whereas methanol (93%) is the major organic product obtained from **2**, followed by formaldehyde (7%), **3** (96%), and **4** (4%).[13] Scheme I outlines a mechanistic interpretation of these results. Both **1** and **2** undergo PMe_3 dissociation followed by deinsertion leading to intermediate hydroxymethyl hydride **5** and methoxy hydride **6**. These intermediates then undergo competing reductive elimination leading to methanol and **3** and β-hydride elminination forming formaldehyde and $H_2R(PMe_3)_2COCl$. The latter, which was not observed, undoubtedly reacts with PMe_3 to yield the isolated complex **4**, but it can also reductively eliminate hydrogen to form **3**. Indeed, when **4** is treated with 1 atm of CO at 25 °C in acetone, immediate H_2 elimination takes place to yield **3**. Since two modes for formation of **3** are operative, the relative importance of processes a and b as well as c and d is determined by the ratio of methanol to formaldehyde rather than **3** to **4**. Both the reductive elimination and the β-elimination processes are irreversible: **3** does not react with methanol and **4** does not react with formaldehyde (in the presence or absence of CO).

The disappearance of **1** and **2** in dioxane-d_8 at 70 °C was followed by ^1H NMR. In both cases, first-order dependence was observed for at least 3 half-lives. Significantly, almost the same rate constants are observed (Figure 1): for **1**, $k_{obsd} = 4.74 \times 10^{-4}$ s^{-1}, and for **2**, $k_{obsd} = 4.85 \times 10^{-4}$ s^{-1}. This is most likely a result of both processes having the same rate-determining step. Various elimination modes of octahedral *cis*-acylrhodium hydride–PMe_3 complexes[2b,14] as well as reductive elimination from *cis*-alkylrhodium hydride–PMe_3 complexes[2b,15] were shown to proceed via an unsaturated five-coordinate intermediate formed by a rate-determining PMe_3 dissociation from the position trans to the hydride. This is also most likely the case for the hydroxyacetyl complex **1** and thus also for **2**. Although careful rate measurements in the presence of added PMe_3 have not been carried out yet, retardation of the decomposition rate of both **1** and **2** upon addition of PMe_3 has been observed. It is thus possible to conclude that PMe_3 dissociation from **1** and **2**, required to allow for the migration process, is rate-determining. This tends to exclude a mechanism for methanol formation from **2** by deprotonation involving a methoxide anion generated from the carbomethoxy ligand. Additional support for this exclusion is obtained by partial decomposition of **2** in the presence of CD_3OD. At 50% decomposition, no incorporation of deuterium into **2** was observed. It is noteworthy that these results indicate, by microscopic reversibility, a concerted migratory mechanism for CO "insertion" into Rh–OCH_3, in agreement with results obtained for Pt(dppe)(OCH_3)CH_3.[16] Carbonylation of $Ir(PPh_3)_2(CO)(OR)$, however, is thought to proceed via an ionic mechanism.[17]

Regardless of the exact mechanism by which the intermediates **3** and **4** eliminate methanol and formaldehyde, we conclude that in our system methanol formation via an alkoxy hydride intermediate is preferred over methanol elimination from an hydroxymethyl hydride complex, which favors β-hydride elimination to yield formaldehyde.[18,19] This conclusion is relevant not only to CO hydrogenation mechanism but also to the mechanism of aldehyde hydrogenation[20,21] and formaldehyde hydroformylation[22] favoring alcohol formation by O–H rather than C–H reductive elimination.

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(18) It is instructive to consider the thermodynamics of these reactions. Since the order of thermodyanic stability is $CH_2O + H_2 < CH_3OH$ and apparently $H_2Rh(CO)(PMe_3)_2Cl < Rh(CO)(PMe_3)_2Cl{+}H_2$ (since $H_2Rh(CO)(PMe_3)_2Cl$ apparently undergoes spontaneous reductive elimination of hydrogen), it follows that formation of $H_2Rh(CO)(PMe_3)_2Cl + CH_2O$ is thermodynamically less favored than $Rh(CO)(PMe_3)_2Cl + CH_3OH$. Thus, prevalence of the β-elimination process for **5** is probably kinetic in nature.

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An Unusual Methoxy Group Migration: Synthesis of *cis*-CH_3OSF_4NCO and *cis*-$CH_3OSF_4NHC(O)OCH_3$

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In 1977 we reported the synthesis of $SF_4{=}NC(O)N(C_2H_5)_2$ from the reaction of pentafluorosulfanyl isocyanate with (diethylamino)trimethylsilane.[2] At that time the only other compound known to contain the $SF_4{=}N$ moiety was $SF_4{=}NCF_3$.[3] Since then several other $SF_4{=}NR$ derivatives have been prepared, where R = CH_3,[4] C_2H_5,[5] F,[6] C_2F_5,[7] and SF_5.[8] Shreeve and co-workers have also described a series of related $SF_3X{=}NR_f$[9] compounds. Recently, we have obtained additional spectroscopic data on $SF_4{=}NC(O)N(C_2H_5)_2$ and have prepared its dimethylamido analogue as well as the products $R_2NSF_3{=}NC(O)NR_2$ (R = CH_3, C_2H_5) which result from the addition of a second equivalent of the nucleophile.[10]

$$SF_5NCO + (C_2H_5)_2NSi(CH_3)_3 \rightarrow SF_4{=}NC(O)N(C_2H_5)_2 + (CH_3)_3SiF \quad (1)$$

In an attempt to synthesize further compounds containing the $SF_4{=}N$ moiety, we carried out the reaction of SF_5NCO with trimethylmethoxysilane. Initially, stoichiometric amounts of reactants were used, and since the isocyanate moiety did not disappear as expected, the reaction mixture was heated to 60 °C. The unexpected isolation of *cis*-methoxytetrafluorosulfanyl iso-

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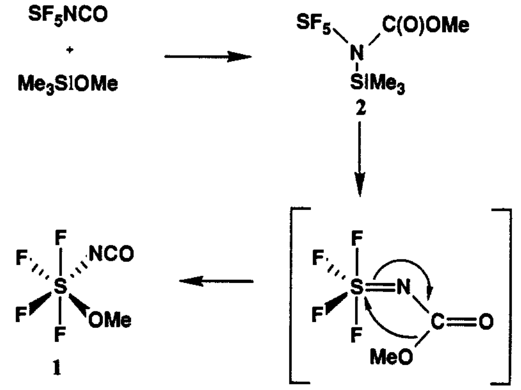
cyanate (**1**) upon reaction workup explained the persistance of the NCO functionality. When the reaction was carried out at room temperature, we were able to isolate the reaction intermediate $SF_5N[Si(CH_3)_3]C(O)OCH_3$ (**2**) thus eliminating the possibility of direct attack by the nucleophile at the sulfur atom in SF_5NCO. The formation of **1** must result from an unusual methoxy group migration which follows the loss of trimethylfluorosilane from **2**. The rate of this rearrangement is deemed to be rapid with respect to the loss of trimethylfluorosilane because we observe no evidence for the expected five-coordinate sulfur(VI) product $SF_4{=}NC(O)OCH_3$. The fact that only the cis isomer of **1** is observed strongly suggests that the methoxy group migration is intramolecular. Further support of the proposed reaction pathway (eq 2) is found in the reaction of SF_5X (X = Cl, Br) with (dimethylamino)trimethylsilane, where direct attack of the nucleophile at the sulfur atom gives exclusively trans products (eq 3).[11]



(2)

$$SF_5X + (CH_3)_2NSi(CH_3)_3 \rightarrow trans\text{-}(CH_3)_2NSF_4X + (CH_3)_3SiF \quad (3)$$

Of the few known examples of methoxy group migrations in intramolecular rearrangements,[18] we failed to find even one example involving a migration from carbon to sulfur. The unimolecular rearrangement described herein is reminiscent of the Curtius rearrangement.[18a] In fact, the first evidence for a Curtius-type rearrangement involving a pentacoordinate (phosphorus) atom was only recently reported.[19] One postulates that the corresponding molecular rearrangement is not observed in $SF_4{=}NC(O)N(C_2H_5)_2$ because of additional resonance stabilization by the carbonyl group, the greater steric bulk of NEt_2 vs. OMe, and a weaker nitrogen–sulfur bond strength.

In a typical reaction, SF_5NCO (15.0 mmol) and $(CH_3)_3SiOCH_3$ (13.0 mmol) were allowed to react in an FEP tube reactor for $3^1/_2$ weeks at room temperature. Repeated trap-to-trap distillation of the volatile products gave *cis*-CH_3OSF_4NCO (1.8 g, 9.9 mmol) in 76% yield in the −78 °C trap and $(CH_3)_3SiF$ and excess SF_5NCO collected in the −196 °C trap. If the reaction is allowed to proceed for only 4 days, $SF_5N[Si(CH_3)_3]C(O)OCH_3$ can be isolated in 88% yield. Samples of **2** were monitored by NMR spectroscopy and found to decompose cleanly to **1** and $(CH_3)_3SiF$ over a period of several weeks. Heating the initial reaction mixture to 60–80 °C greatly shortens the reaction time; however, this causes both lower yield and product purity.

cis-Methoxytetrafluorosulfanyl isocyanate is a colorless liquid [estimated bp 98 °C, $\ln P(\text{torr}) = 17.353 - (3977.6/T)$, $\Delta H_{vap} = 7.90$ kcal/mol, $\Delta S_{vap} = 21.3$ eu] which freezes to a glass below −130 °C. The infrared spectrum of the gas[12] shows intense bands attributable to the NCO and OCH_3 functionalities as well as the sulfur(VI)–fluorine bonds. The ^{19}F NMR spectrum gives the expected AB_2C pattern[13] with δ(A) 106.0, δ(B) 84.8, and δ(C) 61.3, and $J_{AB} = 133.1$, $J_{AC} = 156.4$, and $J_{BC} = 137.6$ Hz.[14] As no long-range coupling is observed between the methoxy protons and the sulfur fluorines, it becomes impossible to assign the B and C fluorines with any degree of certainty. The ^1H and ^{13}C NMR spectra[12] are consistent with the assigned structure. The electron impact mass spectrum[12] failed to exhibit a molecular ion, but the observed fragmentation pattern supports **1**'s identity. Anal. $(C_2H_3NO_2SF_4)$ C, H, N.

The reaction intermediate **2** is a colorless liquid (vp < 0.1 torr at 0 °C) which melts at 10 °C. Important infrared absorptions[15] occur at 1650 cm^{-1} for the carbonyl group and at 845 and 593 cm^{-1} for the SF_5 group. The ^{19}F NMR is a typical AB_4 pattern with δ(A) 87.8, δ(B) 72.2, and $J_{AB} = 156.1$ Hz; again the ^1H and ^{13}C NMR spectra[15] are consistent with the proposed structure. The mass spectrum[15] displays both the molecular ion and the expected fragmentation pattern. Anal. $(C_5H_{12}NO_2SSiF_5)$ C, H, N.

The identity of **1** is further confirmed by the synthesis of the methoxy urethane derivative *cis*-$CH_3OSF_4NHC(O)OCH_3$ (**3**). The reaction of **1** (3.0 mmol) with excess methanol gives **3** as white, sublimable crystals (mp 56–58 °C) in quantitative yield (0.64 g) (eq 4). Spectroscopically **3**[16] parallels $SF_5NHC(O)OCH_3$[17] with the notable exception of the AB_2C splitting pattern observed in the ^{19}F NMR (δ(A) 85.9, δ(B) 64.9, and δ(C) 62.1 and $J_{AB} = 120.1$, $J_{AC} = 148.1$, and $J_{BC} = 133.3$ Hz). Anal. $(C_3H_7NO_3SF_4)$ H, N. C: calcd 16.90, found 16.35.

$$cis\text{-}CH_3OSF_4NCO + CH_3OH \rightarrow cis\text{-}CH_3OSF_4NHC(O)OCH_3 \quad (4)$$

Recently we have found that the rearrangement described herein is not limited to the methoxy group but takes place with the ethoxy and *n*-propoxy groups as well. A more detailed mechanistic study including reactions utilizing bulkier alkoxy groups as well as silylated sulfur and carbon nucleophiles is under active investigation and will be reported separately.[10]

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Supplementary Material Available: Experimental and computer-simulated ^{19}F NMR spectra (3 pages). Ordering information is given on any current masthead page.

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(12) **1**: IR (gas) 2970 (ss), 2270 (ss), 1450 (wb), 1370 (m), 1290 (s), 1060 (sb), 910 (s) 895–810 (vsb), 600 (m) cm^{-1}; ^1H NMR 3.77 (s, OCH_3) ppm; $^{13}C\{H\}$ NMR (CCl_3F) 130.2 (br m, NCO), 58.6 (m, OCH_3) ppm; mass spectrum (70 eV), *m/z* 150 (SF_4NCO^+, 18%), 147 (OSF_3NCO^+, 41%), 139 (25%), 128 (OSF_2NCO^+, 18%), 105 (25%) , 89 (SF_3^+, 100%), 70 (SF_2^+, 12%), 67 (SOF^+, 12%), 51 (SF^+, 11%).

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(15) **2**: IR (film) 2982 (m), 1650 (vs), 1461 (s), 1340 (s), 1267 (s), 1001 (m), 845 (vs br), 768 (vs), 680 (m), 650 (m), 624 (m), 593 (m) cm^{-1}; ^1H NMR (CCl_3F) 3.49 (s, 3 H, OCH_3), 0.08 (s, 9 H, $SiMe_3$) ppm; $^{13}C\{H\}$ NMR (CCl_3) 152.9 (CO), 55.3 (OCH_3), −1.8 ($SiMe_3$) ppm; mass spectrum (70 eV) major, *m/z* 273 (M^+, 3%), 254 ($[M - F]^+$, 3%), 150 (32%), 127 (SF_5^+, 65%), 118 (35%), 104 (15%), 89 (SF_3^+, 100%), 77 (47%), 73 (53%), 59 (75%), 45 (30%), 44 (20%), 43 (24%).

(16) **3**: IR (mull) 3290 (sb), 2990 (m), 2970 (m), 1735 (vs br), 1505 (mb), 1465 (mb), 1230 (vsb), 1025 (sb), 880 (s), 830 (vs br), 725 (s), 610 (w), 590 (w) cm^{-1}; ^1H NMR (CH_2Cl_2) 7.78 (br s, 1 H, NH), 4.00 (s, 3 H), 3.70 (s, 3 H); mass spectrum (70 eV) major, *m/z* 213 (M^+, <1%), 194 ($[M - F]^+$, <1%), 182 ($[M\text{-}OCH_3]^+$, 6%), 162 ($CH_3OSF_3NCO^+$, 10%), 139 ($CH_3OSF_4^+$, 100%), 128 (8%), 105 (OSF_3^+, 100%), 104 (33%), 89 (64%), 74 (22%), 70 (12%), 67 (14%), 59 (90%), 58 (16%), 46 (14%), 45 (30%), 44 (41%).

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