elevated temperatures to a lower fluoride and fluorine,[3] the equilibrium (3) was examined for its potential as a fluorine gas

$$2CoF_3 \rightleftarrows 2CoF_2 + F_2 \qquad (3)$$

generator. The CoF_3 system was found to exhibit the following drawbacks: (i) relatively high temperatures (in excess of 500 °C) were required for the generation of even moderate fluorine pressures (about 268 Torr at 514 °C); (ii) long reaction times were required to reach equilibrium; (iii) on cooling of the system, the back-reaction to CoF_3 consumed most of the fluorine formed; (iv) reaction of the fluorine with the hot reactor walls was difficult to suppress; (v) the yields of fluorine were disappointingly low. These drawbacks appear to be generally true for equilibrium reactions of this type and therefore render these reversible systems unattractive for fluorine gas generator applications.

Table I. Results from Solid-Propellant Pure Fluorine Gas Generator Experiments

run no.	starting materials (amt, mmol)	amt of F_2 generated, mmol	peak pressure, Torr	F_2 yield, mol %
1	K_2NiF_6 (1.47), BiF_5 (4.51)	1.1	990	75[a]
2	Cs_2CuF_6 (2.01), BiF_5 (3.95)	0.9	836	46[a]
3	Cs_2MnF_6 (4.86), BiF_5 (14.85)	1.0	929	41[b]
4	K_2NiF_6 (6.31), TiF_4 (6.25)	0.87	810	14[a]
5	K_2NiF_6 (1.94), TiF_4 (1.94), BiF_5 (1.94)	0.88	820	45[a]

[a] Yields based on the limiting reagent and the stoichiometry $A_2MF_6 + 2BiF_5 \rightarrow 2ABiF_6 + MF_2 + F_2$. [b] Yield based on the limiting reagent and the stoichiometry $Cs_2MnF_6 + 2BiF_5 \rightarrow 2CsBiF_6 + MnF_3 + 0.5F_2$.

Generation of F_2 by Irreversible Reactions. Most of the above drawbacks of the reversible reactions can be avoided by the use of irreversible reactions. This principle has been applied by us in previous work.[1] For example, the thermal decomposition of NF_4BF_4 (eq 4) in an NF_3–F_2 gas generator is irreversible; i.e.,

$$NF_4BF_4 \rightarrow NF_3 + F_2 + BF_3 \qquad (4)$$

NF_3, F_2, and BF_3, even at elevated temperature and pressure, do not re-form NF_4BF_4.[4] This concept of irreversibility was further exploited[2,5] by replacing the BF_4^- anion in the NF_4^+ salt by anions such as NiF_6^{2-} or MnF_6^{2-}, which are themselves stable but are derived from thermodynamically unstable parent molecules. In the thermal decomposition of these $(NF_4^+)_2MF_6^{2-}$ type salts, thermodynamically unstable MF_4 molecules are formed (eq 5), which then decompose in a second irreversible step to a stable lower fluoride and F_2 (eq 6). The concept of generating a thermodynamically unstable fluoride from its stable anion, followed by its irreversible decomposition with spontaneous fluorine evolution, has recently been utilized for the purely chemical generation of elemental fluorine.[6] By use of starting materials, i.e. K_2MnF_6 and SbF_5, that can be prepared from HF, elemental fluorine was generated by the simple displacement reaction (7), followed by the irreversible decomposition of the unstable MnF_4 (8). If, in this scheme, the liquid Lewis acid SbF_5 is replaced by a solid Lewis acid of sufficient strength and suitable melting or sublimation point, a pure fluorine, solid-propellant-based gas generator is obtained, as demonstrated by eq 9 and 10, where A can be an alkali metal and M can be Ni, Cu, or Mn. The results of five typical experiments are summarized in Table I. Although no systematic effort was made to maximize the F_2 yields, the results of Table I show that the F_2 yields are generally very good. From both yield and molecular weight considerations, K_2NiF_6 appears to be the most attractive starting material. Of the two Lewis acids tested, BiF_5 (mp 151.4 °C, bp 230 °C) appears to be superior to TiF_4 (sublimation pt 283.1 °C), although on a weight basis, the considerably lighter bifunctional acid TiF_4 might be attractive, particularly as an additive to other Lewis acids as shown by run 5 of Table I.

$$(NF_4^+)_2MF_6^{2-} \rightarrow 2NF_3 + 2F_2 + [MF_4] \qquad (5)$$

$$[MF_4] \rightarrow MF_{4-x} + (x/2)F_2 \qquad (6)$$

$$K_2MnF_6 + 2SbF_5 \rightarrow 2KSbF_6 + [MnF_4] \qquad (7)$$

$$2[MnF_4] \rightarrow 2MnF_3 + F_2 \qquad (8)$$

$$A_2MF_6 + 2BiF_5 \rightarrow 2ABiF_6 + MF_{4-x} + (x/2)F_2 \qquad (9)$$

$$A_2MF_6 + TiF_4 \rightarrow A_2TiF_6 + MF_{4-x} + (x/2)F_2 \qquad (10)$$

The starting materials used in this study can be readily premixed at ambient temperature and stored safely. When the mixture is heated to about 60–70 °C, fluorine evolution starts. The fluorine evolution was measured as a function of time and temperature, and a typical curve for the K_2NiF_6–BiF_5 system is shown in Figure 1. The fluorine evolution is rapid, the gas can be generated at

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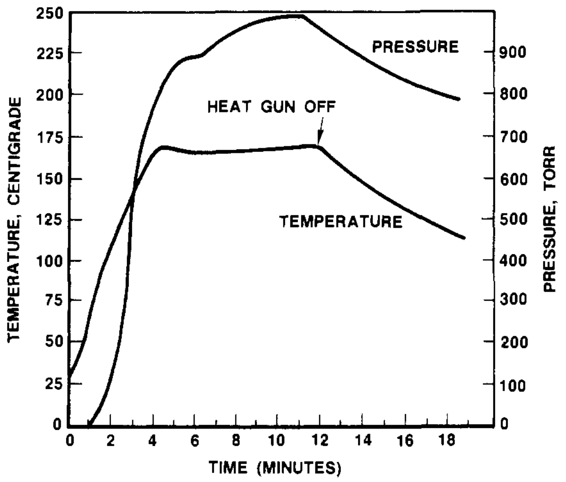

Figure 1. Pressure and temperature vs. time curves for the K_2NiF_6–BiF_5 system.

superatmospheric pressure, and there is no evidence for any reversible reactions. Furthermore, the F_2 is evolved at such moderate temperatures that reaction of the fluorine with the container walls is of no concern. The purity of the generated fluorine was shown to be in excess of 99% by its quantitative reaction with mercury.

Conclusion. Application of the same principle that was recently used for the chemical synthesis of elemental fluorine[6] to solid Lewis acids results in useful, solid-propellant-based, pure fluorine gas generators. The validity of the concept has been demonstrated for A_2MF_6 salts (A = K, Cs and M = Ni, Cu, Mn) and BiF_5 and TiF_4 as the Lewis acids. Further improvements in the attainable fluorine yields are anticipated by variation of the starting materials and Lewis acids and an optimization of the stoichiometries and reaction conditions.

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Registry No. K_2NiF_6, 17218-47-2; Cs_2CuF_6, 43070-30-0; Cs_2MnF_6, 16962-46-2; BiF_5, 7787-62-4; TiF_4, 7783-63-3; F_2, 7782-41-4.

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An Arbuzov-like Reaction in the Trimethyl Phosphite–η^2-Silaacyl Adduct (η^5-C_5Me_5)$Cl_3Ta\{\eta^2$-$OC(SiMe_3)[P(OMe)_3]\}$

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and Steven J. Geib[‡]

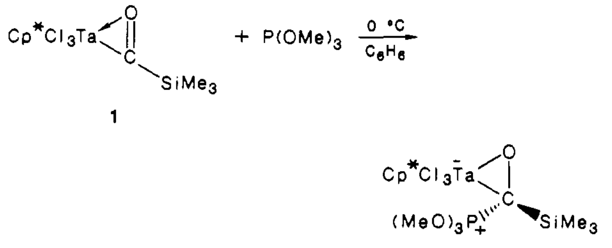
Received November 19, 1986

Our studies concerning the carbonylation chemistry of early-transition-metal silyl complexes[1] have led to the discovery of $Cp^*Cl_3Ta(\eta^2$-$COSiMe_3)$ (**1**, $Cp^* = \eta^5$-C_5Me_5), a reactive η^2-silaacyl derivative.[1b,c] Recently we have found that **1** readily reacts with Lewis bases to form complexes of the type $Cp^*Cl_3Ta[\eta^2$-$OC(L)SiMe_3]$, in which the Lewis donor binds to the η^2-silaacyl carbon atom.[1c] Here we report the preparation and characterization of the trimethyl phosphite adduct $Cp^*Cl_3Ta\{\eta^2$-$OC(SiMe_3)[P(OMe)_3]\}$ (**2**) and its spontaneous Arbuzov-like dealkylation to MeCl and $Cp^*Cl_2Ta[\eta^4$-$OC(SiMe_3)P(OMe)_2O]$ (**6**). The latter compound, which has been characterized by X-ray crystallography, contains an unusual η^4-phosphonatosilaacyl(2–) ligand.

The dealkylation of trialkyl phosphites is promoted by a number of transition-metal complexes.[2] Dealkylation is usually preceded by coordination of phosphite to the transition metal. In a few cases this process appears to follow attack of the phosphite onto an electrophilic ligand bound to the metal,[3] as in the reaction reported here.

Results and Discussion

Silaacyl adduct $Cp^*Cl_3Ta\{\eta^2$-$OC[P(OMe)_3](SiMe_3)\}$ (**2**) is obtained upon addition of trimethyl phosphite to a benzene solution of the silaacyl $Cp^*Cl_3Ta(\eta^2$-$COSiMe_3)$[1c] (**1**, eq 1). A more



1 **2** (1)

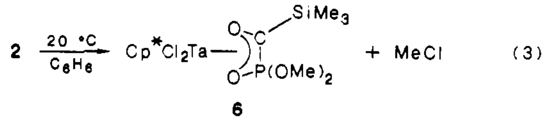
convenient method for the preparation of **2** involves pressurizing a pentane solution of $Cp^*Cl_3TaSiMe_3$[4] (**3**) and trimethyl phosphite (1:1) with 10–100 psi of carbon monoxide (eq 2). With a rapid,

$$\underset{\mathbf{3}}{Cp^*Cl_3TaSiMe_3} + P(OMe)_3 \xrightarrow[0\ °C,\ pentane]{CO} \mathbf{2} \qquad (2)$$

low-temperature workup (see Experimental Section), dark red crystals of **2** can be isolated in high yield.

Spectroscopic data indicate that **2** is structurally analogous to other silaacyl adducts, $Cp^*Cl_3Ta[\eta^2$-$OC(L)SiMe_3]$[1c,e] (**4**, L = pyridine; **5**, L = triethylphosphine). X-ray structures of the latter two compounds show that coordination of the Lewis base to the electron-deficient η^2-silaacyl results in reduction to an sp^3-hybridized carbon atom. Formation of these adducts is accompanied by a large upfield ^{13}C NMR chemical shift for the silaacyl carbon (δ 351) to δ 117.1 for **4**, δ 78.0 for **5**, and δ 103.1 for **2**.

Benzene-d_6 solutions of **2** change color from maroon to orange within a few minutes at 20 °C. Examination of ^1H NMR spectra of these solutions reveals shifts in the resonances for the C_5Me_5 (from δ 2.18 to 2.11) and $SiMe_3$ (from δ 0.15 to 0.49) groups and replacement of the doublet for the $P(OMe)_3$ group in **2** (δ 3.52, J_{PH} = 12.6 Hz) by a pair of doublets (δ 3.16, 3 H, J_{PH} = 11.1 Hz; δ 3.56, 3 H, J_{PH} = 10.8 Hz) and a singlet (δ 2.30, 3 H). The latter signal is due to MeCl, as determined by NMR and GC comparisons to an authentic sample. The remaining resonances are assigned to the new product **6**, isolated as orange crystals from a preparative-scale reaction (eq 3). Monitoring the reaction by ^{31}P NMR reveals gradual replacement of a singlet at δ 60.7 due to **2** by a peak at δ 36.6 for the Arbuzov reaction product **6**.



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This reaction also occurs quantitatively in the solid state. Though slow at 22 °C under nitrogen, the reaction occurs rapidly

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