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Organometallic fluorides

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The compound Cp^*TiF_3 ($Cp^* = C_5Me_5$) has been prepared previously from the corresponding chloride by reaction with the fluorinating agent AsF_3. However, attempts to isolate the homologous zirconium and hafnium compounds via this method were unsuccessful. We have now found that a suitable fluorinating agent is Me_3SnF. This compound reacts in stoichiometric amount with the corresponding chlorides to yield Group 4 organometallic fluorides in nearly quantitative yield.

$$Cp'MCl_3 + 3Me_3SnF \longrightarrow Cp'MF_3 + 3Me_3SnCl$$

($M = Ti, Zr, Hf$; $Cp' = C_5Me_5, C_5H_4Me, C_5Me_4Et, C_5H_5$)

X-Ray structural analysis of Cp^*ZrF_3 shows that the compound exists as a tetramer in the solid state, with the structure consisting of a symmetric arrangement of four Cp^*ZrF_3 molecules. The fluorine atoms connect the zirconium atoms through alternating single and triple bridging configurations. In addition, one fluorine atom is terminally bonded to each zirconium atom. Reaction of the compound with $AlMe_3$ yields the dimer $[Cp^*ZrMeF_3AlMe_2]_2$ and the Al–Zr cluster $[(Cp^*Zr)_3Al_6Me_8(CH)_5(CH_2)_2]$. Both products are interesting catalysts in the polymerization of olefins.

Reduction of Cp^*TiF_3 with sodium, magnesium, calcium and aluminium either yields organometallic clusters containing the molecular solids NaF, MgF_2 and CaF_2, or Werner-type coordination compounds of composition $(Cp^*_2TiF_2)_3Al$.

Reaction of the organotitanium(III) chlorides $(Cp_2TiCl)_2$, Cp^*_2TiCl and $[(C_5H_4Me)_2TiCl]_2$ with Me_3SnF gave the corresponding fluorides $(Cp_2TiF)_2$, Cp^*_2TiF and $[(C_5H_4Me)_2TiF]_2$, respectively, as new compounds. An alternative method for the preparation of $(Cp_2TiF)_2$ and $[(C_5H_4Me)_2TiF]_2$ involves the reduction of the titanium(IV) compounds using sodium amalgam.

The structures of the various compounds have been determined by single crystal X-ray diffraction.

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