SYNTHESIS AND PROPERTIES OF TRIFLUOROSILYL

COBALT TETRACARBONYL

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(Received 25 November 1969)

It was found by Chalk and Harrod (2) that compounds having the general formula $R_3SiCo(CO)_4$ (R = organic groups, Cl) could be synthesized by the interaction of a substituted silane, R_3SiH , with $Co_2(CO)_8$; Aylett and Campbell (3) have reported the synthesis of $H_3SiCo(CO)_4$ from H_3SiI and the $[Co(CO)_4]$ anion. The present investigation was carried out in order to ascertain whether $F_3SiCo(CO)_4$ could be synthesized and, if so, whether it would be sufficiently thermally stable to study at room and elevated temperatures. This compound is of particular interest since it is the silicon analog of $F_3CCo(CO)_4$, the simplest organic cobalt tetracarbonyl stable at room temperature (4, 5).

It was found that $F_3SiCo(CO)_4$ could be formed readily in 84% yield based upon the amount of $Co_2(CO)_8$ employed, by the reaction of F_3SiH at an ideal gas pressure of 40 atmospheres at room temperature in the absence of solvent during 24 hours at room temperature, viz.,

$$2F_3SiH + Co_2(CO)_8 \longrightarrow 2F_3SiCo(CO)_4 + H_2$$
 (1)

Reaction also occurred at a measurable but slower rate at lower pressures. This compound could also be formed by the reaction of F_3SiH with HCo(CO)₄ at an ideal gas pressure of 2 atmospheres during one hour at room temperature, according to the equation

$$F_3SiH + HCo(CO)_4 \longrightarrow F_3SiCo(CO)_4 + H_2$$
 (2)

Trifluorosilyl cobalt tetracarbonyl is sufficiently volatile to be handled easily in a vacuum system (2.7 mm vapor pressure at 0°). It readily forms large (approx. 1 mm) transparent amber crystals by sublimation and it melts at 19.4° with some decomposition. No decomposition is observed TRIFLUOROSILYL COBALT TETRACARBONYL

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in the solid state on warming to the melting point or in the gas phase at room temperature for extended periods of time. At room temperature a small sample of liquid $F_3SiCo(CO)_4$ decomposed, in vacuo, during 18 hours to SiF₄, CO, and a material of much smaller volatility having a gross composition corresponding to a mixture of Co₄(CO)₁₂, Co₂(CO)₈, and silicon in the relative molar proportions 1.0: 2.0: 2.0, respectively, viz.

$${}^{8}F_{3}SiCo(CO)_{4} \rightarrow Co_{4}(CO)_{12} + 2Co_{2}(CO)_{8} + 2Si + 6SiF_{4} + 4CO$$
 (3)

Fifty-six percent of a large sample of liquid $F_3SiCo(CO)_4$ was recovered unchanged after six hours at 65°. After two hours at 138° a sample had decomposed according to the equation

$$4F_{3}SiCo(CO)_{4} \longrightarrow 3SiF_{4} + 16CO + [4Co + Si]$$
(4)

and all of the fluorine was liberated as SiF_{4} . Decomposition of liquid $F_{3}SiCo(CO)_{4}$ appears to be promoted by glass surfaces (or by material absorbed on the glass), since the thermal stability was reduced when small quantities of liquid compound were held in a relatively large glass container.

A reaction occurs between $F_3SiCo(CO)_4$ and $HgCl_2$ at 60° during three hours according to the equation

$$2F_{3}SiCo(CO)_{4} + HgCl_{2} \longrightarrow 2F_{3}SiCl + Hg[Co(CO)_{4}]_{2}$$
(5)

to give 90% yields of F_3SiCl based on the $F_3SiCo(CO)_4$ consumed. No reaction was observed between $F_3SiCo(CO)_4$ and HgI_2 under similar conditions, although considerable thermal decomposition of the $F_3SiCo(CO)_4$ occurred. The Si-Co bond was cleaved at room temperature by water with the formation of HCo(CO)₄ and a white solid, presumably SiO_2 . No reaction was observed between $F_3SiCo(CO)_4$ and PF₃ at ideal gas pressures up to 40 atmospheres at room temperature.

The ¹⁹F (6), ²⁹Si (6), mass (7), and infrared [CO stretching region only] (8) spectra have been reported previously. The two strong bands in the Si-F stretching region at 940 cm⁻¹ and 825 cm⁻¹ are assigned to the E and A₁ modes, respectively. The weighted average $(2E + A_1)/3$, 902 cm⁻¹, is approximately 50 cm⁻¹ less than this weighted average in species of the type F₃SiX (where X = F, H, H₃C, (H₃C)₃SiO, (H₃C)₂N, etc.)(9). A similar, although somewhat greater, reduction in C-F stretching

frequencies in perfluoroalkyl transition metal carbonyl derivatives has been interpreted in terms of partial $(d \rightarrow \sigma^*)\pi$ double bond character in the C-metal bond (10). It has been suggested previously that there may be some $(d \rightarrow d)\pi$ double bond character in the Si-Co bond in $F_3SiCo(CO)_4$ (8). The Si-F stretching frequency data reported here suggests that there may also be some $(d \rightarrow \sigma^*)\pi$ double bond character involving an interaction between filled cobalt 3d orbitals with σ^* orbitals of appropriate symmetry on the F_3Si group.

<u>Acknowledgement:</u> This work was sponsored by AFOSR(SRC)-OAR, USAF, Contract No. AF49(639)-1519.

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