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## THE FLUOROSULFATE ION ACCEPTOR ABILITY OF SELECTED TRANSITION METAL FLUOROSULFATES

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The acceptor ability of transition metal fluorosulfates towards the  $\text{SO}_3\text{F}^-$  ion is restricted almost entirely to binary fluorosulfates with the metal from the 4d or the 5d block. Two general manifestations of acceptor behavior are found: (i) The formation of complexes containing the anion  $[\text{M}(\text{SO}_3\text{F})_n]^{m-}$  and (ii) acidic behavior of  $\text{M}(\text{SO}_3\text{F})_n$  in fluorosulfuric acid. The availability of a general, convenient synthetic route to complexes with  $[\text{M}(\text{SO}_3\text{F})_n]^{m-}$  ions has afforded a large number of examples generally containing the  $[\text{M}(\text{SO}_3\text{F})_6]^{m-}$  ion. However acidic behavior is restricted to very few examples, where  $\text{M} = \text{Au}$  or  $\text{Pt}$ , for two main reasons: (i) The unavailability of suitable binary fluorosulfate with  $\text{M}$  in a sufficiently high oxidation state, or (ii) their lack of solubility in  $\text{HSO}_3\text{F}$ . The discussion will center around some unusual complexes and some acidity measurements supported by sample calculations.

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## SYNTHESIS OF TRANSITION METAL ALKYL AND $\sigma$ -BONDED METAL COMPOUNDS BY THE COCONDENSATION OF METAL VAPOR AND FREE RADICALS: A GENERAL SYNTHETIC TECHNIQUE

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The study of  $\sigma$ -bonded metal compounds has received much attention in the past several years. A problem which has hindered this study has been the unsuccessful preparation of some metal alkyls. Reaction conditions are often such that a slightly stable metal alkyl compound is decomposed by the reaction conditions or the reactants themselves. An idea which shows promise for such syntheses is the cocondensation of metal vapor with radical species on cryogenic surfaces:



Using this technique, novel electron deficient metal alkyls of marginal thermal stability such as  $\text{Cd}(\text{CF}_3)_2$ ,  $\text{Pd}(\text{CF}_3)_2$ ,  $\text{Ni}(\text{CF}_3)_2$ ,  $\text{Co}(\text{SiF}_3)_2$ ,  $\text{Pd}(\text{SiF}_3)_2$ , and  $\text{Ni}(\text{SiF}_3)_2$  have been prepared. Complexation of these unstable compounds with phosphine or with arenes gives stable, albeit reactive species such as  $\text{Ni}(\text{CF}_3)_2(\text{PMe}_3)_2$ ,  $\text{Pd}(\text{CF}_3)_2(\text{PMe}_3)_2$ ,  $(\eta^6\text{-toluene})\text{Ni}(\text{SiF}_3)_2$ , and  $(\eta^6\text{-mesitylene})\text{Co}(\text{SiF}_3)_2$ . The radicals, such as  $\cdot\text{CF}_3$  and  $\cdot\text{SiF}_3$  are produced in a low temperature glow discharge of a symmetrical gas having a weak central bond (i.e.,  $\text{C}_2\text{F}_6$  and  $\text{Si}_2\text{F}_6$ ). We have found that many radicals can be cleanly generated in this manner such as  $\cdot\text{CH}_3$ ,  $\cdot\text{NF}_2$ ,  $\cdot\text{PF}_2$ ,  $\cdot\text{SH}_3$ ,  $\cdot\text{SCF}_3$ ,  $\cdot\text{OCF}_3$ , and  $\cdot\text{C}(\text{CF}_3)_3$ . Characterization of the products and future applications of this technique will be discussed.