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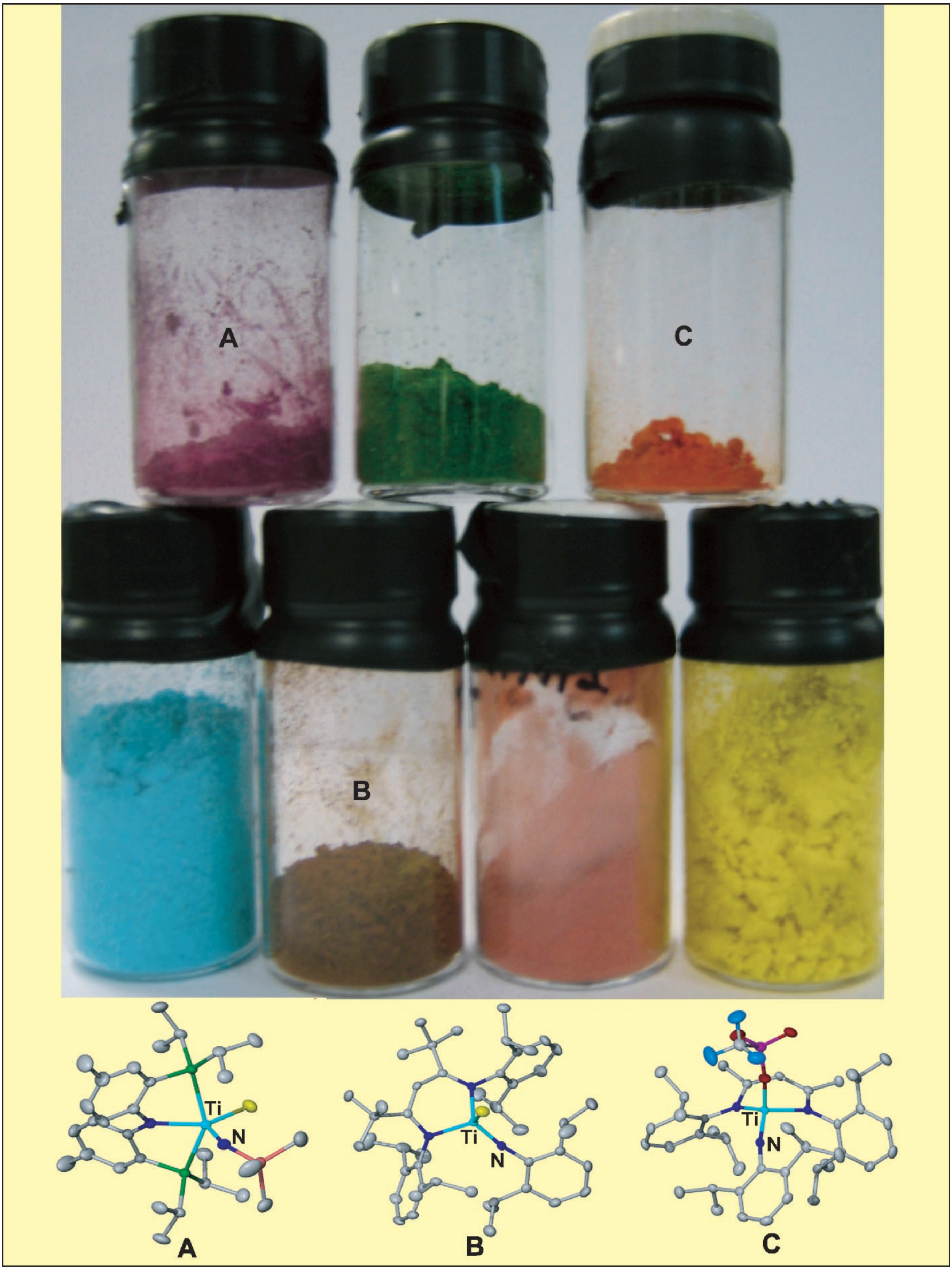

The Progression of Synthetic Strategies to Assemble Titanium Complexes Bearing the Terminal Imide Group

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Abstract: The synthesis of terminal titanium imides is described in this account. The incorporation of this functional group has evolved from more simplistic approaches to more complex or unusual methods. Past and current synthetic strategies to incorporate the terminal imide functionality are explained with particular emphasis on low-coordinate titanium environments bearing this ubiquitous but vital type of motif. More recently, the imide functionality has demonstrated to be a key intermediate for modeling important industrial processes such as the hydrodenitrogenation of crude oil.

Keywords: hydroamination · imides · titanium · transmetalation

Introduction

The imide functionality is an important ligand class in the realm of high-oxidation-state early-transition-metal chemistry and has been utilized in fields such as inorganic, organic, bioinorganic, materials, and medicinal chemistry as well as the chemical industry.[1–6] As a result, this field continues to burgeon over the years given the practical use of the imide in multiple areas of research.[3–7] For example, this type of functionality is responsible for fundamentally important reactions such as the intermolecular activation of aliphatic (including methane)[8,9] as well as aromatic C–H bonds.[7,10–13] The ubiquitous imide group can also participate in other processes such as cycloaddition reactions with substrates like carbon dioxide,[14–21] carbon disulfide,[14–16,19,22] ketones,[16,22,23] alkenes (intra- and intermolecularly),[24,25] alkynes,[22,24–26] nitriles,[23,27] isonitriles,[16,28] imines,[16,23,29,30] carbodiimides,[4,16,30–32] allenes,[4,24,33] allylic alcohols,[34] and carboxamides[35] along with several other polar reagents.[4–7] Depending on the complex, incomplete or complete metathetical reactions can often take place (even catalytically) with these types of substrates, thus leading to Wittig-like chemistry and extrusion of organic products in which the imide group has been swiftly incorporated. In addition to behaving as a reactive ligand, high-oxidation-state metal imides can also function as supporting ancillary ligands. This role has important implications to catalysis and medicinal chemistries. In the context of materials chemistry, imides are known precursors to thin metal nitride films for metal–organic chemical vapor deposition methods (MOCVD).[36–43]

As described previously, the imide functionality (in a closed-shell formalism) has also been utilized as a supporting ligand. For example, metal imides can be used as ancillary ligands for the study of important industrial reactions such as olefin metathesis[44] and polymerizations,[29,38,44–46] as well as models for processes such as propylene ammoxidation[47] and hydrodenitrogenation.[2] The chemical behavior of the imide ligand is often governed by the role of the lone pair of electrons on nitrogen, which may or may not contribute to the formation of a pseudo-triple bond. Therefore, imides can resonate in the form $\mathrm{M{=}NR \leftrightarrow M^{-}{\equiv}N^{+}R}$. One clear illustration of such a resonance has been demonstrated by the Schrock alkylidene–imide catalyst, $\mathrm{[(RO)_2Mo{=}NAr(CHR)]}$ (R = perfluoro alkyl, aryl, or chelating ligand), a system which typically displays no reactivity at the imide motif.[48] However, for the molybdenum complex the imide group does play a critical role from an electronic and structural standpoint, since formation of the $\mathrm{Mo{\equiv}NAr}$ bond controls isomerization about the $\mathrm{Mo{=}CHR}$ bond to form the two corresponding rotamers, *syn* and *anti*.[48] Apart from imides stabilizing the metal ion during the catalytic process, this type of ligand can simply act as ancillary framework to solubilize and protect the metal ion. For example, stable radiopharmaceutical agents composed of Tc have often been prepared using the prototypical ancillary imide ligand.[3]

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From a bioinorganic perspective and outside the scope of the early-transition-metal regime, terminal[49,50] imide motifs involving the biologically relevant element iron are now beginning to flourish. Such a development could have important implications as nitrogenase models involved in dinitrogen sequestration and subsequent functionalization.[51,52]

As noted earlier, metal imides play pivotal roles in stoichiometric "NR" group-transfer processes in which the metal center acts as a delivery vehicle. In general, terminal and early-transition-metal imides are expected to be reactive, given the polarized nature of the M−N multiple bond, especially for complexes with low-coordination environments. For these reasons, it is not surprising that titanium imides are often required for several catalytic reactions such as the intermolecular and intramolecular hydroamination of alkynes and allenes,[4,24,33,53–55] hydrohydrazination of alkynes,[6] multi-coupling reactions to generate α,β-unsaturated β-aminoimines,[6,28] guanylations,[32] imine metathesis,[56] carbodiimide metathesis,[31] carboamination of alkynes with aldimines,[57,58] transamidations,[35] and cyclization reactions to produce multisubstituted quinolines[58] among other important processes.[4–7]

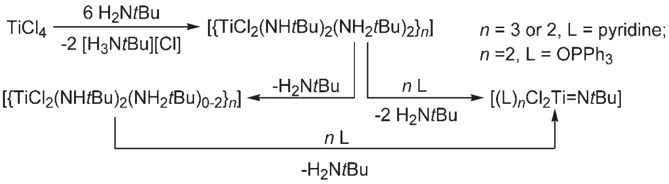
Given the tremendous amount of literature recounting transition-metal–nitrogen multiple bonds, we will cover only descriptive chemistry surrounding the assembly of the terminal imide motif onto titanium. Specifically, we will concentrate our attention on synthetic efforts to incorporate the imide functionality on titanium systems that have low-coordination environments given their inherent reactivity and catalytic promise. Reaction chemistry deriving from the imide functionality will not be reported in this document, unless it relates to a synthetic protocol to assemble the imide ligand itself. Dimers and polynuclear bridging imido complexes will be covered only briefly in this concepts review, and we refer the reader to more comprehensive reviews describing this area.[4,5] Small-molecule chemistry and catalysis relating to the reactivity of the imide group will not be discussed in this concepts article.

Early Synthesis of Terminal Titanium Imides

Buerger and Wannagat most likely reported the first example of a terminal titanium imide [$Me_3SiN{=}TiCl_2(pyridine)_2$],[59] a compound that was prepared by trimethylsilylchloride elimination. Attempts to prepare this compound in the absence of pyridine did not succeed; instead oligomerization through bridging halides or the imides occurred to yield [$(\{Cl_2Ti{=}NSi(Me)_3\}_2)_x$] ($x=8$ or ∞).[60–62] The first structurally characterized terminal titanium imides were documented by Roesky[63] and Rothwell,[64] namely the complexes [$Ph_2PN{=}TiCl_2(pyridine)_3$] and [$(ArO)_2Ti{=}NPh(py')_2$] ($Ar=2,6\text{-}i Pr_2C_6H_3$, py′ = 4-pyrrolidinopyridine), respectively. Since then, inorganic chemists have developed new synthetic strategies to generate the terminal imide functionality. These strategies often involve novel approaches or a combination of well-known procedures. The following protocols summarize most of the reported methods to access the terminal titanium imide ligand.

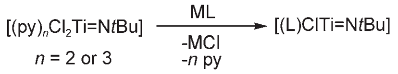
Dehydrohalogenation, Deprotonation, and α-Hydrogen Abstraction Reactions

Dehydrohalogenation, deprotonation, and α-hydrogen abstractions are perhaps the most common and convenient protocols to access the Ti=NR motif. Typically, coordinatively saturated titanium imides are prepared from the reaction of $TiCl_4$ and the corresponding primary amine such as H_2NtBu (excess, over 6 equiv) in the presence of donor ligands to generate five- or six-coordinate titanium complexes of the type [$(L)_nCl_2Ti{=}NtBu$] ($n=2$ or 3, L = pyridine; $n=2$, L = bulky pyridine such as NC_5H_4tBu; $n=2$, L = $O{=}PPh_3$), concomitant with formation of the ammonium salt (Scheme 1).



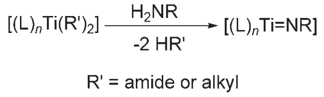
Scheme 1.

The use of excess H_2NtBu promotes dehydrohalogenation to form the Ti−NHtBu linkage and the ammonium salt [H_3NtBu][Cl], while the donor ligands (e.g, pyridine, phosphine oxides) likely play several roles such as displacement of the metal-bound amine, α-hydrogen deprotonation, and formation of the titanium imide monomer. Winter's seminal work has demonstrated that the presence of a Lewis base such as $O{=}PPh_3$ is critical in these reactions, since it prevented formation of the amide–amine oligomers [$\{TiCl_2(NHtBu)_2(NH_2tBu)_{0-2}\}_n$].[36] Mountford[5,65–67] also applied an analogous strategy, generating the terminal imide group by using other donors such as pyridine, monoamines, *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TMEDA), among many others. Such an approach is practical given the availability of the starting materials, $TiCl_4$ and H_2NtBu, and the ability to produce the corresponding titanium *tert*-butyl imide in multigram quantities for subsequent reactions. Hence, compounds such as [$(py)_nCl_2Ti{=}NtBu$] are excellent precursors to a broad class of titanium complexes bearing the terminal Ti=NtBu scaffold (Scheme 2) through transmetalation reactions (with neutral, mono, or dianionic ligands).[4,5,14,68]

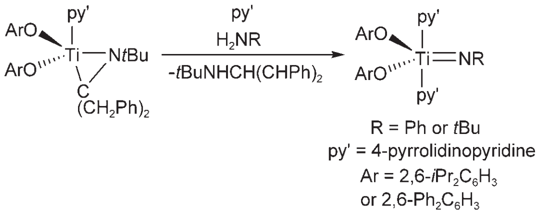


Scheme 2.

However, generating an ammonium salt in the aforementioned reactions can sometimes be a hindrance, since it can act as a conjugate acid. In addition, separation of the salt from the imide product can also be problematic, because of the partial solubility of the former in organic solvents. To avoid this type of limitation, terminal titanium imides can often be prepared by generating a much weaker conjugate acid, which would be the case for byproducts such as amines and alkanes. For example, $[L_nTi(NMe_2)_2]$ and $[L_nTi(R)_2]$ (R = alkyl group) can be treated with the primary amine H_2NR to form the imide product $[L_nTi{=}NR]$, concurrent with $HNMe_2$ and RH elimination (2 equiv of each), respectively (Scheme 3). Most notably, the deprotonating ligands are not limited to amides or alkyls only. For example, Rothwell and co-workers have shown that titanium imide ligation can be accomplished by double deprotonation of the amine with a strained titanoaziridine framework (Scheme 4).[64]

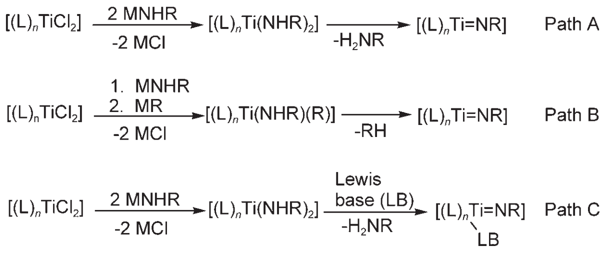


Scheme 3.



Scheme 4.

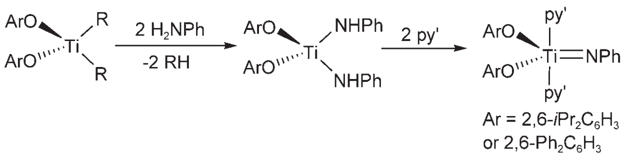
Terminal titanium imides are also commonly prepared from salt elimination reactions with primary amide salts such as LiNHR or powerful bases such as MR (in which M = alkali metal; R = H or alkyl group) with the corresponding metal halide precursor.[3] The advantage of this route over the previous one is the ability to generate low-coordinate surrogates by using a better leaving group. In addition, this approach results in elimination of insoluble inorganic salts as opposed to the ammonium byproducts (vide supra). α-Hydrogen abstraction can also be base promoted with the use of these substrates. For example, titanium bis-anilide complexes can be treated with Lewis bases, such as pyridines, to create a sterically crowded environment, and subsequently undergo α-hydrogen abstraction (vide infra).[64] Scheme 5 depicts three prototypical pathways often applied for the assembly of the terminal titanium imide group. Path A applies a dehydrohalogenation route with primary amide salts in which an alkali metal salt and amine are leaving groups. Path B invokes a two-step process in which a primary amide is incorporated, and then the primary amide complex is transmetallated with an alkyl reagent to afford the amide–alkyl species.[69,70] This last system would then be poised to extrude RH and form the titanium imide product. For this path, one can also envision a protocol in which the alkylation takes place prior to addition of the primary amine or transmetalation with the primary amide salt (in the case of 1 equiv of alkyl). Sometimes, elimination of the alkane or primary amine can be promoted by addition of a Lewis base (LB).[64] Path C invokes a double transmetalation step with the primary amide, followed by addition of a Lewis base to promote the α-hydrogen abstraction. These Lewis bases include ethers, amines, phosphines, phosphine oxides, and *N*-heterocycles, such as pyridine or substituted pyridines.



Scheme 5.

Dehydrohalogenation reactions often combine two steps, a transmetalation and an α-hydrogen abstraction, the latter which can be essentially juxtaposed with the term α-deprotonation. It has been determined that the steric bulk of the base plays an essential role in the α-hydrogen abstraction step.[69] Consequently, bulkier bases are more likely to abstract the proton. In dehydrogenation reactions, Lewis bases or heat can also promote α-hydrogen abstraction, which is similar to the protocol applied in the synthesis of high oxidation state early-transition-metal alkylidenes. Rothwell and co-workers have clearly shown some of the earlier examples in which a titanium bis-anilide system, prepared by treatment of a metal bis-alkyl (dimethyl and/or diethyl amines can also be used instead of an alkyl group) with two equivalents of aniline, can undergo smooth α-hydrogen abstraction when treated with strong Lewis bases such as 4-pyrrolidinopyrine or 3,4,7,8-tetramethyl-1,10-phenanthroline (py′) to afford 5-coordinate titanium imides (Scheme 6).[71] The use of a Lewis base in these reactions most likely prevented dimerization through the bridging of the imide ligand, but also promoted α-hydrogen abstraction by steric crowding.[64]

In some cases, however, the amine can be coordinated to the titanium(IV) center without formation of the ammonium salt, and then such an adduct can be dehydrohalogenat-



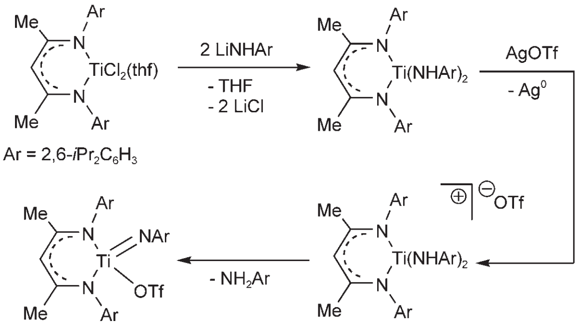
Scheme 6.

ed with a Brønsted base to afford the monomeric imide. Winter and co-workers have applied this strategy using the precursor $TiCl_4(NH_3)_2$, NaH, and $OPPh_3$, to afford a rare example of a Group 4 terminal parent imide, namely $[(OPPh_3)_2Cl_2Ti{=}NH]$ (Scheme 7).[72] Intermediates leading to formation of the parent imide were not reported, but likely involve a parent amide precursor generated through H_2 and NaCl elimination (Scheme 7).[72]

$$[TiCl_4(thf)_2] \xrightarrow[-2\ THF]{2\ NH_3} [TiCl_4(NH_3)_2] \xrightarrow[\substack{-\ NH_3\\ -\ 2\ NaCl\\ -\ 2\ H_2}]{2\ OPPh_3} [(OPPh_3)_2Cl_2Ti{=}NH]$$

Scheme 7.

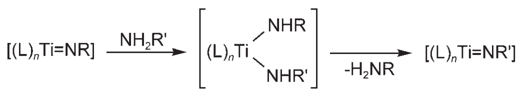
Another synthetic strategy to assemble the terminal imide functionality in low-coordination environments is through an α-hydrogen abstraction step that can be accomplished by a simple one-electron oxidation reaction. This approach applies a one-electron oxidation of a Ti^{III} radical precursor to promote α-hydrogen abstraction via a putative, coordinately saturated Ti^{IV} intermediate.[73] The advantage of such a tactic is that rare examples of four-coordinate titanium imides[45,73–80] can be prepared by this synthetic route. Most notably, a substitutionally labile group such as a triflate, can be readily incorporated in conjunction with the terminal imide motif. For example, the dichloride precursor $[(nacnac)TiCl_2(thf)]$[73] ($nacnac^- = [ArNC(Me)]_2CH$, Ar = 2,6-$i$$Pr_2C_6H_3$) reacts readily with two equivalents of LiNHAr to afford the bis-anilido titanium(III) complex $[(nacnac)Ti(NHAr)_2]$ in excellent yield (Scheme 8).[74] Chemical oxidation of the latter with AgOTf caused a color change from green to orange-red concomitant with formation of a Ag^0 mirror. Immediate workup of the reaction afforded the bis-anilido salt $[(nacnac)Ti(NHAr)_2][OTf]$ (Scheme 8).[74] This salt complex is relatively stable as a solid, but solutions of it gradually transform to the four-coordinate titanium imide $[(nacnac)Ti{=}NAr(OTf)]$ and H_2NAr, the former which can be isolated as red prisms in moderate yield (Scheme 8).[74] Electrochemical studies of the complex $[(nacnac)Ti(NHAr)_2]$ revealed a reversible oxidation wave at −0.89 V for the Ti^{III}/Ti^{IV} couple, thus suggesting that the one-electron oxidation step is NOT rate-determining for this type of transformation. The role of the anion in the α-hydrogen abstraction step is critical in that treatment of $[(nacnac)Ti(NHAr)_2]$ with an oxidant containing a weakly coordinating anion (e.g., $[FeCp^*_2][B(C_6F_5)_4]$) results in formation of the bis-anilide cation $[(nacnac)Ti(NHAr)_2][B(C_6F_5)_4]$ rather than the corresponding imide species.[74] Hence, the anion must play a crucial role in the α-hydrogen abstraction step, but we are unsure whether anion binding or α-hydrogen abstraction is rate-determining for the aforementioned reaction.



Scheme 8.

Transiminations

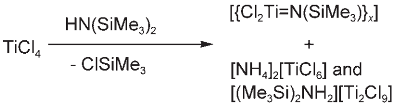
Combining protonation and α-hydrogen abstraction using an amine can be described as a transimination reaction.[3] Mountford and co-workers have commonly applied this strategy to assemble terminal aryl imide compounds of titanium.[16,17,21,81–84] Likewise, Odom and co-workers have also used this tactic to prepare silyl imides.[85] However, this approach to incorporate the imide group relies on having an already assembled, highly donating (e.g., tBu), imido ligands. Transimination likely operates by protonation of the basic imide site to generate a transient nondegenerate bis-amide intermediate, which then undergoes α-hydrogen abstraction to furnish the less basic imide group (Scheme 9).



Scheme 9.

Trimethylsilyl Chloride Elimination Reactions

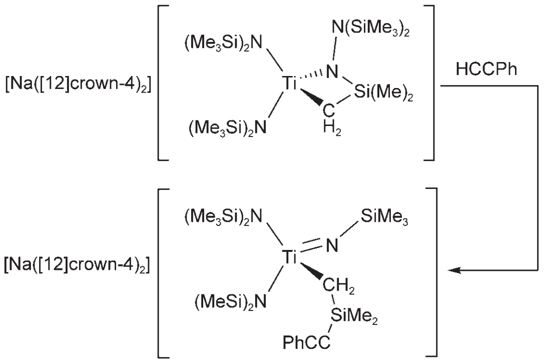
N−H bonds are not the only linkage amenable to activation by a one-electron oxidation. The fragile nature of N−Si linkages coupled with the high bond-dissociation enthalpy of Si−Cl (≈406 kJ mol^{-1}) makes trimethylsilyl elimination a thermodynamically feasible process. This approach was perhaps the first documented method to incorporate the terminal titanium imide functionality.[59] Despite this finding, trimethylsilylimide ligands bound to titanium are exceedingly rare, which is a surprising fact given the availability of hexamethyldisilazane and $[MN\{Si(Me)_3\}_2]$ salts (M = Li and Na). As a result of the availability of starting material, bridging trimethylsilylimide oligomers of titanium, $[\{Cl_2Ti{=}N(SiMe_3)\}_x]$ (x = 8 or ∞) can be readily assembled by treatment of $HN(SiMe_3)_2$ with $TiCl_4$ in CH_2Cl_2 (Scheme 10).[60–62] $TiCl_4$ and the amine are used to sequester the HCl to generate $TiCl_6$ and Ti_2Cl_9 anions stabilized by ammonium counterions.[62] Upon thermolysis (>250 °C), this imide precursor



Scheme 10.

can degrade to [{TiNCl}$_x$] and a second equivalent of Me_3SiCl.[86] Therefore, complexes such as [{$Cl_2Ti{=}N(SiMe_3)$}$_x$] can be excellent precursors to terminal trimethylsilylimide titanium complexes by salt elimination and breaking of the metal oligomers (vide infra).[86]

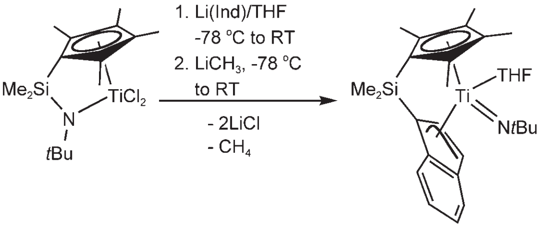
Silyl elimination reactions can also lead to terminal titanium imides with both aliphatic and aromatic groups on nitrogen. For example, secondary amines of the type HN*t*Bu($SiMe_3$) react readily with $TiCl_4$ in CH_2Cl_2 or THF to generate oligomers with a terminal imide group.[87] However, if a donor such as pyridine is used in the reaction, the monomer [$Cl_2(py)_2Ti{=}N$*t*Bu] can be obtained.[87] Tertiary amines such as $RN(SiMe_3)_2$ can also be used to assemble the terminal titanium imide ligand (R = 1-adamantyl, Ph, C_6F_5, 3,5-$(CF_3)_2C_6H_3$) when treated with $TiCl_4$. For these last cases, the use of THF as solvent results in formation of edge-sharing octahedral dimers such as [{Cl(μ_2-Cl)(thf)$_2$Ti=NR}$_2$].[88] Rupture of the N−Si bond in silazanes concurrent with Ti=N bond formation can also be accomplished with strained systems[89,90] and with the aid of nucleophiles.[91,92] In the case of nucleophiles, the cyclometallated salt [Na([12]crown-4)$_2$][$(Me_3Si)_2N]_2TiCH_2SiMe_2N(SiMe_3)$] can be disilylated (also resulting in oxidation to Ti^{IV}) at the cyclometallated N−Si linkage with HC≡CPh to afford the imide–alkyl salt [Na([12]crown-4)$_2$][{$(Me_3Si)_2N$}$_2Ti{=}NSiMe_3(CH_2SiMe_2CCPh)$] (Scheme 11).[91]



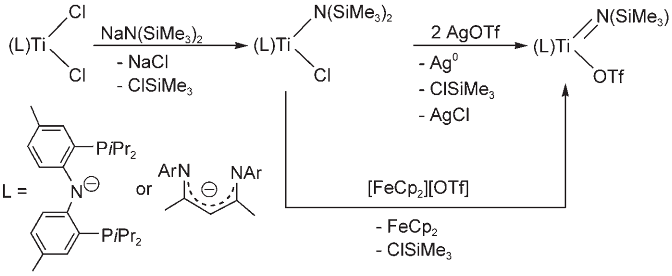
Scheme 11.

Other strained N−Si linkages in monoanionic ligands such as $Me_2Si(\eta^5\text{-}C_5Me_4)$(N*t*Bu) can be broken in the presence of a nucleophile such as Li(indene) to generate the terminal titanium imide. Subsequent treatment with LiMe in THF results in dehydrohalogenation to form the chiral *ansa*-metallocene imide–THF adduct depicted in Scheme 12.[92]

One-electron oxidation can also promote trimethylsilyl chloride elimination. Hence, when a solution of the Ti^{III} hexamethyldisilazide complexes [(L)ClTiCl($N(SiMe_3)_2$)] (L^- = N[2-P$(CHMe_2)_2$-4-methylphenyl]$_2$ (PNP), or nacnac) in THF , both prepared from one equivalent of $NaN(SiMe_3)_2$ and the corresponding dichloride precursor, are treated with [$FeCp_2$][OTf], oxidation rapidly ensues to generate the trimethylsilylimides [(L)(OTf)Ti=N($SiMe_3$)] along with Me_3SiCl and $FeCp_2$ (Scheme 13).[93] Separation of the trimethylsilylimide from $FeCp_2$ is readily achieved by fractional crystallization from diethyl ether or pentane. Alternatively, the Ti^{III} precursors [(L)ClTi{$N(SiMe_3)_2$}] can be treated with two equivalents of AgOTf to yield compounds [(L)(OTf)Ti=N($SiMe_3$)] in isolated yields greater than 76% (Scheme 13).[93] This last process is more convenient given the ease of separation of the Ag^0 from the mixture. Ag^+ not only acts as an oxidant, but also participates in the salt metathesis of Cl^- for OTf^- as well, since treatment of (L)ClTi{$N(SiMe_3)_2$} with one equivalent of AgOTf results in a mixture of chloro and triflate imide compounds.[93]



Scheme 12.

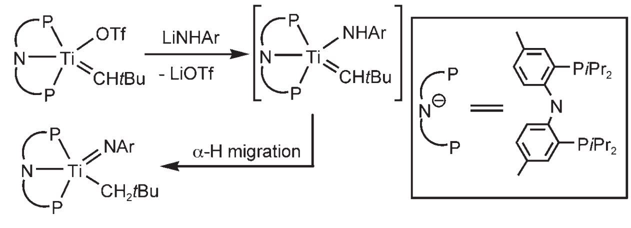


Scheme 13.

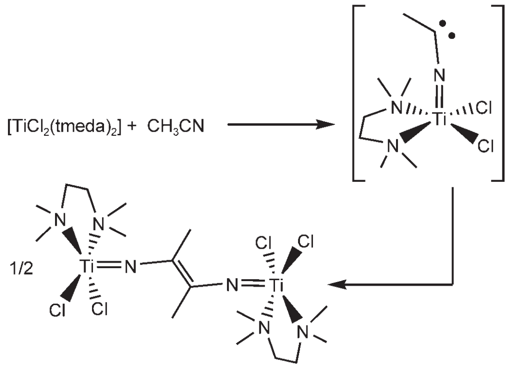
α-Hydrogen Migration Reactions

Tautomerization or α-hydrogen migration can be used to generate terminal imide functionalities when a more basic site is adjacent to the primary amide group. For example, Schrock and co-workers have applied this synthetic strategy to prepare tungsten alkylidene–imide and alkylidene–oxo compounds.[94] Mindiola and co-workers have prepared titanium alkyl–imides[71] as well as titanium[57] and vanadium[73] alkyl–phosphinidenes using a similar protocol by utilizing highly nucleophilic and terminal alkylidene groups.[95] To prepare a terminal titanium imide functionality by an α-hydrogen migration, the titanium alkylidene–triflato complex [(PNP)(OTf)Ti=CH*t*Bu] was treated with LiNHAr (Ar =

$2,6\text{-}i\mathrm{Pr_2C_6H_3}$), resulting in transmetalation to form a putative alkylidene–anilide intermediate $[(\mathrm{PNP})\mathrm{Ti{=}CH}t\mathrm{Bu(NHAr)}]$, which immediately tautomerized to a rare example of a titanium alkyl–imide $[(\mathrm{PNP})\mathrm{Ti{=}NAr(CH_2}t\mathrm{Bu)}]$ (Scheme 14).[95]



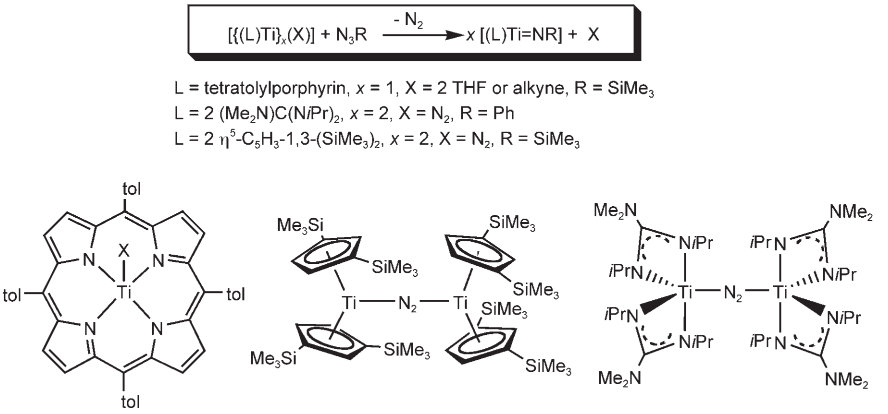
Scheme 14.



Scheme 15.

Reductive Coupling Reactions

To date, the only clear example of a C=C bond formation reaction coupled with the assembly of a $\mathrm{Ti{=}N_{imide}}$ group was documented by Gambarotta and co-workers, and it involved a powerful $\mathrm{Ti^{II}}$ reducing reagent.[96–98] Upon treatment of $[\mathrm{TiCl_2(tmeda)_2}]$ with excess MeCN, the dinuclear imide complex $[\mathrm{Cl_2(tmeda)Ti{=}NC(Me){=}C(Me)N{=}TiCl_2(tmeda)}]$ was generated along with free TMEDA. Formation of the *trans*-olefinic imide dimer likely occurs via a putative titanium imide–carbene species, which subsequently dimerizes through C=C bond formation (Scheme 15).



$$[\{(L)\mathrm{Ti}\}_x(X)] + \mathrm{N_3R} \xrightarrow{-\mathrm{N_2}} x\,[(L)\mathrm{Ti{=}NR}] + X$$

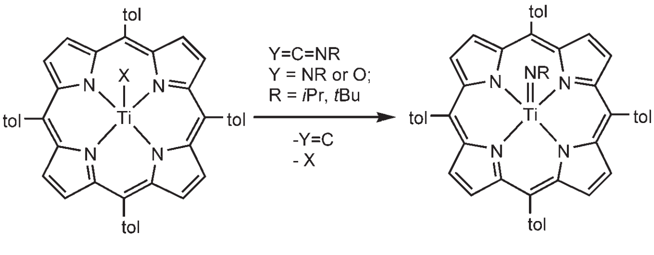
L = tetratolylporphyrin, $x = 1$, X = 2 THF or alkyne, R = $\mathrm{SiMe_3}$
L = 2 $\mathrm{(Me_2N)C(N}i\mathrm{Pr)_2}$, $x = 2$, X = $\mathrm{N_2}$, R = Ph
L = 2 $\eta^5\text{-}\mathrm{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2}$, $x = 2$, X = $\mathrm{N_2}$, R = $\mathrm{SiMe_3}$

Scheme 16.

Reduction of *N*-Cumulenes

The few reported examples of low-valent $\mathrm{Ti^{II}}$ reagents that employ *N*-cummulenes as an imide source, are rare for this transition metal. To date, the only documented examples of titanium imide formation by reduction of an organic azide were reported by Woo,[99] Arnold,[100] and Chirik.[101] In all cases, the titanium reagent in question was a low-valent complex capable of promoting the two-electron reduction of the organic azide resulting in $\mathrm{N_2}$ extrusion (Scheme 16). While Woo's $\mathrm{Ti^{II}}$ was a porphyrin complex solvated with THF, $[(\mathrm{ttp})\mathrm{Ti(thf)_2}]$ (ttp = *meso*-5,10,15,20-tetra-*p*-tolylporphyrinato dianion),[99] Arnold and Chirik's reducing reagents were low-valent titanium complexes stabilized by atmospheric nitrogen, namely the guanidinate complex $[\{\mathrm{(Me_2N)C(N}i\mathrm{Pr)_2}\}_2\mathrm{Ti}(\mu_2{:}\eta^1,\eta^1\text{-}\mathrm{N_2})]$[100] and metallocene $[\{(\eta^5\text{-}\mathrm{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2})_2\mathrm{Ti}\}_2(\mu_2{:}\eta^1,\eta^1\text{-}\mathrm{N_2})]$,[101] respectively (Scheme 16). The $\mathrm{Ti^{II}}$ porphyrin and metallocene complexes are unique in the sense that these represent the only documented cases of trimethylsilylazide reduction to generate rare examples of the titanium trimethylsilylimide functionality.[93,99–103]

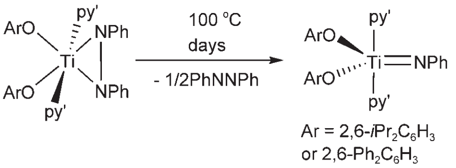
Woo and co-workers have also described reductive decarbonylation of isocyanates and reductive deisocyanation of carbodiimides, with a masked $\mathrm{Ti^{II}}$ alkyne–porphyrin complex (X = alkyne) to generate terminal titanium imides supported by a tetratolylporphyrin scaffold (Scheme 17).[104] Arnold and co-workers reported a similar transformation presumably invoking the reduction of an N–C linkage via a putative "$[\{\mathrm{PhC(NSiMe_3)}\}_2\mathrm{Ti^{II}}]$" intermediate.[105]



Scheme 17.

Cleavage of N=N Bonds

Rothwell and co-workers reported the first example of a titanium imide, $[(ArO)_2Ti{=}NPh(py')_2]$, formed through N=N bond cleavage. The aforementioned complex is the result of slow N=N bond cleavage of azobenenze by a masked source of Ti^{II}, $[(ArO)_2Ti(\eta^2\text{-}PhNNPh)(py')_2]$ ($Ar = 2,6\text{-}i Pr_2C_6H_3$, py′ = 4-pyrrolidinopyridine), as depicted in Scheme 18.[64]

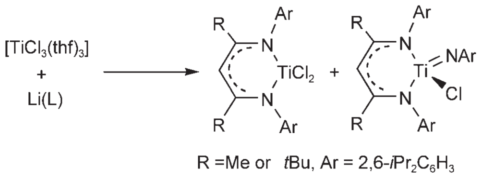


Scheme 18.

Rothwell also detailed the N=N bond cleavage in strained diazenes such as benzo[c]cinnoline, but the mechanism to formation of the Ti=N bond was not discussed.[106] N=N bond reductive cleavage was further explored by Gambarotta[96] and Woo[107] using highly reactive Ti^{II} reagents.

Reductive Cleavage of N−C Bonds

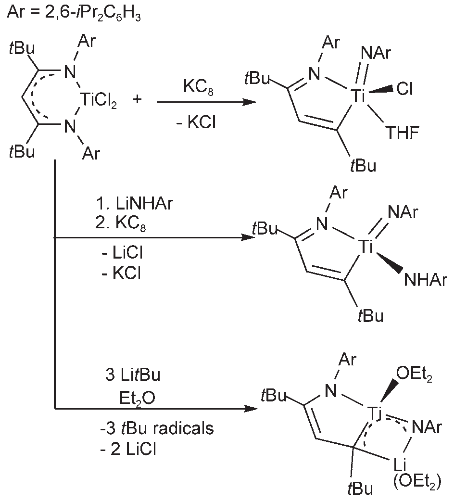
Radical reductive cleavage of N−C bonds with a low-valent titanium radical center is a rare occurrence, but has been documented. Roesky[108] and Mindiola[45] have reported the isolation of terminal titanium imides of the type [(L)Cl Ti=NAr] (L^- = nacnac or $[ArNC(tBu)]_2CH$, $Ar = 2,6\text{-}iPr_2C_6H_3$) by the transmetalation of LiL with $[TiCl_3(thf)_3]$ (Scheme 19). In addition to the imide–chloride, the expected



Scheme 19.

Ti^{III} complex $[(L)TiCl_2]$ is also isolated from the mixture (when L is the less hindered nacnac, the Ti^{III} material is a dimer composed of bridging chlorides). Formation of the Ti=N linkage from the β-diketiminate "NAr" fragment has been proposed to occur via formation of a putative $[(L)_2TiCl]$ intermediate. A mechanism to formation of the imide has not been proposed, but Roesky and co-workers have observed the cation of $[(L)_2TiCl]$ by EI-MS (L = nacnac).[108] Most notably, by employing a less hindered β-diketiminate ligand such as $[iPrNC(Me)]_2CH$, they were able to show that a monomer $[\{[iPrNC(Me)]_2CH\}_2TiCl]$ could be isolated, and such species could then slowly decompose to the imide dimer $[\{([iPrNC(Me)]_2CH)Ti{=}NAr(\mu_2\text{-}Cl)\}_2]$ over a period of three months.[108]

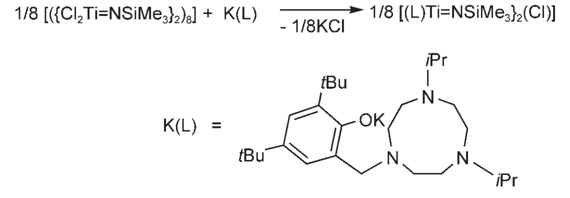
β-Diketiminates can also act as "NAr" transfer reagents in certain multi-electron redox processes. For example, the compound $[\{[ArNC(tBu)]_2CH\}TiCl_2]$ ($Ar = 2,6\text{-}iPr_2C_6H_3$) can be treated with KC_8 or three equivalents of a reductant such as Li*t*Bu to form titanium imides supported by the azabutadienyl scaffold, namely $[(ArN\{tBu)CCHC(tBu)\}Ti{=}NAr(thf)Cl]$ and $[Li(Et_2O)][(ArN(tBu)CCHC(tBu))Ti{=}NAr(Et_2O)]$ (Scheme 20).[109] Likewise, C−N cleavage occurred to form the imide–anilide $[\{ArN(tBu)CCHC(tBu)\}Ti{=}NAr(NHAr)]$ when $[\{[ArNC(tBu)]_2CH\}TiCl(NHAr)]$ was reduced with KC_8 (Scheme 20).[109] Stephan and co-workers have proposed compounds similar to $[\{ArN(tBu)CCHC(tBu)\}Ti{=}NAr(thf)Cl]$ as likely intermediates in their reduction studies of Ti^{III} precursors using a less hindered β-diketiminate ligand, nacnac.[110] Similarly, Tokitoh and co-workers have shown that two- and one-electron reductions of Ti^{IV} and Ti^{III} precursors, respectively, can lead to C−N rupture when applying the unsymmetrically substituted β-diketiminate ligand MesNC(Me)CHC(Me)N(Tbt) (Tbt = 2,4,6-$\{(Me_3Si)_2CH\}_3C_6H_2$ and Mes = 2,4,6-$Me_3C_6H_2$).[111,112] A Ti^{II} intermediate was implicated in these studies, since treatment of the lithium β-diketiminate salt with Gambarotta's Ti^{II} precursor, $[TiCl_2(tmeda)_2]$, generated the identical Ti^{IV} imides resulting from reductive C−N bond rupture.[111]



Scheme 20.

Oligomerization Breakup

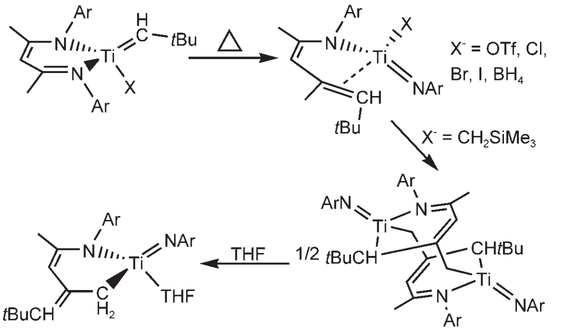
Imide aggregates can sometimes be broken into the corresponding monomer by salt elimination reactions or treatment with strong donating ligands such as pyridine, TMEDA, and other chelates. One clear illustration of such an approach has been reported by Mountford and co-workers using $[\{Cl_2Ti{=}NSi(Me)_3\}_8]$ and eight equivalents of K(L) to break the bridging chlorides and afford the terminal and monomeric imide $[\mathrm{(L)ClTi{=}N\{Si(Me)_3\}}]$ (Scheme 21).[46] This process is versatile in the sense that the ligand in question can also be neutral to make cationic imide chlorides. Bridging imides can be broken into their monomers; such is the case when $[\{\{\mathrm{(CyN)_2C(Me)}\}_2\mathrm{TiCl}(\mu_2\text{-N}t\mathrm{Bu})\}_2]$ is treated with LiCp to generate the monomeric and terminal imide complex $[\{\mathrm{(CyN)_2C(Me)}\}\mathrm{Ti{=}N}t\mathrm{Bu(Cp)}]$.[113] Other examples of monomeric terminal imides prepared by breaking dimers or oligomers have been documented.[27,38,113–115]



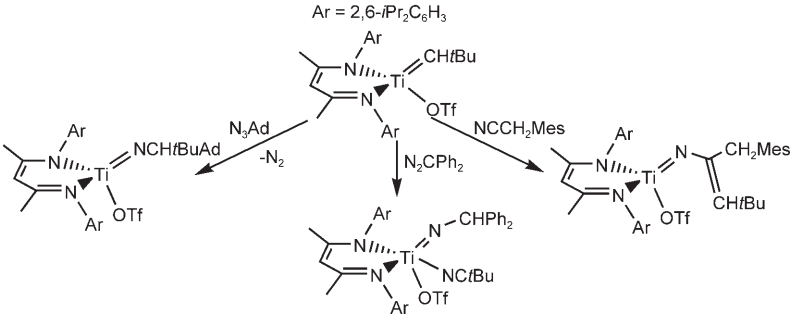
Scheme 21.

Wittig-Like Reactions

The paucity of kinetically stable complexes bearing the highly polarized Ti=C and Ti=P functional groups has limited the exploration of Wittig-like reactions involving imines or aldimines to afford the corresponding Ti=NR ligand. Doxsee and co-workers have reported Wittig-like chemistry for transient "$[\mathrm{Cp_2Ti{=}CH_2}]$" with nitriles to make titanium imides.[23,98,116] Recent studies by Mindiola and co-workers have shown that $[\mathrm{(nacnac)(X)Ti{=}CHR}]$ ($\mathrm{R} = t\mathrm{Bu}$, $\mathrm{X^-} = \mathrm{OTf}$, Cl, Br, I, $\mathrm{BH_4}$, and $\mathrm{CH_2SiMe_3}$;[73,75,76] $\mathrm{R} = \mathrm{SiMe_3}$, $\mathrm{X^-} = \mathrm{OTf}$[117]), can undergo intramolecular Wittig-like reactions of the alkylidene ligand with the imine residue of the β-diketiminate to form the titanium imide group (Scheme 22 displays Wittig-like reaction when $\mathrm{R} = t\mathrm{Bu}$). When $\mathrm{X} = \mathrm{CH_2SiMe_3}$, the Wittig-like transformation results in additional activation of the ligand (by C–H activation, Scheme 22).[76] Removal of steric bulk from the alkylidene, but increased steric hindrance at the β-carbon group of the diketiminate (e.g., tBu), as in the case of $[\{[\mathrm{ArNC}(t\mathrm{Bu})]_2\mathrm{CH}\}\mathrm{Ti{=}CH}i\mathrm{Pr(OTf)}]$, also results in Wittig-like chemistry to generate the imide functionality.[118] However, intermolecular Wittig-like reactions can be exploited if the substrate in question is reactive enough to surpass the rate of the intramolecular Wittig-like transformation. Hence, $[\mathrm{(nacnac)(OTf)Ti{=}CH}t\mathrm{Bu}]$ reacts rapidly with $\mathrm{N_3Ad}$ (Ad = 1-adamantyl), $\mathrm{NCCH_2Mes}$ ($\mathrm{Mes} = 2,4,6\text{-}\mathrm{Me_3C_6H_2}$), and $\mathrm{N_2CPh_2}$ to afford titanium products in which the imide group has been swiftly incorporated (Scheme 23).[75] Formation of the imide and nitrile group from N=N cleavage in the diazoalkane unit is unique and could be classified best as an N=N bond cleavage reaction rather than a Wittig-like process.[75] A similar version of this reaction has also been observed between a titanium phosphinidene and $\mathrm{N_2CPh_2}$.[78]

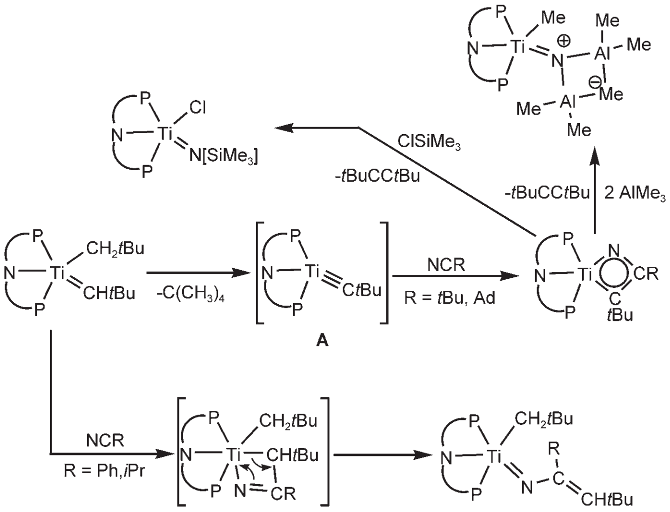


Scheme 22.



Scheme 23.

The ability to generate transient titanium alkylidynes[119,120] from the PNP pincer-type framework prompted the exploration of Wittig-like reactions with this rare ligand type. For example, sterically hindered nitriles such as NCtBu and NCAd react with $\mathrm{(PNP)Ti{\equiv}C}t\mathrm{Bu}$ (generated from $[\mathrm{(PNP)Ti{=}CH}t\mathrm{Bu(CH_2}t\mathrm{Bu)}]$) to afford the first examples of stable azametallacyclobutandienes rings, namely $[\mathrm{(PNP)Ti\{C(}t\mathrm{Bu)C(R)N\}}]$ ($\mathrm{R} = t\mathrm{Bu}$, Ad).[103] Addition of $\mathrm{Me_3SiCl}$ to the latter leads to the formation of the imide $[\mathrm{(PNP)ClTi{=}N(SiMe_3)}]$ concurrent with extrusion of the alkyne tBuCCR, thus clearly indicating that a triple bond alkylidyne with nitrile metathesis has taken place (Scheme 24). The use of ^{15}N-enriched nitrile, ^{15}NCAd, unambiguously confirmed that the imide nitrogen in $[\mathrm{(PNP)Cl\,Ti{=}N(SiMe_3)}]$ originated from the nitrile. If less bulky nitriles are used, such as NCR ($\mathrm{R} = i\mathrm{Pr}$ and Ph), Wittig-like chemistry occurs at the alkylidene moiety of $[\mathrm{(PNP)Ti{=}CH}t\mathrm{Bu(CH_2}t\mathrm{Bu)}]$ to yield the imides, $[\mathrm{(PNP)Ti{=}NC(R){=}CH}t\mathrm{Bu(CH_2}t\mathrm{Bu)}]$, depicted in Scheme 24.[103] Extrusion of the alkyne is not limited to $\mathrm{Me_3SiCl}$ alone, inasmuch as two equivalents of $\mathrm{AlMe_3}$ also promotes metathesis in $[\mathrm{(PNP)Ti\{C(}t\mathrm{Bu)C(}t\mathrm{Bu)N\}}]$ to yield the zwitterionic titanium

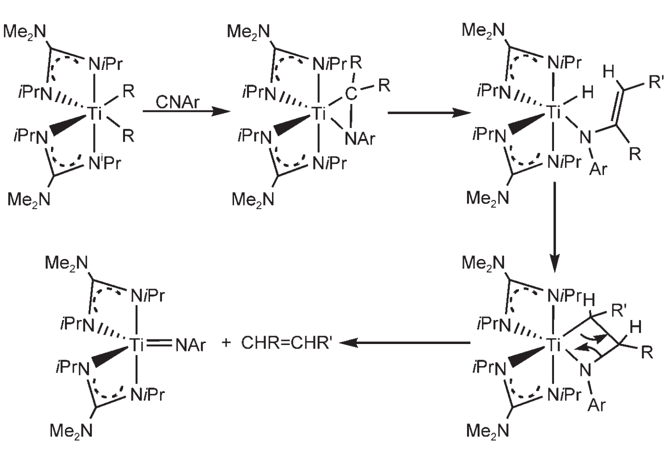


Scheme 24.

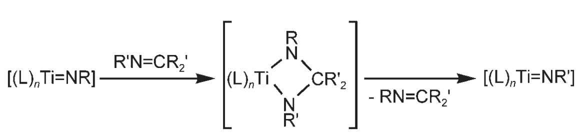
imide complex [(PNP)Ti=N{$Al_2(Me)_4$(μ-Me)}(Me)] (Scheme 24).[103]

Another documented case of a Wittig-like reaction to produce titanium imides was reported by Richeson and coworkers.[54] In their studies a bis-guanidinate titanium bisalkyl underwent double insertion of a bulky isonitrile NCAr (Ar = 2,6-$Me_2C_6H_3$) to eventually afford the terminal aryl imide [{(Me_2N)C(N*i*Pr_2)$\}_2$Ti=NAr] (Scheme 25). Formation of the imide was proposed to occur by isonitrile insertion into the Ti−R bond (R = Me or CH_2Ph) to form a metalla-azaridine intermediate, followed by β-hydride elimination and reinsertion to generate an azatitanacyclobutane complex, which would then undergo [2+2] retrocycloaddition to furnish the titanium aryl imide and olefin.[54] We refer to this transformation as a Wittig-like reaction since the last step leading to imide bond formation conceptually involves the metathesis of an alkylidene group with an imine moiety.

Lastly, aldimines[26] and imines,[56] can undergo metathesis with titanium imides to generate new imide ligands via a ureate intermediate.[4] Likewise, carbodiimides can also undergo exchange with the titanium imide group.[31] Scheme 26 displays a prototypical imine cross-metathesis reaction. As in the case of transimination, this approach requires a preassembled and reactive titanium imide in order to achieve “NR” transfer.



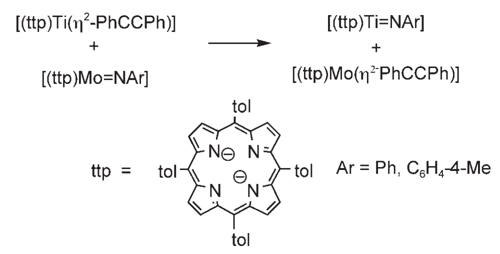
Scheme 25.



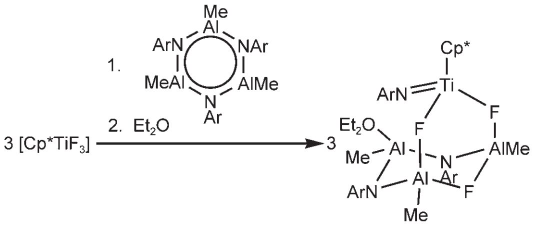
Scheme 26.

Intermetal Imide-Group Transfer

The concept of intermetal imide-group transfer is a rare occurrence in titanium chemistry. To date, the two only documented cases of titanium imide formation by the use of a M=NR transfer reagent were reported by Woo[121] and Roesky.[122] Woo's strategy was to treat a low-valent Ti^{II} precursor with a “NAr”-group transfer reagent such as Mo^{IV}=NR (Scheme 27).[121] For Roesky's system, the imide-group transfer reagent in question was a trimeric iminoalane reagent [{MeAlNAr$\}_3$] (Ar = 2,6-*i*$Pr_2C_6H_3$, Scheme 28).[122] Accordingly, when the titanium trifluoride precursor [Cp*TiF_3] is treated with [{MeAlNAr$\}_3$], and the intermediate treated with Et_2O, the terminal imide complex depicted in Scheme 28 is obtained. Et_2O is used to break any Al···N(Ar)Ti interactions in order to make the imide group on titanium terminal.[122]



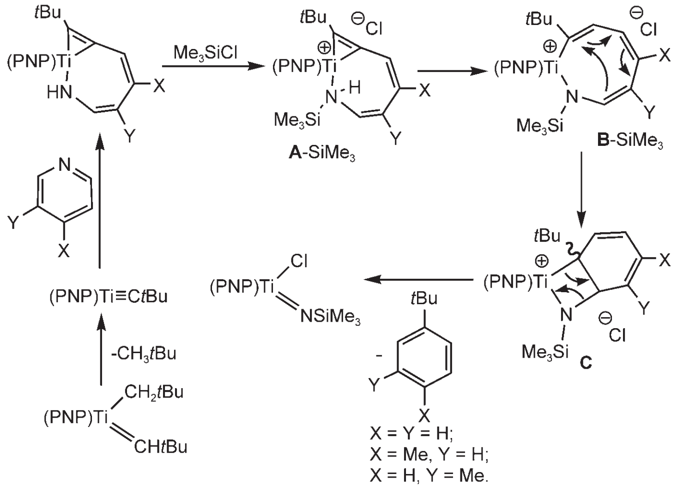
Scheme 27.



Scheme 28.

Nitrogen-Atom Transfer by Denitrogenation of N-Heterocycles

The use of N-heterocycles as a source of nitrogen is an unprecedented phenomenon in organometallic chemistry and represents an elegant entry to a nitride or imide group. Given the ability of the titanium alkylidyne $[(PNP)Ti{\equiv}C\mathit{t}Bu]$ to ring-open N-heterocycles, such as pyridines and picolines, this system provides interesting azametallabicyclic frameworks that are poised to undergo arene extrusion processes.[123] Accordingly, when the synthon to $[(PNP)Ti{\equiv}C\mathit{t}Bu]$, $[(PNP)Ti{=}CH\mathit{t}Bu(CH_2\mathit{t}Bu)]$, reacts with pyridine or 3- or 4-picolines, the azametallabicyclic compounds $[(PNP)Ti\{C(\mathit{t}Bu)CC_4H_3RNH\}]$ (R = H or Me) are formed in quantitative yield (Scheme 29).[102,123] Treatment of the latter compounds with $ClSiMe_3$ at 65 °C over three days generates the trimethylsilylimide $[(PNP)ClTi{=}N(SiMe_3)]$ by Ar*t*Bu extrusion (Ar = C_6H_5, 4-MeC_6H_4, 3-MeC_6H_4). Formation of $[(PNP)ClTi{=}N(SiMe_3)]$ from $[(PNP)Ti\{C(\mathit{t}Bu)CC_4H_3RNH\}]$ and Me_3SiCl is proposed to occur through silylation of the α-nitrogen composing the azametallabicyclic ring (intermediate **A**), followed by a ring expansion applying a 1,3-hydrogen shift to afford the 8-membered ring intermediate **B**. Invoking an electrocyclic rearrangement, it is proposed that intermediate **B** would ring-contract to generate intermediate **C**, which undergoes a [2+2] retrocycloadditon to extrude the substituted benzene product and to finally engender trimethylsilylimide-chloride formation (Scheme 29).[102]



Scheme 29.

Future Outlook

Simplistic to rather sophisticated synthetic strategies have been applied to incorporate low-coordinate, terminal imides of unparalleled reactivity. These syntheses have now evolved from the more common deprotonation pathways to more elegant methods such as denitrogenation. The latter being useful as a model for the purification of crude oil, an industrial process known as hydrodenitrogenation. Preliminary results indicate that compounds such as $[(PNP)ClTi{=}N(SiMe_3)]$ can be converted readily to $[(PNP)TiCl_3]$ by deimination with two equivalents of $MoCl_5$ (Me_3SiCl and insoluble $[Mo_2Cl_7(\mu_2\text{-}N)]$ are byproducts). The compound $[(PNP)TiCl_3]$ can be then smoothly transformed to $[(PNP)Ti(CH_2\mathit{t}Bu)_2]$ by a one-electron reduction and subsequent alkylation. The latter is a known precursor to $[(PNP)Ti{=}CH\mathit{t}Bu(CH_2\mathit{t}Bu)]$, thereby closing the cycle for the denitrogenation of N-heterocycles by a titanium reagent.[102] This result implies that such a reaction has the potential to becoming catalytic, and that the imide ligand in question plays a crucial role in the cycle for the denitrogenation of N-heterocycles. In addition, titanium imides play an important role in other industrial processes such as olefin metathesis and polymerizations, sometimes either stabilizing the active catalyst or simply contributing as an ancillary ligand on the metal center. The imide functionality also offers a unique opportunity to be utilized as a precursor in the formation of the unknown terminal titanium nitride, a molecule that will more than likely possess comparable reactivity to transient titanium alkylidynes. Given that titanium imides are transferable groups in organic reactions as well as potential precursors to nitrides, this class of ligand will constantly challenge current paradigms of reactivity.

Acknowledgements

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