The Synthesis and Characterization of New, Robust Titanium (IV) Scorpionate Complexes

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INTRODUCTION

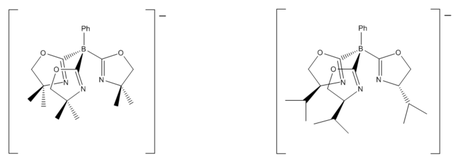
Titanium complexes possessing sterically encumbered ligands have allowed for the preparation of reactive moieties (imido, alkylidene, and alkylidyne species) relevant to a wide range of reactions, including:

•Olefin polymerization

and

•Alkyne hydroamination

We have previously prepared two bulky ligands, tris(4,4-dimethyl-2-oxazolinyl)phenyl borate $[To^M]^-$ and the related chiral ligand, tris(4-isopropyl-2-oxazolinyl)phenyl borate $[To^P]^-$ for use in the synthesis of transition metal complexes:

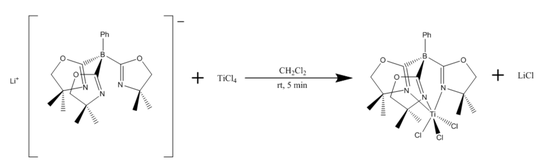


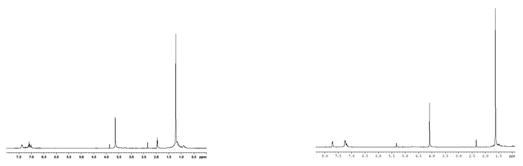
$[To^M]^-$ **$[To^P]^-$**

These ligands have been used to synthesize a series of new titanium (IV) complexes.

SYNTHESIS OF $[Ti(\kappa^3\text{-}To^M)Cl_3]$

The complex $[Ti(\kappa^3\text{-}To^M)Cl_3]$ was prepared in moderate yield (43%) by the rapid (< 1 min at room temperature) reaction of $Li[To^M]$ and $TiCl_4$:



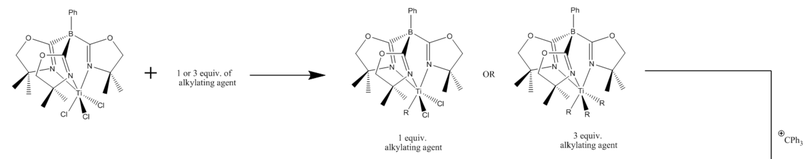


^{1}H NMR spectrum of Li[To^M] in acetonitrile-d_3

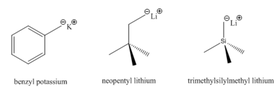
^{1}H NMR spectrum of $[Ti(\kappa^3\text{-}To^M)Cl_3]$ in methylene chloride-d_2

ALKYLATIONS OF $[Ti(\kappa^3\text{-}To^M)Cl_3]$

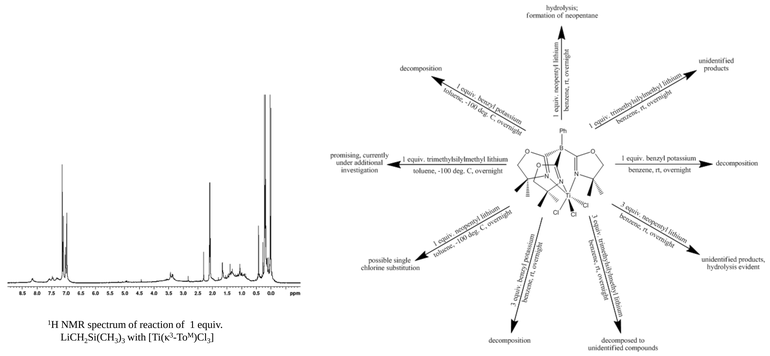
The synthesis of titanium alkyl complexes by salt metathesis was attempted using one or three of equivalents of alkylating agent under either low temperature or ambient temperature conditions:



Alkylating agents used:



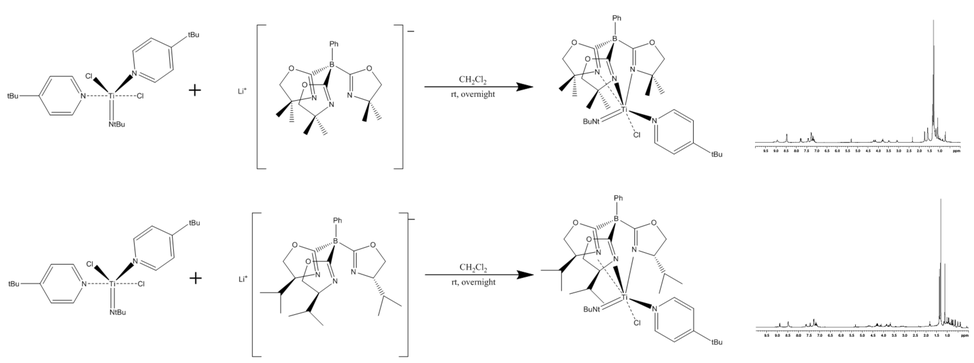
Results of alkylation attempts:



^{1}H NMR spectrum of reaction of 1 equiv. $LiCH_2Si(CH_3)_3$ with $[Ti(\kappa^3\text{-}To^M)Cl_3]$

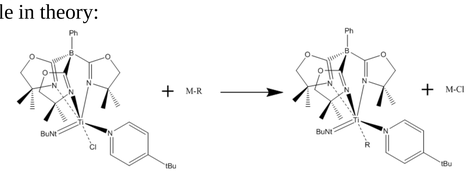
SYNTHESIS OF $[Ti(=NBu^t)(\kappa^3\text{-}To^M)(Cl)(Bu^tpy)]$ AND $[Ti(=NBu^t)(\kappa^3\text{-}To^P)(Cl)(Bu^tpy)]$

$[Ti(=NBu^t)(\kappa^3\text{-}To^M)(Cl)(Bu^tpy)]$ (Bu^tpy = 4-*tert*-butylpyridine) and $[Ti(=NBu^t)(\kappa^3\text{-}To^P)(Cl)(Bu^tpy)]$ were synthesized by reaction of the known Ti imido $[Ti(=NBu^t)(Cl)_2(Bu^tpy)_2]$ with $Li[To^M]$ or $Li[To^P]$, respectively:

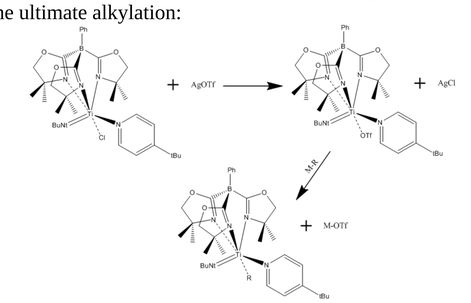


PATHWAYS TO TITANIUM IMIDO ALKYLS

Direct alkylation (via salt metathesis) of $[Ti(=NBu^t)(\kappa^3\text{-}To^M)(Cl)(Bu^tpy)]$ is possible in theory:



Alkylation using trimethylsilylmethyl lithium, however, resulted in the formation of an unidentifiable product. In an alternative approach suggested by Mindiola and coworkers, a triflate complex is synthesized before the ultimate alkylation:



This approach has shown promise and is currently under additional investigation.

FUTURE RESEARCH

•Alkylations of $[Ti(\kappa^3\text{-}To^M)Cl_3]$ with trimethylsilylmethyl lithium have proven promising and will be further investigated.

•Further alkylation attempts will be made by alkylating the triflyl complex $[Ti(=NBu^t)(\kappa^3\text{-}To^M)(Cl)(Bu^tpy)]$.

•The utility of $[Ti(\kappa^3\text{-}To^M)Cl_3]$ in promoting polymerization reactions will be explored.

•The complex $Ti(\kappa^3\text{-}To^M)Cl_2$ will be synthesized by reaction of $Li[To^M]$ and $TiCl_3$. Attempts will be made to oxidize this complex into a Ti (IV) cation.

ACKNOWLEDGEMENTS

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