



## Review

## A survey of titanium fluoride complexes, their preparation, reactivity, and applications

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**Abbreviations:** Cp, η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>; Cp\*, η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>; Ar, aromatic group; Me, methyl; Et, ethyl; Et<sub>2</sub>O, diethyl ether; <sup>n</sup>Bu, butyl; <sup>t</sup>Bu, tert-butyl; <sup>n</sup>Pr, propyl; <sup>i</sup>Pr, iso-propyl; Ph, phenyl; Cy, cyclohexyl; Py, pyridine; THF, tetrahydrofuran; DMF, dimethylformamide; DEF, diethylformamide; DME, dimethoxyethane; NacNac, β-diketiminato ligand ArNC(R)CHC(R)NAr; L, ligand; R, alkyl group; IR, infrared; NMR, nuclear magnetic resonance; UV–VIS, ultraviolet–visible spectroscopy; X-ray, X-ray diffraction; DFT, density functional theory; chem.an., chemical analysis; n.r., not reported.

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## ABSTRACT

A significant amount of information regarding the synthesis, reactivity, and catalytic activity of titanium fluoride complexes is available in the literature. However, the reports are mostly nonsystematic and spread over a large number of specific journals. An attempt is made to collect and organize all available information. Emphasis is given on work published after 1990 with links to the previous reviews, but earlier work is also included if no systematic report was done before.

Published synthetic methods to access titanium fluoride complexes are covered in the present review, as well as the properties and reactivity of titanium fluoride complexes. In particular, the behavior of  $TiF_4$  in non-aqueous solvents, as well as the interaction of  $TiF_4$  with neutral and charged ligands in non-aqueous solvents is reviewed. All published tetrafluoride complexes  $TiF_4L_2$  ( $L$  – neutral ligand) are presented. Mixed chloro and fluoro titanium complexes supported by neutral ligands, their preparation, and isomerism are surveyed. DFT calculations were performed to estimate the relative basicities of molecular ligands in titanium fluoride complexes as well as the relative stability of fluoride bridged titanium complexes.

The reactivity of heterometallic titanium–alkali metal, titanium–alkaline earth metal fluoride complexes, the interaction of titanium fluoride complexes with silicon substrates, and the reactivity of titanium complexes toward organofluorine compounds are presented later in the review.

Titanium fluoride complexes have found numerous applications in organic synthesis, and in many cases, the fluoride complex shows better performance than do complexes supported by other types of ligands. Organotitanium fluoride complexes show antitumor activity, and their values of cytotoxicity are comparable to that of the “gold standard” cisplatin.

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## 1. Introduction

In 1795, the German chemist Klaproth discovered a sample of  $TiO_2$  now known as rutile. He named the element titanium after the Titans. According to Greek mythology, the Titans are the children of heaven and earth condemned to live among the hidden fires of the earth. In 1791, William Gregor, a vicar from Cornwall, discovered ilmenite ( $FeTiO_3$ ), a black mineral. This mineral is broadly used for the preparation of titanium metal. Titanium is an abundant chemical element of the earth's crust (it comprises 0.63%), holding the ninth position among all elements.

Titanium complexes play an important role in chemistry. In recent decades, transition metal fluorides have shown continuous growth in many applications. The element–fluorine bond is the strongest single bond among elements.

It is now recognized that transition-metal fluoride complexes are distinctive, exhibiting reactivity patterns that are remarkably different from those of their more well known alkoxy, chloro, bromo, and iodo counterparts [1].

The difference in reactivity has prompted reviews of the chemistry of fluoride complexes and their application in catalysis. The preparation, properties, and structural characterization of the main group metal fluoride complexes [2,3], *f*-block fluorides [3–6], and *d*-block fluorides [3,5–8] have been covered in several reviews. The organometallic fluorine chemistry of palladium and rhodium complexes was reviewed by Serafin and Müller [9] and later by Grushin [10]. The CH arylation of five-membered heteroaromatic compounds such as thiazoles and thiophenes promoted by palladium fluoride complexes has been summarized by Mori and Sugie in 2008 [11]. These reactions allow the preparation of a wide variety of 2,5-diarylthiazoles. Cross-coupling reactions utilizing organosilicon substrates that are promoted by palladium fluoride complexes were summarized in a shorter account by Hiyama in 2002 [12]. An excellent review about the role of transition-metal fluoride complexes in asymmetric catalysis had been presented in 1999 by Pagenkopf and Carreira [13]. Halide effects, including the fluoride effect in transition-metal catalysis were reviewed by Fagnou and Lautens in 2002 [14].  $AgF$ ,  $ZnF_2$ , and  $CuF$  were used in catalyzed asymmetric allylation and reviewed by Yamamoto and Wadamoto in 2007 [15]. The catalysis of copper fluoride complexes was summarized by Shibasaki and Kanai in 2008 [16]. Gold-catalyzed organic transformations in the presence of fluorinating reagents

were described by Gouverneur et al. in 2010 [17]. Dual activation of electrophile and nucleophile in asymmetric catalysis by transition-metal fluoride complexes was summarized by Ma and Cahard in 2004 [18].

Titanium has received considerable attention since many titanium compounds are nontoxic and almost all compounds in the environment transform titanium into nontoxic titanium dioxide. In particular,  $TiO_2$  is employed as a pigment to impart whiteness to products such as paints, coatings, plastics, papers, inks, foods, medicines (*i.e.*, pills and tablets), and most toothpastes [19].

Titanium fluoride complexes were extensively reviewed in 1991 [6], 1997 [5], and 1999 [20]. The activity of titanium fluoride complexes in olefin polymerization has been reviewed by Mandal and Roesky in 2011 [21], and their application in asymmetric catalysis has been reviewed by Pagenkopf and Carreira in 1999 [13]. Fluoride-bridged complexes of transition metals, including the titanium complexes, were reported in 1999 [3]. Some titanium(IV) fluoride complexes supported by neutral donor ligands were discussed in 2013 [8].

The reviews mostly describe the titanium cyclopentadienyl complexes. A large part of titanium complexes is uncovered to date, namely, titanium complexes with nonmetallocene ligands. This is surprising because most of the reported titanium fluoride complexes possessing catalytic activity are supported by the non-pentadienyl-type ligands. The most important application of titanium fluoride complexes in catalysis was not reviewed since 1999, although a number of publications appeared in this area.

The body of this review has been divided into several sections. Initially, emphasis is placed on the synthesis of titanium fluoride complexes from nonfluorinated titanium compounds and titanium tetrafluoride. Further, the properties and application of titanium fluoride complexes in organic reactions are summarized.

Homo- and heterometallic complexes of titanium fluoride and solutions of titanium tetrafluoride in donor solvents have found application as stoichiometric reagents and catalysts for various organic transformations. Therefore, the behavior and reactivity of titanium tetrafluoride in donor solvents and the properties of heterometallic fluoride complexes containing titanium and alkali or alkaline earth metals are reviewed. Moreover, numerous reports mention that titanium fluorides promote a range of C–C coupling reactions utilizing organosilicon compounds. This prompted revision of the reactivity series of titanium fluoride complexes

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