

Preliminary communication

Synthesis of fluoro-Group IV metal-organotransition metal compounds. Novel tetrafluoroborate fluorination

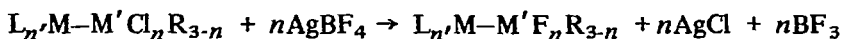
TOBIN J. MARKS and AFIF M. SEYAM★

Department of Chemistry, Northwestern University, Evanston, Ill. 60201 (U.S.A.)

(Received July 9th, 1971)

That fluorocarbon organometallics¹ and Group IV metal-transition metal compounds² exhibit considerably enhanced thermal stability over their alkyl and aryl analogs suggested to us that fluoro-silicon, -germanium and -tin organotransition metal molecules might possess a variety of interesting properties³. At present, only a few trifluorosilyl compounds have been characterized⁴⁻⁶ and these were synthesized by difficult and inefficient methods. No effective synthetic route of any generality has been developed. We wish to communicate such a route for the convenient synthesis of a number of fluoro-Group IV metal-transition metal molecules and also to report the surprising observation that silver tetrafluoroborate can be a highly effective fluorinating agent in both coordinating (*e.g.* acetone, tetrahydrofuran) and non-coordinating (*e.g.* benzene) solvents. The latter result is of significance in its own right since the tetrafluoroborate anion enjoys widespread use in organometallic chemistry as what is generally regarded to be an "innocent" counterion.

The reaction of readily accessible² chloro-Group IV metal-organotransition metal compounds with stoichiometric quantities of silver tetrafluoroborate dissolved in aromatic or coordinating solvents results in rapid, quantitative precipitation of silver chloride. The mixture can then be filtered and in most cases, the corresponding fluoro compound can be easily isolated from the filtrate in high yield by unexceptional techniques. Tin compounds sometimes yield stable, covalent tetrafluoroborates which cannot always be converted to the fluorides; a similar situation exists for $(\text{CH}_3)_2\text{SnCl}_2$ ⁷, and we will report more detailed results at a later date. The generalized reaction is:



(M = transition metal, M' = Si, Ge, Sn)

As an example, $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{GeCl}_3$ reacts with three equivalents of AgBF_4 in acetone (15 min) to give pale yellow crystals of $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{GeF}_3$ in 80% yield after recrystallization from acetone/hexane and sublimation. Table 1 presents examples of fluorinated compounds which can be synthesized in similarly high yields. It can also

★UNESCO Fellow, on leave from the University of Jordan

TABLE 1

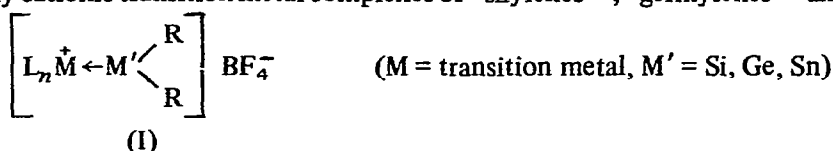
INFRARED SPECTRA IN THE C—O STRETCHING REGION FOR CORRESPONDING PAIRS OF FLUORO- AND CHLORO-GROUP IV METAL-TRANSITION METAL COMPOUNDS ^a

Compound	X = F	X = Cl
(C ₅ H ₅)Mo(CO) ₃ GeX ₃ ^b	2052s,1987vs,1976vs	2047s,1985vs,1975vs
(C ₅ H ₅)Mo(CO) ₃ Ge(C ₆ H ₅) ₂ X ^b	2019s,1958s,1929s	2016s,1960s,1933s
(OC) ₅ MnGe(C ₆ H ₅) ₂ X ^b	2112s,2052m,2027vs,2020vs	2105s,2045m,2023vs,2011vs
(C ₅ H ₅)Fe(CO) ₂ SiX ₃ ^b	2033s,1990vs	2034s,1995vs
(OC) ₄ CoGe(C ₆ H ₅) ₂ X ^b	2102s,2044s,2024vs,2012vs	2109s,2051s,2031vs,2019vs
(OC) ₄ CoGeX ₃ ^b	2119s,2059m(sh),2051vs	2116s,2062s,2044vs
(OC) ₄ CoSiX ₃ ^c	2128s,2073s,2049vs	2125s,2071s,2049vs

^a In cm⁻¹; m = medium; v = very; s = strong; (sh) = shoulder. ^b This work. Spectra were recorded on a Beckman IR9 spectrophotometer in dilute cyclohexane or benzene solutions. Corresponding pairs of compounds were recorded in the same solvent, and frequencies are considered accurate to ± 2 cm⁻¹. All new compounds have satisfactory analytical data. ^c Gas phase spectra from reference 6.

be seen from comparison of C—O stretching frequencies that chloro and fluoro substituents have nearly identical electronic effects on the transition metal. Initial qualitative experiments indicate that fluorine substitution does not markedly alter the thermal stability of most of the complexes.

An intriguing possibility is that the reactions under discussion involve what are formally cationic transition metal complexes of "silylenes"⁸, "germylenes"⁸ and "stannylenes"⁸ (I).



Mechanistic studies are in progress to resolve this question; the results presented here imply that species such as (I) will probably not be isolable. In contrast, analogous carbene complexes have been isolated⁹ and are stable with respect to fluorination. An approximate thermodynamic cycle indicates that the stability of the M—M'—F functionality is the major driving force for fluorination. Hence, the coordinated divalent Group IV species is expected to be a strong Lewis acid (especially with respect to hard bases such as fluoride). We have observed similar fluorination reactions with silver hexafluorophosphate, and the full scope of this reaction and related ones is under investigation.

ACKNOWLEDGEMENTS

We thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank Ethyl Corp., W.R. Grace, and American Metal Climax, Inc. for generous gifts of chemicals.

REFERENCES

- 1 P.M. Treichel and F.G.A. Stone, *Advan. Organometal. Chem.*, 1 (1964) 143.
- 2 J.F. Young, *Advan. Inorg. Chem. Radiochem.*, 11 (1968) 92.
- 3 R.S. Nyholm, *Quart. Rev.*, 24 (1970) 1.
- 4 R.R. Schrieke and B.O. West, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 141.
- 5 S.K. Gondal, A.G. MacDiarmid, F.E. Saalfeld and M.V. McDowell, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 351.
- 6 A.P. Hagen and A.G. MacDiarmid, *Inorg. Chem.*, 6 (1967) 686.
- 7 H.C. Clark and R. Goel, *J. Organometal. Chem.*, 7 (1967) 263.
- 8 (a) P.L. Timms, *Prep. Inorg. React.*, 4 (1968) 59; (b) W.H. Atwell and R.D. Weyenberg, *Angew. Chem.*, 81 (1969) 485; *Angew. Chem. Int. Ed. Engl.*, 8 (1969) 469; (c) G. Schmid and H.J. Balk, *Chem. Ber.*, 103 (1970) 2240.
- 9 M.L.H. Green, L.C. Mitchard and M.G. Swanwick, *J. Chem. Soc.*, A (1971) 794.

J. Organometal. Chem., 31 (1971) C62-C64