IN THE NAME OF GOD

Shiraz University
Faculty of Sciences

Ph.D. Dissertation in Organic Chemistry

NEW APPLICATIONS OF TRICHLOROTITANIUM(IV) TRIFLUOROMETHANESULFONATE, $TiCl_3(OTf)$ & PREPARATION AND APPLICATION OF SILICA BOUND Ti(IV), $TiCl_2(OTf)$-SiO_2 AS A HETEROGENEOUS CATALYST IN ORGANIC TRANSFORMATIONS

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دانشکده‌ی علوم

پایان نامه دکترا در رشته شیمی آلی

کاربردهای جدید تری کلرو تیتانیوم تریفلات $TiCl_3(OTf)$ و تهیه و کاربردهای تیتانیوم پیوند شده بر سیلیکا ژل: $TiCl_2(OTf)$-SiO_2 بعنوان یک کاتالیزور هتروژن در تبدیلات آلی

به وسیله ی:

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اردیبهشت ۱۳۸۸

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DECLARATION

Hereby, Soghra Farahi (832848) student of Organic Chemistry College of Sciences certify that this thesis results from my own research and whenever I have utilized other sources, I have clearly reference them. I also declare that the research and the title of my thesis are novel and I promise, without the permission from the university, the results never be published or bring to someone else. The copyright of this thesis is the property of Shiraz University.

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BY:

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Dedicated to:

My Family Specially My Dear Mother

And

All My Teachers Specially

Professor Habib Firouzabadi, Professor Nasser Iranpoor

&

Professor Ali Reza Sardarian

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ABSTRACT

NEW APPLICATIONS OF TRICHLOROTITANIUM(IV) TRIFLUOROMETHANESULFONATE, $TiCl_3(OTf)$ & PREPARATION AND APPLICATION OF SILICA BOUND Ti(IV), $TiCl_2(OTf)$-SiO_2 AS A HETEROGENEOUS CATALYST IN ORGANIC TRANSFORMATIONS

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In this thesis, we have utilized two titanium (IV)-based compounds; $TiCl_3(OTf)$ and $TiCl_2(OTf)$-SiO_2 as catalysts for some organic reactions.

At first, catalytic applications of solid $TiCl_3(OTf)$ was extensively investigated in esterification and transesterification reactions. $TiCl_3(OTf)$ catalyzed acylation of alcohols, phenols, thiols and α-hydroxyphophonates with acid anhydrides in the absence of organic solvents at room temperature or at 70 and 80 °C. In the presence of $TiCl_3(OT)$, formylation of alcohols and amines and acetylation of alcohols were achieved in refluxing ethyl formate and ethyl acetate. Direct esterification of different alcohols with different carboxylic acids was also experienced in the presence of this catalyst at 115 °C.

Protection of aldehydes with acetic anhydride was also achieved in the presence of $TiCl_3(OTf)$. The generality of this method for the conversion of various aldehydes to their corresponding acylals has been shown.

$TiCl_3(OTf)$ has also been applied for efficient silylation of –OH functional groups of α-hydroxyphosphonates, alcohols and phenols with HMDS at room temperature under neat conditions. High chemo- and regioselectivity were observed between different substrates using $TiCl_3(OTf)$ as a catalyst.

We also prepared $TiCl_2(OTf)$-SiO_2, which is a moisture tolerant Ti(IV) silica bound compound. Then, we investigated applications of this new compound as a catalyst in some organic reactions.

Preparation of α-trimethylsiloxyphosphonates and silyl ethers using HMDS as silylating agent was achieved in the presence of $TiCl_2(OTf)$-SiO_2 as a catalyst under neat conditions. Here again, high chemo- and regioselectivity were observed between different substrates using this catalyst. The catalyst is separated from the reaction mixture by simple filtration and was reused for six consecutive runs without appreciable loss in its catalytic activity.

We also reported *N*-derivatization of α-aminophosphonates *via* Michael addition reactions using $TiCl_2(OTf)$-SiO_2 as a catalyst for the first time. The generality of the catalyst for C-C and C-N bond formation reactions through 1,4-conjugate addition of structurally diverse amines, indoles and pyrrole to electron deficient C-C double bonds has been shown. Recyclablity of the catalyst was also investigated in these reactions. The catalytic activity of $TiCl_2(OTf)$-SiO_2 is maintained during four consecutive runs.

Finally, we applied $TiCl_2(OTf)$-SiO_2 as an effective recyclable catalyst for cyanosilyltion of aldehydes under neat conditions.

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ABBREVIATIONS

TMSCl	Trimethylsilyl chloride
DPAT	Diphenyl ammonium triflate
CAN	Ceric (IV) ammonium nitrate
AcOH	Acetic acid
Ac_2O	Acetic anhydride
AT	Ammonium triflate
DBSA	Dodecylbenzene sulfonic acid
CDBS	Copper dodecylbenzene sulfonate
DMAP	4-(Dimethylamino)pyridine
PPY	4-Pyrrolidinopyridine
Bu_3P	Tributylphosphine
PMA	Phosphomolybdic acid
TBDMS	*t*-Butyl dimethyl silyl
DEAD	Diethyl azodicarboxylate
DMF	N,N-Dimethylformamide
HMDS	Hexamethyldisilazane
NBS	N-bromosuccinimide
SDS	Sodium dodecyl sulfate
TMSCN	Trimethylsilyl cyanide
MS	Molecular sieve
GC	Gas chromatography
TLC	Tin layer chromatography
EtOAc	Ethyl acetate
THF	Tetrahydrofuran

Bu Butyl

LD_{50} =The LD_{50} is a standardized measure for expressing and comparing the toxicity of chemicals.

The LD_{50} is the dose that kills half (50%) of the animals tested (LD = "lethal dose"). The animals are usually rats or mice, although rabbits, guinea pigs, hamsters, and so on are sometimes used.

TON = Turnover number; the number of moles of substrate that a mole of catalyst can convert before becoming inactivated.

TOF = Turnover frequency is used to refer to the turnover per unit time.