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Reactivity of terminal imido complexes of group 4—6 metals: stoichiometric and catalytic reactions involving cycloaddition with unsaturated organic molecules

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Abstract

Imido complexes of early transition metals are key intermediates in the synthesis of many nitrogen-containing organic compounds. The metal—nitrogen double bond of the imido moiety undergoes [2+2] cycloaddition reactions with various unsaturated organic molecules to form new nitrogen—carbon and nitrogen—heteroatom bonds. This review article focuses on reactivity of the terminal imido complexes of Group 4—6 metals, summarizing their stoichiometric reactions and catalytic applications for a variety of reactions including alkyne hydroamination, alkyne carboamination, pyrrole formation, imine metathesis, and condensation reactions of carbonyl compounds with isocyanates.

Keywords

Terminal imido complex; Early transition metals; Group 4—6 metals; Cycloaddition; Nitrogen-containing organic compound

1. Introduction

Early transition metal imido complexes bearing a dianion of primary amines, $[\text{RN}]^{2-}$, as a supporting ligand have attracted considerable attention in the field of organometallic chemistry due to their diverse utility as reactive intermediates in organic synthesis as well as electron-donating supporting ligands for many types of metal catalysts, such as those used in olefin polymerization and alkene metathesis [1–3]. The metal—nitrogen double bond of

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terminal imido complexes undergoes various types of reactions, including cycloaddition with unsaturated bonds [4]; aliphatic and aromatic C—H bond activation [5,6]; and imido group transfer [7,8]. Among them, [2+2] cycloaddition of imido ligands with unsaturated organic molecules such as alkynes, alkenes, carbonyls, and imines is perhaps the most attractive fundamental reaction owing to its wide applicability to various stoichiometric and catalytic organic transformations. Many nitrogen-containing organic compounds can be produced via the corresponding four-membered [2+2] cycloadducts **A** and **B** followed by protonation or further insertion of additional unsaturated organic molecules, as representatively shown in Scheme 1.

Given the synthetic attractiveness of terminal imido complexes, comprehensive studies on the synthesis of the terminal imido moiety have been conducted [9]. The most common routes for metal imido synthesis are shown in Figure 1, and include: (1) dehydrohalogenation of metal halides and primary amines in the presence of two equivalents of base (Figure 1(a)) [10]; (2) deprotonation of primary amines by alkyl- and amidometal complexes (Figure 1(b)) [11]; (3) 2-electron oxidation of a low valent metal center by organic azides (R-N₃), with expulsion of N₂ (Figure 1(c)) [12]; (4) metathesis of metal oxos and isocyanates along with release of CO₂ (Figure 1(d)) [13]; and (5) bimetallic 4-electron cleavage of the N=N double bond of azo compounds (R-N=N-R) by low-valent metal centers (Figure 1(e)) [14]. Each of these methods have advantages and disadvantages; for example, while dehydrohalogenation reactions rely on the coupling of simple reagents, removal of salt byproducts is can be challenging; similarly, organic azides benefit from having N₂ as the only byproduct, but suffer from potential explosion hazards.

Depending on the coordination environment of the metal and the stereoelectronic properties of the imido fragment, bridging coordination modes are also possible due to the presence of the L-type lone pair on the nitrogen atom; however, such imido-bridged complexes are often unreactive and are rarely seen in catalytic reactions except as off-cycle intermediates.[15a] In this review, we focus on the reactivity of mononuclear group 4—6 metal complexes having terminal imido ligands, and summarize their stoichiometric and catalytic organic transformations initiated by cycloaddition of the M=N bond with unsaturated organic molecules.

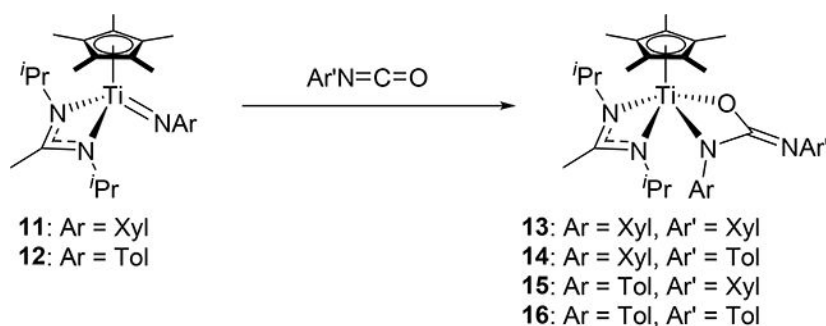
2. Stoichiometric reactions

2.1. Cycloaddition reactions

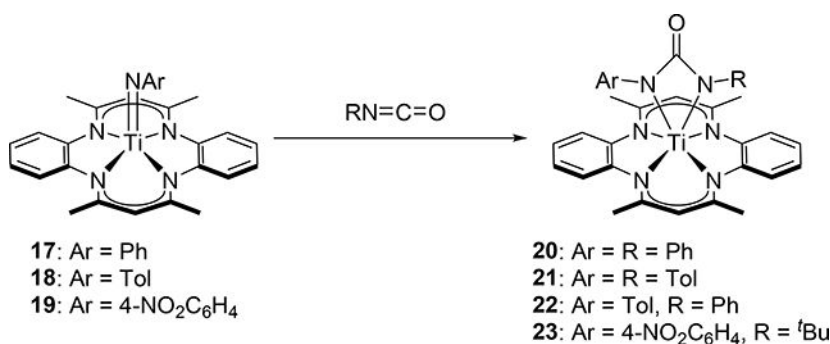
The terminal imido fragment, M=NR, of mononuclear imido complexes undergoes [2+2] cycloaddition with various unsaturated organic compounds such as alkynes, nitriles, alkenes, phosphalkynes, imines, carbonyls, and heterocumulenes to give the corresponding four-membered azametallacycles. Bergman *et al* reported that the Zr=N^tBu fragment of Cp₂Zr(=N^tBu)(thf) (**1**) reacted with alkynes, alkenes, imines, and carbodiimides to provide the corresponding [2+2] cycloaddition products (Scheme 2), during which a coordinatively unsaturated terminal imido species **2** was generated *in situ* by releasing the coordinated THF [15]. Terminal and internal alkynes reacted smoothly to give the corresponding azazirconacyclobutenes **3**, while the reactions with alkenes such as ethylene and norbornene to give the corresponding azazirconacyclobutanes **4** were reversible. When imines or

carbodiimides were used as the substrates, cycloaddition reactions with their C=N bonds led to the formation of diazazirconocyclobutanes **5** and **6**, respectively. In contrast, treatment of **1** with carbonyl compounds such as aldehydes, ketones, and isocyanates gave an oligomeric oxozirconocene **9** along with the corresponding imines and carbodiimides through a metathesis-type fission of the nascent intermediates **7** and **8** due to the thermodynamic stability of the Zr—O bond (Scheme 2) [15e,f]. Organic azides underwent [3+2] cycloaddition with **1** to yield five-membered tetraazametallacycle **10** via the same intermediate **2** (Scheme 2) [15d].

In the same manner as the formation of **8**, Mountford *et al* discovered that the half-titanocene imido complexes **11** and **12** add aryl isocyanates to form azaoxametallacycles **13–16**, which were isolated and crystallographically characterized, in which the Ti=N bond selectively underwent [2+2] cycloaddition with C=O bond of the isocyanates (eq 1) [16]. In sharp contrast, the C=N bond of the isocyanates preferentially reacted with a sterically less bulky Ti=N bond of **17–19** (eq 2) [17]. The different regioselectivity for the cycloaddition of the C=O and C=N moieties to the Ti=N bond is ascribed to the steric crowding around the metal, where the terminal atom or less sterically-hindered side of the substrate interacts with zirconium.



(1)



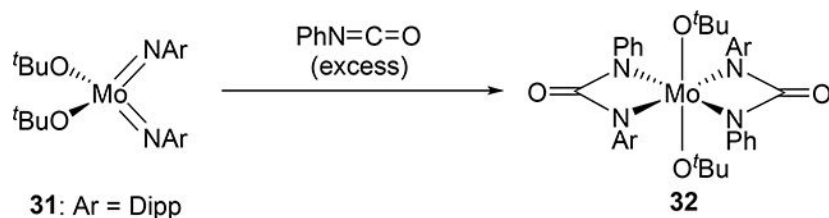
(2)

Titanium complex **24** reacted with carbon-heteroatom triple bonds, i.e. *tert*-butylphosphaalkyne and acetonitrile, to give the corresponding four-membered

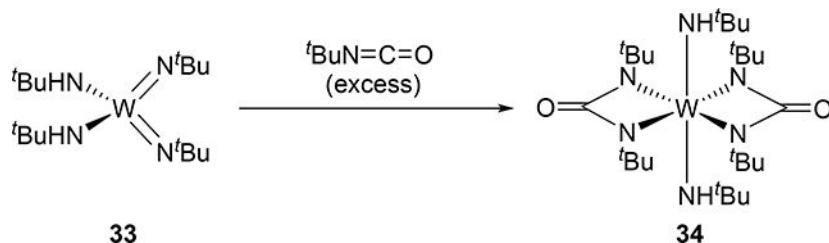
azatitanacycles **25** and **26**, where the pyridyl arm has dissociated from the metal center due to steric crowding around titanium (Scheme 3) [18]. The cycloaddition with *tert*-butylphosphaalkyne afforded titanacycle **25** with the phosphorous atom at the β -position, while cycloaddition with acetonitrile produced diazatitanacycle **26** with the two nitrogen atoms at the α -positions. The opposite regioselectivity for **25** and **26** was attributed to the different polarity of each triple bond.

Titanocene-based imido complexes **28** and **29**, synthesized and recently reviewed by Beckhaus *et al* [19a,b], show similar reactivity patterns to zirconocene-based **2**, including cycloadditions of alkynes, carbodiimides, nitriles, and other small molecules (Scheme 4). However, they are derived from the fulvalene complex **27**, forming the imido group through internal deprotonation of the amine. Additionally, the hydrazido complex **30** is also accessible through this method and shows the same substrate reactivity patterns [19c].

Bis(imido) and tris(imido) complexes react with isocyanates in a manner similar to **2**, where one imido ligand will undergo [2+2] cycloaddition but the other imido ligand will often act as an unreactive spectator ligand [20]. Exceptional examples are that both of the imido ligands of bis(imido) bis(alkoxide) molybdenum complex **31** and bis(imido) bis(amido) tungsten complex **33** reacted with isocyanates to give bis(diazametallacyclic) compounds **32** and **34** (eqs 3 and 4) [21]. These are also notable as group 5 and 6 mono(imido) complexes are typically less reactive than group 4 complexes, and in many cases, the imido ligand on the group 5 and 6 mono(imido) complexes behave only as spectator ligands. Other exceptions are known, however, including a cationic vanadium mono(imido) complex that undergoes [2+2] reactions with alkynes. [22].



(3)



(4)

Unusual [2+2] cycloaddition products were obtained when bis(imido)vanadium complex **35** reacted with 2-butyne and ethylene (Scheme 5) [23]. Horton *et al* reported that the treatment of complex **35** with 2-butyne at 25 °C resulted in C—H bond activation of the imido Si^tBu moiety to give η^3 -azaallyl-coordinated complex **37** via σ -bond metathesis from the intermediate [2+2] cycloadduct **36**. Ethylene also underwent cycloaddition to give **38**, which was converted to an ethenyl complex **39** through retro-[2+2]-cycloaddition to regenerate **35** and subsequent 1,2-addition of the vinylic C—H bond of ethylene. The unusual reactivity of **35** with alkyne and alkene is probably related to high nucleophilicity of the imido nitrogen atom, resulting from competition for the π -donation from the imido nitrogen atom to the vanadium center.

Arnold *et al* investigated the cycloaddition reactivity of the monoazabutadiene bis(imido)niobium complex **40** toward alkynes and alkenes. Treatment of **40** with diphenylacetylene resulted in the formation of eight-membered metallacycle species **41** by the involvement of the phenylimido ligand, whereas reaction with 3-hexyne or norbornene showed different regioselectivity, incorporating the *tert*-butylimido ligand into the eight-membered ring of **42** or **43** (Scheme 6) [24a]. Based on density functional theory (DFT) calculations, the reaction mechanism for the formation of eight-membered metallacycle **41** was proposed to involve [2+2] cycloaddition step with the imido ligand followed by C—C bond formation through a conjugative addition to the monoazabutadiene moiety (Scheme 7). When *para*-bromobenzaldehyde was added to complex **40**, the oxo-bridged imidoniobium dimer **42** was formed via a [2+2] cycloaddition-reversion sequence [24a]. The imido ligand of **40** underwent [3+2] cycloaddition with *tert*-butylazide to afford tetraazametallacyclic species **45** that reversibly converts to a γ -coordinated azido complex **46** [24b]. In addition, [4+2] cycloaddition was observed in the reaction between the Nb=N bond of **47** and (*E*)-4-chlorochalcone [24a].

Azido group activation has also been reported in niobium complex **49** bearing a β -diketiminato (BDI) ligand and an imido group (Scheme 8).[24c] An intermediate analogous to **45** is proposed in this reaction, however, unlike **45**, photolysis of the azido-imido complex **49** is required for its formation. The transient tetraazametallacycle intermediate is unstable and spontaneously releases dinitrogen to form the borane-capped nitride **50**.

A low-valent (BDI)Nb imido complex has also reacted via addition of a Ph-C fragment to the imido bond. When **51** is subjected to hydrogenolysis in α,α,α -trifluorotoluene, the resulting Nb(III) fragment is initially stabilized by the coordination of α,α,α -trifluorotoluene in an η^6 manner in **52** (Scheme 9).[25] DFT studies propose that the bound PhCF₃ is dearomatized via initial C-F bond abstraction, which then undergoes cycloaddition to the imido group. Subsequent C-F abstraction steps ultimately give the product **53** containing a monoanionic η^2 -bound imine. In the presence of aryl fluorides, the C-F bonds are cleaved by niobium, but no cycloaddition occurs.[25b]

2.2. Insertion reactions into azametallacycles

Bergman *et al* demonstrated that it is possible to engender further insertion reactions into the four-membered azazirconacyclobutene **54**, generated by [2+2] cycloaddition between

zirconocene imido complex with 1-phenylpropyne (Scheme 10) [26]. Reactions of **54** with aldehydes, imines, and carbodiimides gave the corresponding six-membered metallacycles **55**, **56**, and **58** *via* insertion of the C=O and the C=N moieties into the metal-carbon bond of the metallacycle **54**. Further heating these complexes over 100 °C in benzene resulted in the formation of Cp₂Zr(=E) (**9**: E = O, Section 2.1; **57**: E = NR) as well as the corresponding dimers and oligomers due to the formation of thermodynamically stable Zr-O and Zr-N bonds accompanied by the release of corresponding α,β-unsaturated imines. Addition of organic azides to **54** afforded seven-membered metallacycle **59**. Insertion reactions of nitriles into azatitanacyclobutenes was reported by Livinghouse *et al.*: titanacycle intermediate **62**, which was generated by intramolecular [2+2] cycloaddition of **61**, reacted with isobutyronitrile to give six-membered titanacycle **63** and further protonation afforded a vinylogous amidine (Scheme 11) [27].

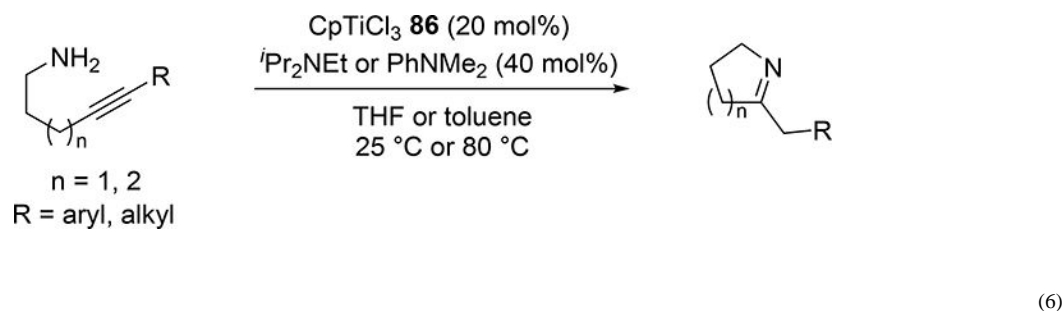
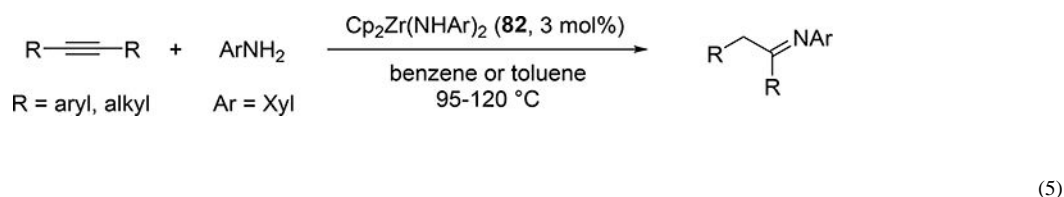
Mountford *et al.* demonstrated that tridentate diamidopyridine Ti imido complexes **64** and **65** reacted with arylacetylenes to form four-membered azametallacyclobutenes **66**–**69** followed by further insertion of one equivalent of arylacetylene into the titanium–carbon bond to give six-membered azametallacyclohexadienes **70**–**74** (Scheme 12) [28]. The four-membered and six-membered metallacycles were each obtained as single isomers as a result of steric repulsion in the [2+2] cycloaddition between the aromatic ring of the arylacetylene and the imido substituent, and in the second insertion between the arylacetylene and the diamidopyridine ligand. Complexes **64** and **65** were found to be catalysts for the hydroamination of arylacetylenes with primary amines *via* four-membered intermediates **66**–**69**; however, the formation of six-membered azatitanacyclohexadienes **70**–**73** was regarded as a deactivation pathway in the catalytic system. Similarly, Odom *et al.* reported that the reaction of bis(imido)metal complexes of molybdenum **74** and tungsten **75** with a ring-strained and highly reactive alkyne, cyclooctyne, gave the corresponding six-membered metallacycles **78** and **79** [29]. In this reaction, one of two imido ligands underwent [2+2] cycloaddition with cyclooctyne to give intermediate azametallacyclobutenes **76** and **77**, followed by the subsequent insertion of cyclooctyne into the M–C bond of the metallacycle, giving the six-membered metallacyclic species **78** and **79** (Scheme 13). Notably, thermolysis of **78** and **79** resulted in the formation of the corresponding pyrrole derivative by reductive elimination together with the low-valent imido species **80** and **81**.

3. Catalytic reactions

3.1. Catalytic hydroamination

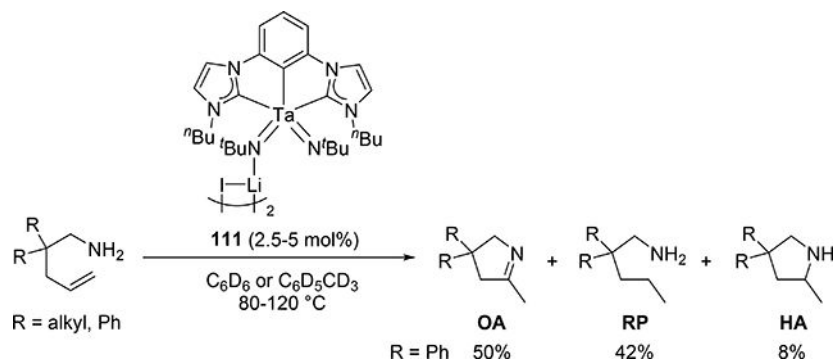
Catalytic hydroamination reaction of alkynes with amines involves a typical [2+2] cycloaddition reaction as the initial step, and subsequent protonolysis of the resulting M–C bond of the four-membered azametallacyclobutene intermediate by amine is a key step to catalytically produce the hydroaminated compounds [30]. Bergman *et al.* developed an intermolecular hydroamination reaction of internal alkynes with aniline derivatives using bis(amido)zirconocene, Cp₂Zr(NHAr)₂ (Ar = Xyl, **82**), as a catalyst to give the corresponding imines (eq 5) [31]. As shown in Scheme 14 for the reaction mechanism, a catalytically active imido species **83**, similar to **2** (Section 2.1), is generated by α-hydrogen elimination of one of two amido ligands of the bis(amido)zirconocene **82** with liberation of

one equiv of an aniline derivative, and *in situ*-generated **83** reversibly undergoes [2+2] cycloaddition with alkynes to form an aziriconacyclobutene intermediate **84**, whose Zr—C bond is subsequently protonated by aniline derivatives, giving an amido-enamido species **85**. Finally, α -elimination of **85** regenerates the imido species **83** together with enamines, the latter of which is isomerized to imines. A kinetic investigation for the catalytic reaction clarified that the reaction obeyed first order rate dependence on the concentration of zirconium catalyst **82** and alkyne, as well as inverse first order rate dependence on the concentration of amine, indicating that the rate-determining step is α -hydrogen elimination of the amido ligand in **82**. Livinghouse *et al* reported an intramolecular version of the hydroamination reaction of γ - and δ -aminoalkynes catalyzed by half-titanocene trichloride, CpTiCl₃ (**86**), in the presence of tertiary amines as bases to afford the corresponding five-membered and six-membered cyclic imines (eq 6) [11d,27]. After these pioneering works by Bergman and Livinghouse, various metallocene, half-metallocene, and non-metallocene catalysts of Group 4 and 5 metals have been intensively investigated, with a wide variety of complexes and ligands discovered to perform this reaction, shown in Figure 2 [32]. Figure 3 shows hydroamination reactions of other unsaturated organic molecules such as alkenes, allenes, and dienes, whose details were highlighted in recent reviews [30,33].



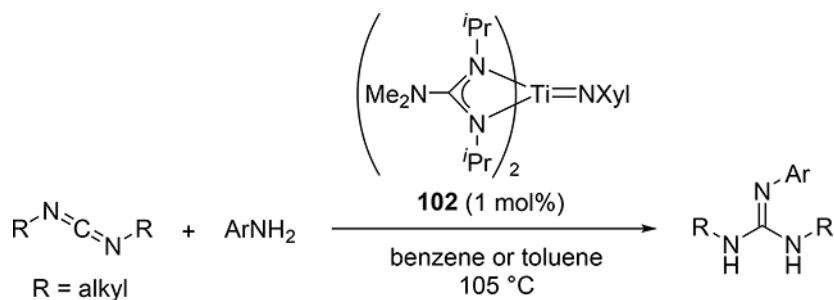
When bis(imido)tantalum complex **111** was combined with 4-pentenylamine derivatives, the major product was determined to be a cyclic imine as oxidative amination product (**OA**) together with reduction product (**RP**) and small amounts of hydroamination product (**HA**) (eq 7) [34]. Several control experiments and DFT studies by Webster *et al* proposed the reaction mechanism as shown in Scheme 15 [35]. One of two imido ligands of **111** exchanges with the substrate, followed by intramolecular [2+2] cycloaddition. The resulting metallacycle intermediate **113** undergoes β -H elimination to give enamido hydrido species **114**, which is protonated by the substrate to yield an enamine. Intermediate **115** catalytically isomerize the enamine to the imine **OA**. Bis(imido) intermediate **116** is regenerated from complex **115** by reduction of the substrate to **RP**. Such a highly active imido Ta=N moiety was achieved by introducing an electron-donating NHC ligand and a second imido ligand.

These factors lead to an extreme π -loading effect, in which the imido π bonds are weakened and rendered more reactive due to multiple π bonds with the same metal orbitals competing for electron density. Reflecting this property, no reaction was observed when 4-pentenylamine was treated with 5 mol% of the mono(imido)tantalum complex bearing the same bis(carbene) ligand, even at 170 °C [36].



(7)

The hydroamination reaction of a C=N bond in carbodiimides with aromatic amines to give guanidines, so-called catalytic guanylation [37], was developed by Richeson *et al* using titanium imido catalyst **102** (eq 8) [38]. The reaction mechanism is essentially the same to the alkyne hydroamination, in which the reaction initiates by [2+2] cycloaddition between Ti=N and C=N bonds of carbodiimides (Scheme 16). Gade *et al* supported this mechanism by characterizing the diazametallacycle intermediate as well as the kinetic study of the hydrohydrazination of carbodiimide catalyzed by titanium hydrazido species [39]. Imido complexes of vanadium [40] and niobium [41] also acted as efficient catalysts for the guanylation reactions of amines with carbodiimides; however, the most plausible mechanism involves insertion of carbodiimides into metal—amido bond, where the imido M=N bond is intact.

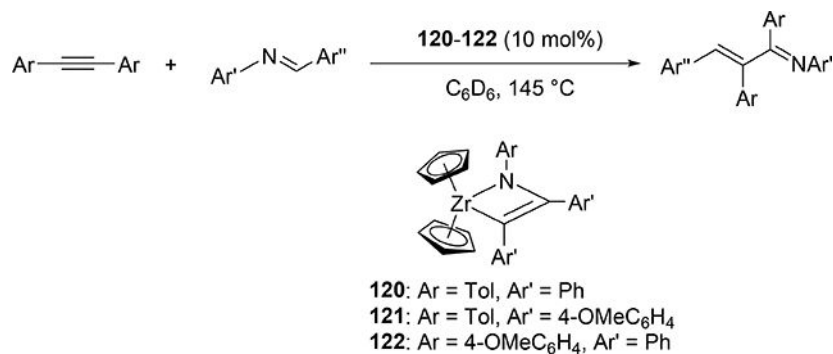


(8)

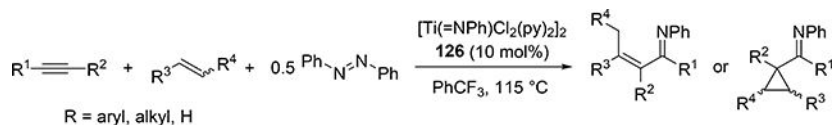
3.2. Catalytic carboamination of alkynes

Carboamination of alkynes is one of the most useful and straightforward methods to form a new C—N bond in organic compounds. Bergman *et al* demonstrated that four-membered

zirronocene catalysts **120**–**122** derived from [2+2] cycloaddition of zirconocene aryl imido species (similar to the alkyl imido-derived complex **3**, Section 2.1) with alkynes served as a catalyst for a carboamination reaction of alkynes with aldimines to give α,β -unsaturated imines (eq 9) [42]. Later, Mindiola *et al* found that cationic β -diketiminate (BDI) titanium imido complexes [(BDI)Ti=NAr(C₆H₅F)][B(C₆F₅)₄] [43a] and [Ti(NMe₂)₃(NHMe₂)] [B(C₆F₅)₄] [42b,c] catalyzed the carboamination of alkynes with aldimines. As shown in Scheme 17, the first step in the catalytic cycle is the formation of azametallacyclobutene **124** *via* [2+2] cycloaddition, and further insertion of aldimines into the M–C bond expands to six-membered intermediate **125**. [4+2]-Retrocycloaddition of **125** regenerates the imido species **123** along with α,β -unsaturated imines. Furthermore, titanium imido complex **126** is a catalyst for the three-component oxidative carboamination of alkynes with alkenes and azobenzenes, generating α,β -unsaturated imines and α -functionalized cyclopropanes (eq 10), in which azobenzene was a source of the imido fragment *via* the N=N bond fission [44]. Scheme 18 shows a plausible reaction mechanism. After the [2+2] cycloaddition of **126** with alkynes to form azatitanacycle **127**, alkene inserts into the metal-carbon bond of **127** followed by β -H elimination and reductive elimination to produce α,β -unsaturated imines (Path A). The alternative pathway is alkene insertion followed by α,γ -reductive coupling to afford α -functionalized cyclopropanes (Path B). Substituents on alkynes differentiate the two reaction pathways from metallacycle **130**. Although Ti^{II}/Ti^{IV} redox mechanism was proposed, a detailed DFT mechanistic study by Wang *et al* suggested that Ti-catalyzed carboamination prefers a redox-neutral mechanism wherein significant backbonding masks the low valent state [45].



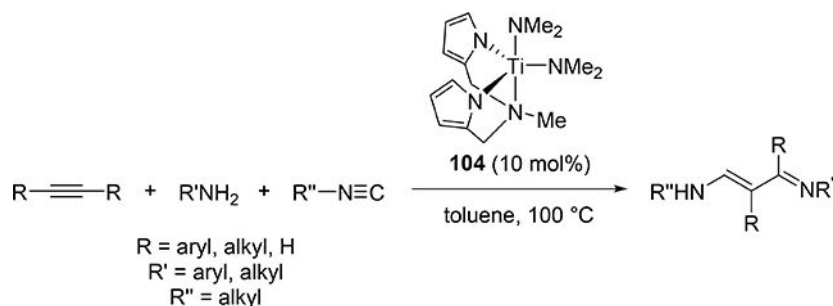
(9)



(10)

Odom *et al* reported that a titanium complex **104** (Section 3.1) catalyzed addition reaction of amines and isocyanides to alkyne to produce α,β -unsaturated β -iminoamines along with a small amount of hydroamination byproducts (eq 11) [46]. The overall reaction is

iminoamination of alkynes; 1,1-insertion of isocyanides into the Ti—C bond of four-membered metallacycle **133** is assumed to be an important step to generate **134**, and subsequent protonolysis by amines gives the final product (Scheme 19).

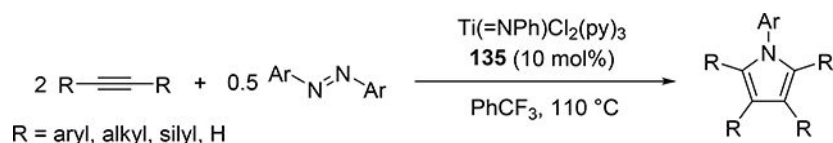


(11)

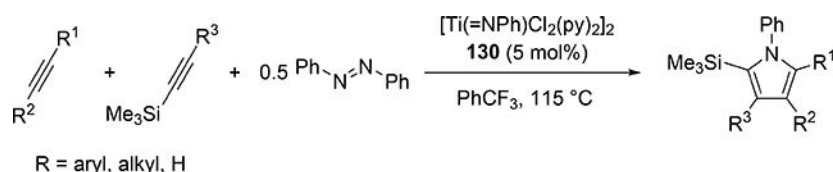
3.3. Catalytic pyrrole formation

Pyrrole skeletons are often present in highly valuable organic molecules [47], and efficient synthetic methods have been extensively investigated [48]. Tonks *et al* reported a catalytic [2+2+1] cycloaddition reaction of 2 equivalents of alkynes and 0.5 equivalent of azobenzene derivatives using titanium imido complex **135** to afford multi-substituted pyrroles in a regioselective manner (eq 12) [49]. The first step is [2+2] cycloaddition of the imido species **135** with one equivalent of alkynes, giving an azatitanacyclobutene **136** (Scheme 20). The second alkyne insertion into the Ti—C bond of **136** produces a six-membered intermediate, azatitanacyclohexadienes **137**, and subsequent reductive elimination affords the corresponding pyrroles and a low valent Ti(II) species **139**, the latter of which is the key species to reductively cleave a N=N bond of azobenzene to regenerate a catalytically active imidotitanium **135**. In fact, low-valent titanium chloride generated in situ from $\text{TiCl}_4(\text{thf})_2$ and zinc powder also worked as a catalyst for the pyrrole formation reaction [50]. Kinetic analysis and theoretical analysis by DFT suggested that the rate determining step is the second alkyne insertion into the titanium-carbon bond [51,52]. Symmetrical and unsymmetrical internal alkynes, terminal alkynes, and diynes were applicable to this pyrrole formation. In addition, chemo- and regio-selective [2+2+1] cross-coupling reactions were achieved when trimethylsilyl-substituted alkynes were used as the substrates (eq 13), in which trimethylsilyl-substituted alkynes are incapable of the initial [2+2] cycloaddition with the Ti=N bond but dominantly insert into the Ti—C bond of the four-membered azatitanacycle intermediate because electron-rich trimethylsilyl alkynes preferentially coordinate to the electron-deficient metal center of azatitanacyclobutenes [53]. Regioselectivity for the insertion of trimethylsilyl-substituted alkynes arises from the α -silyl effect in the transition state (Fig. 4(a)), favoring the SiMe_3 group located at the α -C position in the pyrrole ring to give the 2-silyl pyrrole. Inverse selectivity was observed when the silyl-substituted alkyne bears a Lewis basic directing group such as an *o*-OMe phenyl moiety (eq 14) [54]. The coordination of *o*-OMe group to the Ti center in the alkyne insertion step leads to the selective formation of 3-silyl pyrroles (Fig. 4(b)). In addition, organic azides could be used as an alternative nitrogen source instead of azobenzenes for the [2+2+1] pyrrole

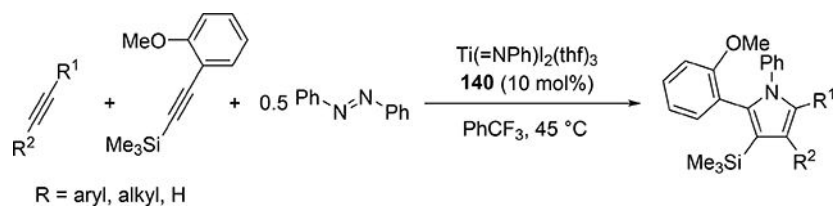
formation when more the Lewis acidic titanium complex, $\text{Ti}(=\text{NTol})\text{I}_2(\text{thf})_3$ (**141**), was used as a catalyst (eq 15) [55]. The use of alkyl azides allows access to *N*-alkyl pyrroles, which cannot be made from the corresponding dialkyl azo compounds due to their radical decomposition under normal catalytic reaction temperatures.



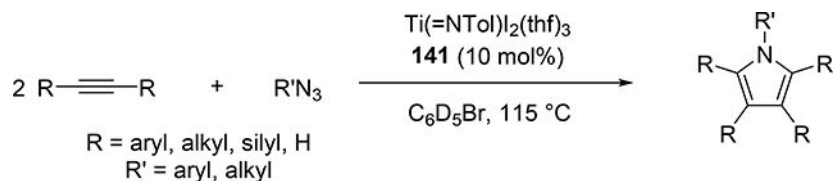
(12)



(13)



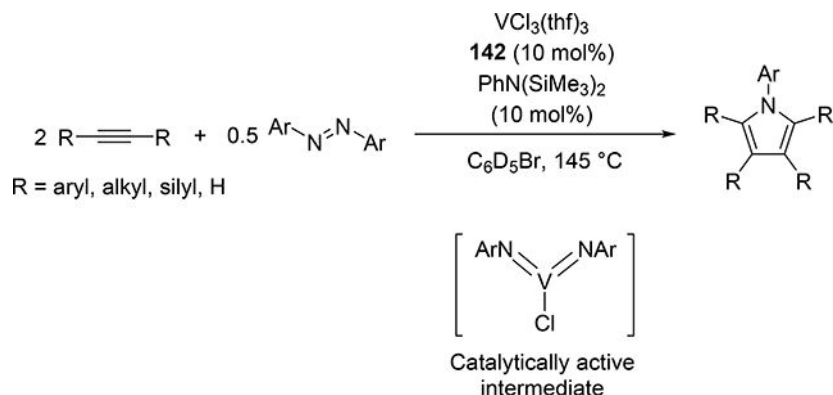
(14)



(15)

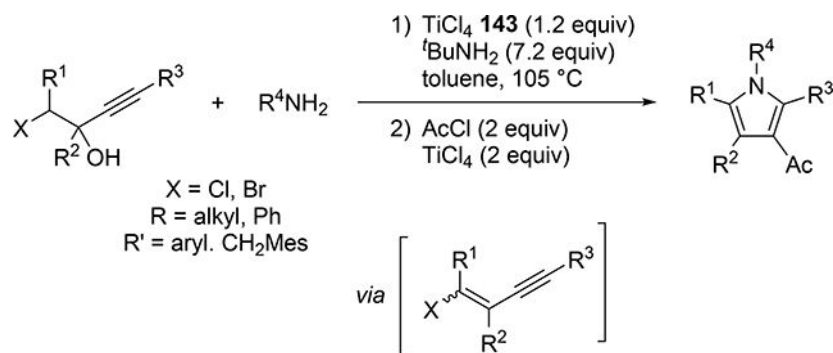
Very recently, Tsurugi, Mashima, Tonks *et al* reported that vanadium(III) chloride THF adduct **142** served as an excellent catalyst in the presence of *N,N*-bis(trimethylsilyl)aniline as an imido source for the [2+2+1] pyrrole formation from alkynes and azobenzenes (eq 16) [56]. In contrast to the Ti-catalyzed system, the bis(imido)vanadium(V) species was found to be a catalytically active intermediate, wherein only one of the two imido ligands participates in the [2+2] cycloaddition with alkynes. Control experiments with a mono(imido)vanadium(V) complex exhibited no catalytic activity. Kinetic studies of the

vanadium-catalyzed system clarified that mono(imido)vanadium(III) species is the resting state, which is consistent with lower reducing ability of V(III) compared to Ti(II).



(16)

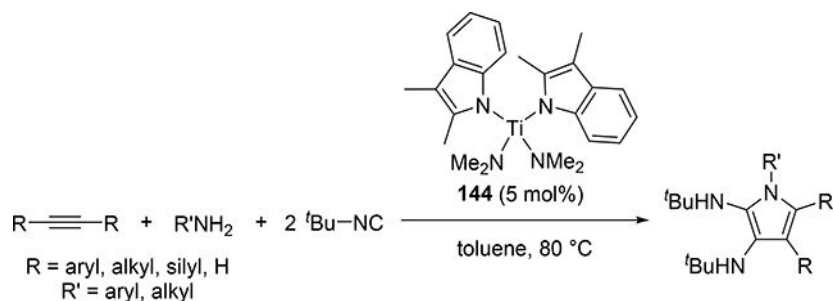
Odom *et al* reported a catalytic pyrrole formation using titanium complexes **96** and **104** (see Section 3.1) *via* an intermolecular hydroamination of 1,4- and 1,5-diyne with primary amines, giving the corresponding iminoalkyne intermediates [57]. These iminoalkynes were thermally converted to the corresponding pyrroles under heating at 100 °C, either by 5-*endo*-dig or 5-*exo*-dig cyclization according to Baldwin rules (Scheme 21). When 1,4-pentadiyne was used as a substrate, a double hydroamination occurred prior to the cyclization of iminoalkynes. A similar hydroamination-cyclization protocol for pyrrole formation was developed by Ackermann *et al* using a simple TiCl₄ (**143**) and ^tBuNH₂ catalyst system. Hydroamination of a triple bond in chloroenynes followed by tautomerization generates α,β-unsaturated imines, which undergoes an intramolecular nucleophilic substitution to yield the corresponding pyrroles (Scheme 22) [58]. Moreover, readily available α-haloalkynol substrates could be applied to the pyrrole synthesis when 1 additional equiv of TiCl₄ (**143**) was used for *in situ* dehydration of the α-haloalkynols into haloenynes (eq 17).



(17)

Another attractive pyrrole formation is a four-component coupling reaction of alkynes, amines, and two equivalents of isocyanides catalyzed by a titanium complex **144**, giving 2,3-diaminopyrroles (eq 18) [59]. In the catalytic cycle, five-membered titanacycle **147** is

formed in the same manner as the Ti-catalyzed iminoamination of alkynes with isocyanides shown in Scheme 23. Further 1,1-insertion of isocyanides into the Ti—C bond followed by protonation of the resulting **148** by amines provides enamine formimines, which spontaneously undergo an intramolecular nucleophilic attack and subsequent tautomerization of the five-membered ring to afford the corresponding pyrrole (Scheme 23). The electron-donating indolyl ligand on the catalyst is crucial to achieve the four-component coupling reaction, where the electron-rich metal center diminishes the protonolysis rate of intermediates **146** and **147** which would normally give hydroamination and iminoamination products, allowing the further insertion of isocyanides into the Ti—C bond.



(18)

3.4. Catalytic imine metathesis

Various imido complexes of Ti (**135**) (Section 3.3) [60], Zr (**149**) [61], Nb (**150**) [62], Ta (**151**) [63], and Mo (**74**) (Section 2.2) [64] served as catalysts for metathesis reaction of carbon—nitrogen double bonds of imines (imine metathesis reaction) (Scheme 24). Two different pathways have been proposed: one is a Chauvin-type mechanism *via* the formation of four-membered diazametallacycle **151**, derived by [2+2] cycloaddition of the imido ligand with imines, similar to olefin metathesis *via* metal alkylidene species (Scheme 25(a)), and the other is an amine-mediated mechanism involving transamination between the imine and a trace amount of amine (Scheme 25(b)). The first mechanism was revealed by Bergman *et al* for the reaction of CpCp'Zr(=NR)(thf) (Cp' = Cp, Cp*) with imines [14d,61]. The second mechanism was proposed by Mountford *et al* on the basis of kinetic studies for the stoichiometric reaction of Ti(=N^tBu)Cl₂(py)₃ with *N*-benzylidenetoluidine, showing that the reaction rate did not depend on the concentration of titanium complex [60]. Various imido and oxo complexes of early transition metals are also catalysts for the metathesis reaction of C=N bonds of carbodiimides to afford mixtures of symmetrical and unsymmetrical carbodiimides as shown in Scheme 27 [65–67]. A four-membered diazametallacyclic species, similar to **152**, was proposed as a reaction intermediate in the catalytic carbodiimide metathesis.

3.5. Catalytic condensation reactions

Some metal oxo complexes can also catalyze the condensation reaction of two isocyanate molecules, giving the corresponding carbodiimide with evolution of CO₂. (Scheme 27) [68,69]. The evolution of CO₂ was attributed to the formation of an imido species **167** from

the metathesis reaction of the metal oxo species **165** and isocyanate via a four-membered [2+2] cycloadduct **166** (Scheme 28). Titanium oxo complex **163** bearing a phthalocyanine ligand and vanadium imido and oxo complexes shown in Scheme 29 worked as effective catalysts, whereas V(=NTol)Cl₃ (**156**) (Section 3.4) displayed no catalytic activity, indicating that the π -donating ability of the ancillary ligands such as alkoxido and amido plays a critical role to activate the M=N bond and accelerate the catalytic reaction. Similarly, Espenson *et al* reported an imine formation reaction between isocyanates and aldehydes, in which vanadium and molybdenum oxo complexes **169–171** reacted with isocyanate or *N*-sulfonylimine to give an imido species *via* metathesis, and subsequent metathesis of the imido species with an aldehyde affords the corresponding imines (Scheme 29) [70]. Molybdenum bis(imido) complex **172** catalyzed the condensation of *N*-sulfinylamines with both aromatic and aliphatic aldehydes, while neither oxo complexes of vanadium (**169**) nor molybdenum (**170** and **171**) were effective for the reaction with aliphatic aldehydes.

3.6. Catalytic isocyanide and carbon monoxide imination reactions

Another method of catalytically forming carbodiimides is from one equivalent of isocyanide and one equivalent of azide, releasing dinitrogen in the process. Unlike isocyanate condensation reactions, these catalytic cycles involve redox changes due to the organic azide acting as an oxidizing agent to regenerate the imido moiety, and consequently are relatively rare among early metal catalysts. Arnold *et al* have demonstrated this with a BDI-niobium complex **173**, where an alkyl isocyanide and *tert*-butyl azide are coupled to form a mixed carbodiimide (Scheme 30).[81] This type of nitrene metathesis is stoichiometric under certain conditions (see below) but is made catalytic upon the addition of azide. In the catalytic cycle, one of the imido groups inserts into a bound isocyanide to give an η^2 -bound carbodiimide **174**. Reductive elimination of the carbodiimide product occurs to give an isolable niobium(III) complex **175** containing an unusual terminal azide, and elimination of dinitrogen regenerates the bis(imido) catalyst **169** through azide complex **176**.

Regarding the above-mentioned catalytic nitrene transfer to the coordinated isocyanide, bis(imido) complex **177** undergoes nitrene metathesis through an isocyanide adduct **178** and a carbodiimide intermediate **179**, where alkyl imido groups are replaced by thermodynamically-favored aryl imido groups upon addition of aryl isocyanide to **177**, forming the mixed aryl-alkyl bis(imido)niobium **180** (Scheme 31).[81] Some alkyl isocyanides can be substituted for other alkyl groups when heated with a large excess of the corresponding alkyl isocyanide; for example, the *t*-butylimido group on **181** can be replaced with a cyclohexyl group to make **182**, and when excess *t*-butyl isocyanide is added to **182**, it again exchanges to the *t*-butylimido complex **183**. DFT calculations propose that these imido metathesis reactions proceed through two η^2 -bound carbodiimide intermediates similar to **179**.

Rather than using a redox-active metal, a redox-active ligand can accomplish catalytic carbodiimide formation through isocyanide imidation. Heyduk *et al* have used this approach with an aminocatechol-type *NNN* ligand on zirconium, **184** (Scheme 32).[71] The same insertion of the imido group into the isocyanide to form **186** with an η^2 -bound carbodiimide occurs, however, there are notable differences between this and the reaction in Scheme 30.

None of the intermediates **185–187** are isolable or detectible by NMR spectroscopy, however, the rate law shows a first-order dependence on azide but an inverse first-order dependence on isocyanide, so the rate determining step is the coordination of azide between **184** and **185** rather than the C-N bond forming step. The imido moiety is only present in the intermediate **185** rather than an isolable complex, although the analogous reaction using aryl isocyanides offers the dimer with bridging imido groups rather than performing catalysis.

Similarly, redox-active ligands can be applied in catalytic nitrene carbonylation to make isocyanates. Wolczanski *et al* have demonstrated this reaction using titanium bearing an *NNNN* tetradentate α -diimine system that enforces pseudo-square planar geometry (Scheme 33).[72] CO appears to directly insert into the Ti-N bond of **188**, as direct binding of CO to the titanium is both electronically and sterically unfavorable. Once the C-N double bond is formed in **189**, the isocyanate is released to give a 4-coordinate titanium species **190**. Subsequently, adamantyl azide coordinates to afford **191**, and dinitrogen is released to regenerate **188**. This reaction was also tested with isocyanides; however, unlike CO, the isocyanide ligand coordinates too strongly to the titanium and the resulting isocyanide adducts are unreactive.

3.7. Catalytic hydrogenation reactions

The high reactivity of bis(imido)metal complexes, as often used for reactions described above, is exemplified for hydrogenation of alkenes. Arnold *et al* reported that cationic bis(imido)vanadium complex, $[V(=N^tBu)_2(PMe_3)_3][Al(pftb)_4]$ (**192**, pftb = perfluoro-*tert*-butoxide), acted as a catalyst for semi-hydrogenation of alkynes to selectively produce *Z*-alkenes, in which 1,2-addition of H₂ to the imine moiety was involved as the key step (Scheme 34)[73]. Two reaction pathways were proposed based on the isolation of the intermediate as well as the DFT calculation. Cationic bis(imido)vanadium **192** activates H₂ via 1,2-addition to give imido-amido species **193**. Further insertion of alkynes into the V—H moiety affords alkenylvanadium **194**. The V—C bond of the alkenylvanadium **194** undergoes σ -bond metathesis with H₂ to release the semi-hydrogenated product with regeneration of imido-amido species **193** (Path A). An alternative pathway is α -NH-elimination from the alkenylvanadium **194** to directly produce the alkene and bis(imido)vanadium species **192** (Path B). The corresponding niobium variant also shows catalytic activity for semihydrogenation of alkynes.

4. Conclusion

Cycloaddition reactions of the M=N fragment of early transition metal imido complexes with unsaturated organic compounds are important steps in bond forming reactions to produce various nitrogen-containing molecules. Stoichiometric reactions of the imido-metal species with unsaturated multiple bonds produces azametallacyclic compounds as key intermediates via [2+2] cycloaddition. Protonation of the four-membered metallacycle by amines is the final step to produce hydroamination compounds, while further insertion of unsaturated organic molecules into the metal-carbon bond of the 4-membered metallacycle is involved in carboamination of alkynes and pyrrole formation. In addition, the 4-membered azametallacycle intermediate was observed in metathesis reaction of C=N bonds in imines,

carbodiimides, and condensation of isocyanates. Modification of supporting ligands for reactivity of the four-membered metallacycle intermediates has been further developed for achieving more versatile transformations starting from imido complexes of early transition metals.

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Abbreviations

Bn	benzyl
Cp	cyclopentadienyl
Dipp	2,6-diisopropylphenyl
<i>i</i>Pr	isopropyl
Mes	mesityl
py	pyridine
<i>t</i>Bu	<i>tert</i> -butyl
THF	tetrahydrofuran
Tol	4-methylphenyl
Xyl	2,6-dimethylphenyl

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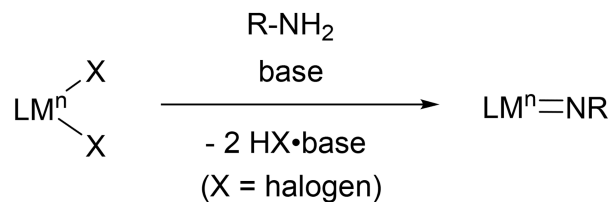
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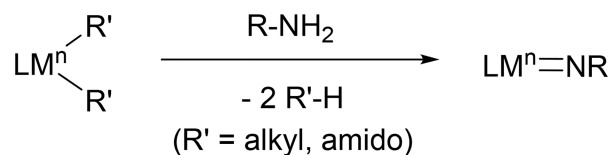
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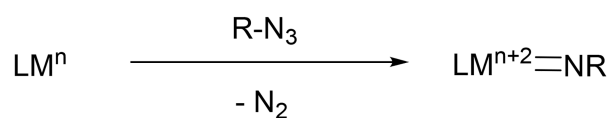
(a) Deprotonation of primary amines by base



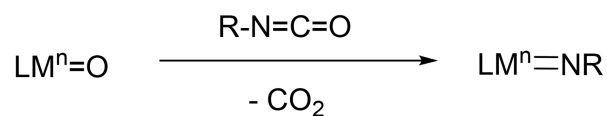
(b) Deprotonation of primary amines by alkyl/amidometals



(c) Decomposition of organic azides



(d) Metathesis of oxo complexes with isocyanates



(e) Cleavage of N=N bond of azo compounds

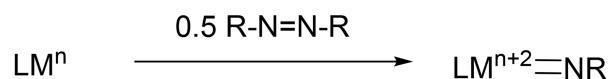


Fig. 1.
Typical synthetic methods of terminal imido complexes

(a) Group 4 metal catalysts

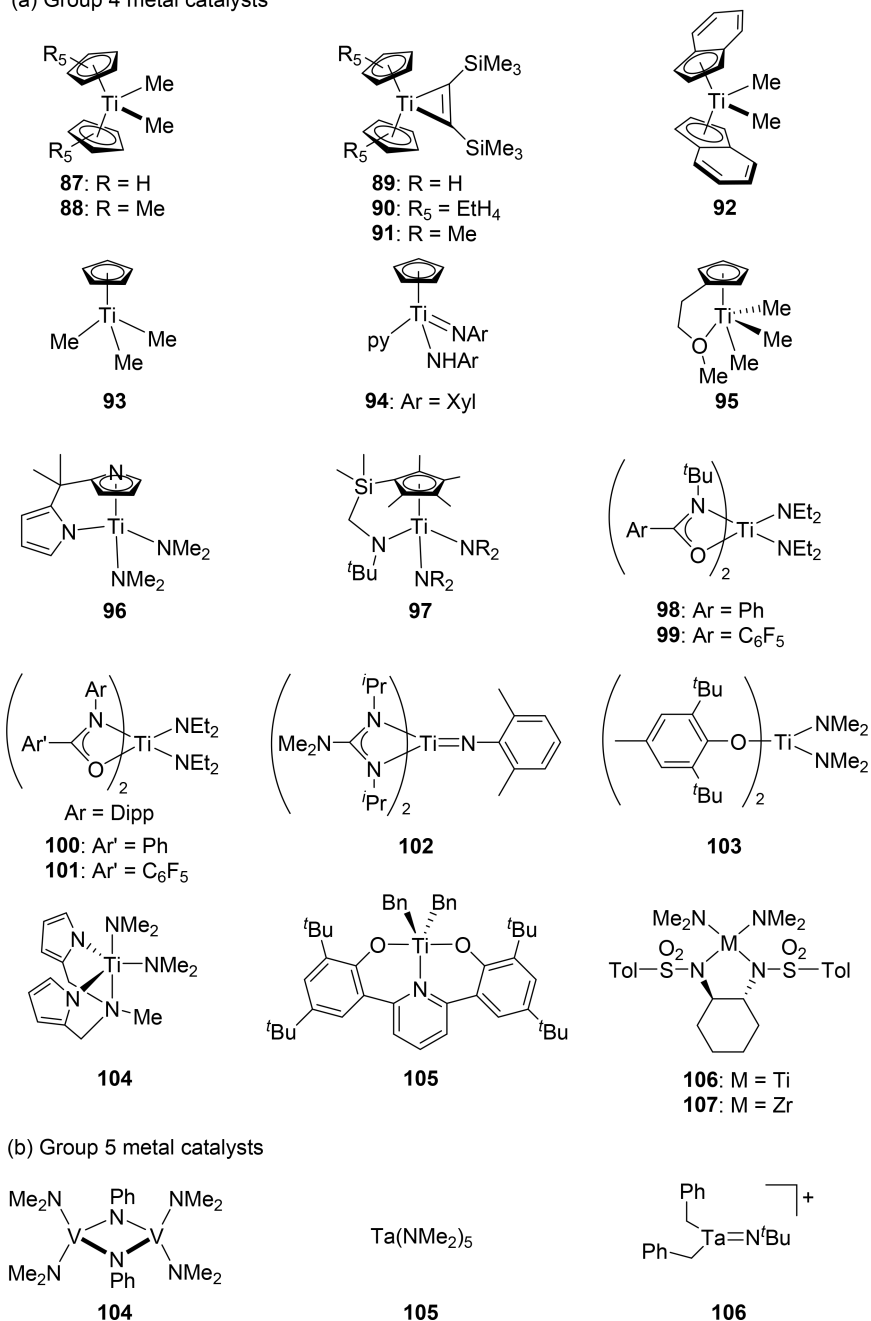


Fig. 2. Examples of early transition metal catalysts and precatalysts for hydroamination of alkynes via cycloaddition.

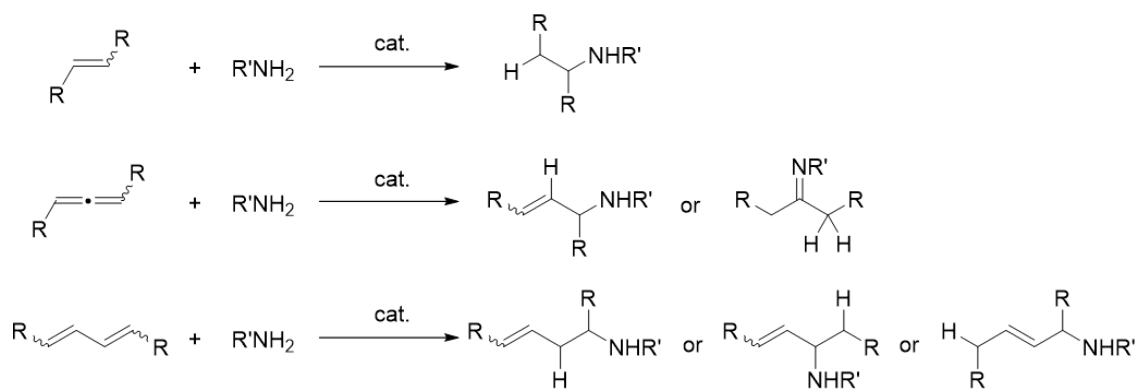


Fig. 3.
Catalytic intermolecular hydroamination reactions of alkenes, allenes, and dienes.

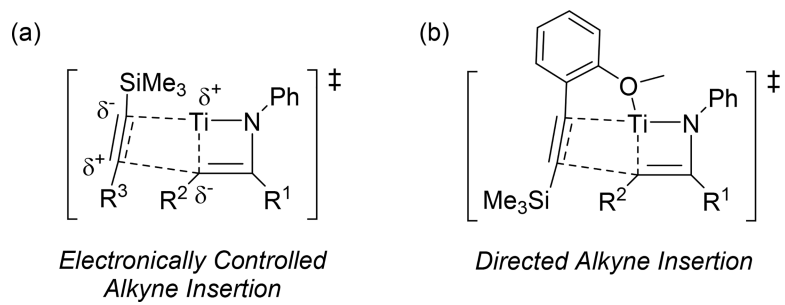
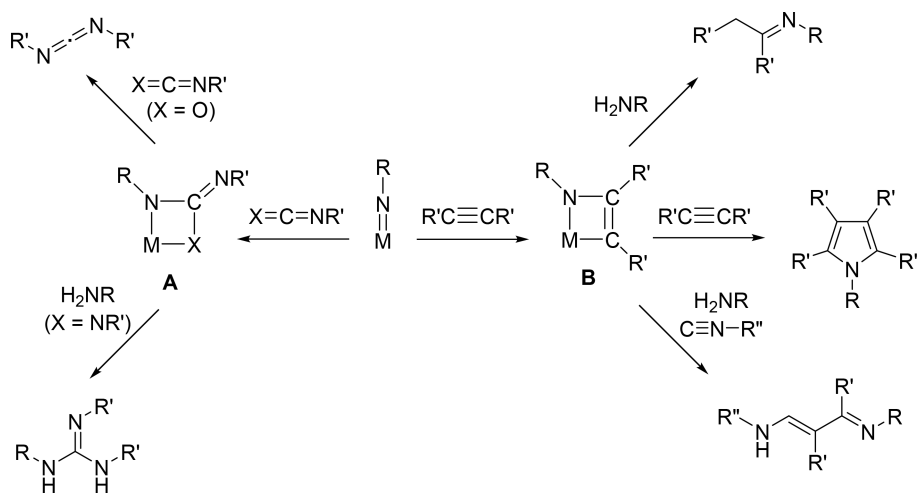
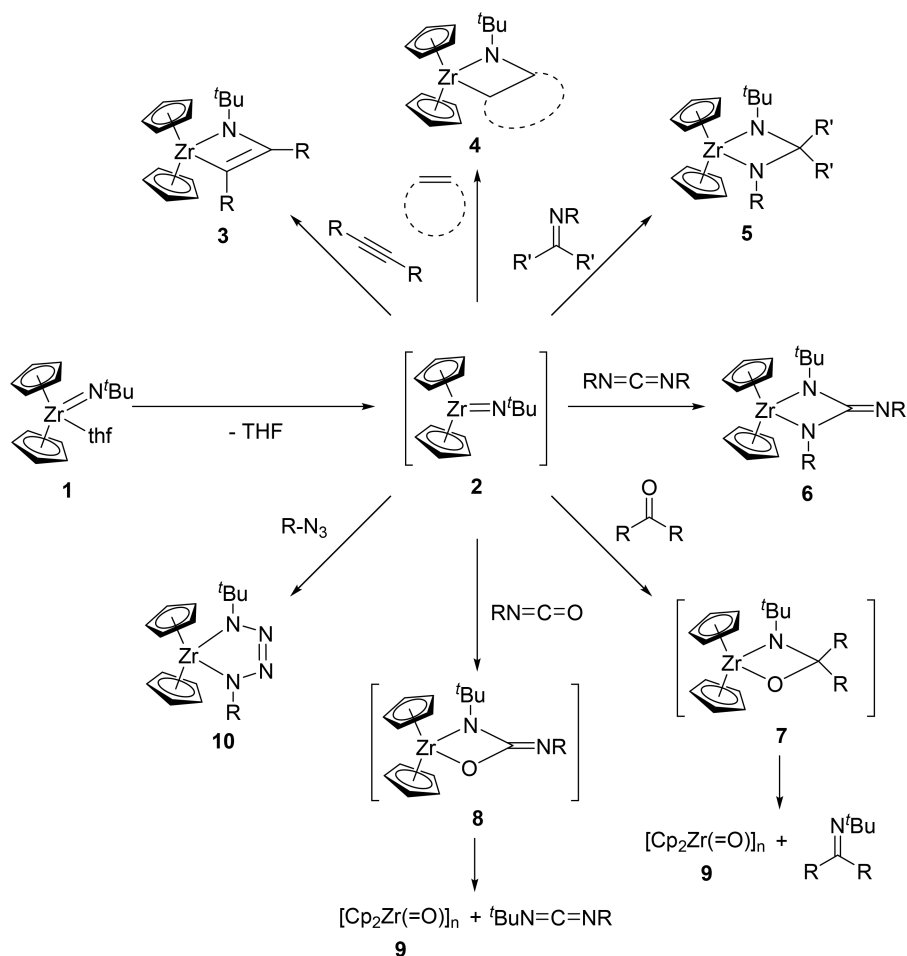


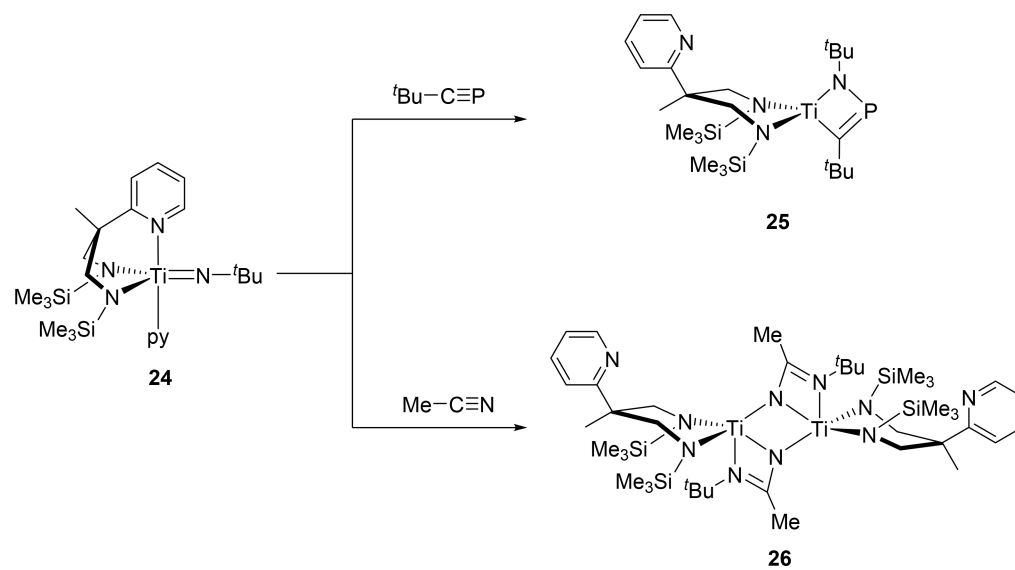
Fig. 4.
Proposed transition states of alkyne insertion into titanacyclobutene



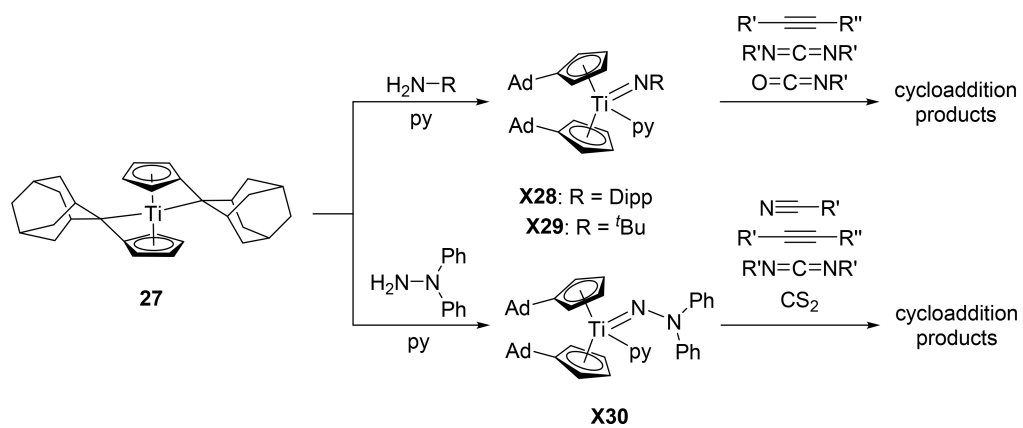
Scheme 1.
Representative Cycloaddition and Subsequent Organometallic Reactions of the Metal Imido Group



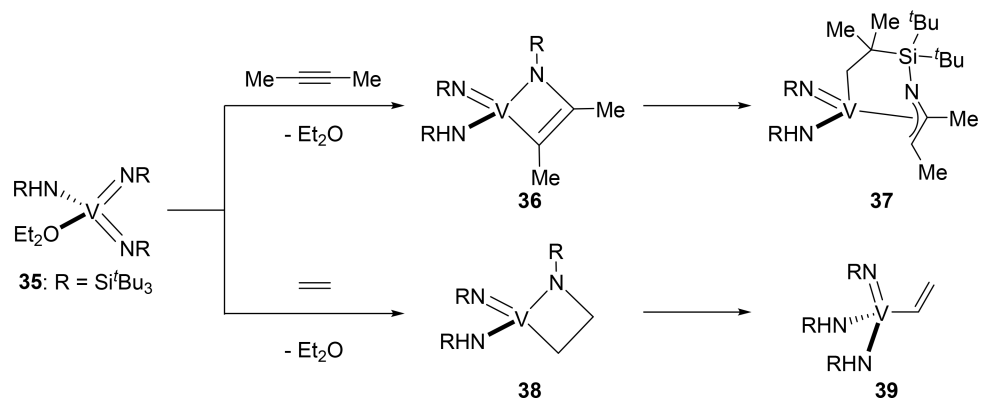
Scheme 2. Cycloaddition Reactions of $\text{Cp}_2\text{Zr}(\text{=N}^t\text{Bu})$ (2) with Alkynes, Alkenes, Imines, Carbonyls, Heterocumulenes, and Organic Azides



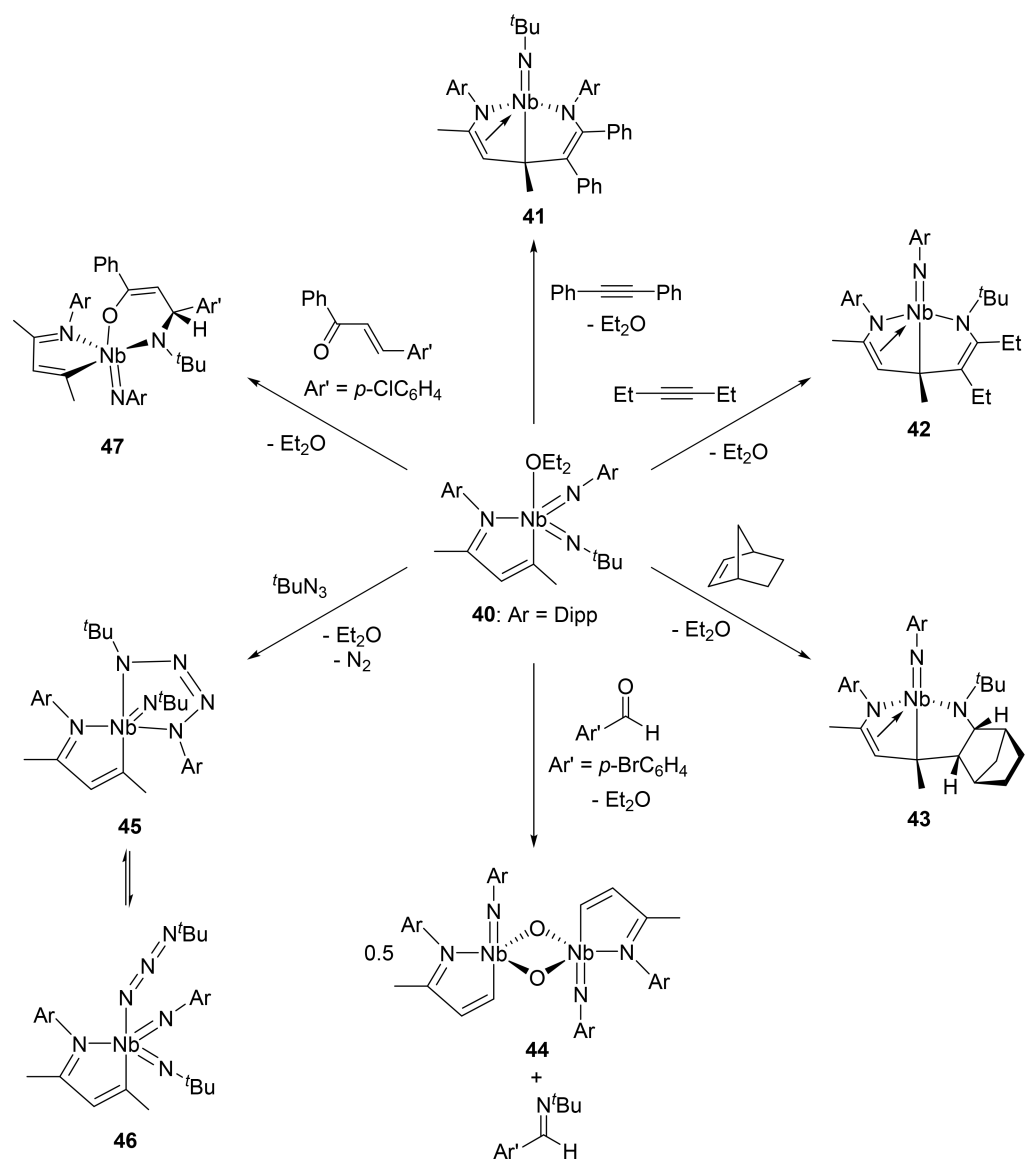
Scheme 3.
Cycloaddition Reactions of Titanium Imido Complex **24** with Phosphaalkyne and Nitrile



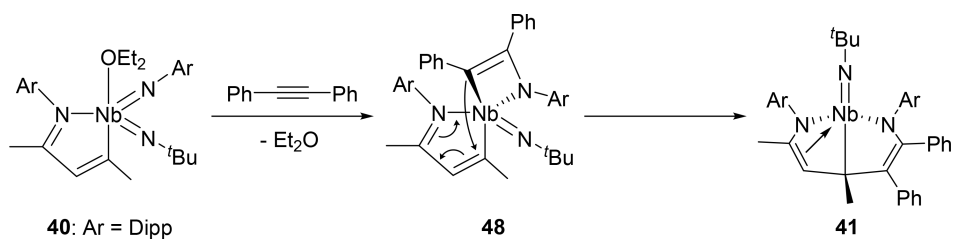
Scheme 4.
 Reactivity of Fulvalene-Derived Titanium Imido Complexes **28–30**

**Scheme 5.**

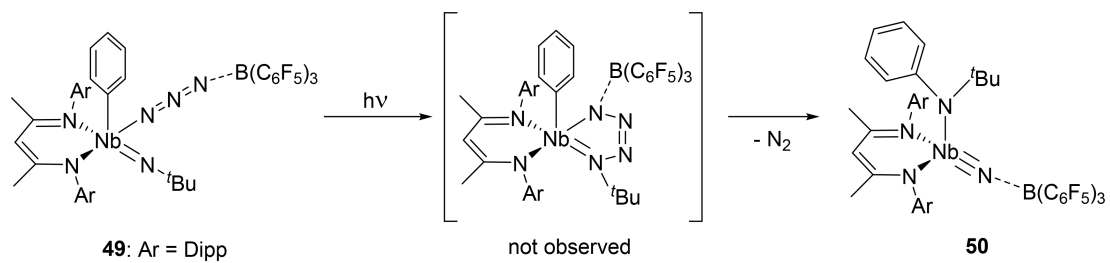
[2+2] Cycloaddition of Bis(imido)vanadium **35** with 2-Butyne and Ethylene

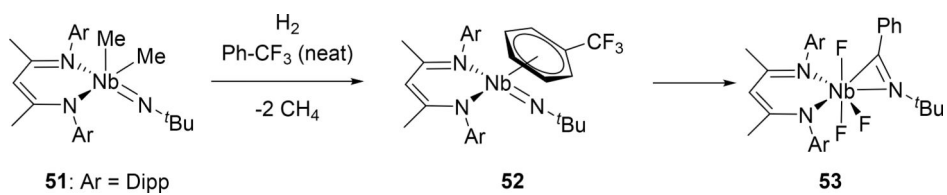
**Scheme 6.**

Cycloaddition Reactions of Bis(imido)niobium Complex **40** with Alkyne, Alkene, Aldehyde, Organic Azide, and α,β -Unsaturated Carbonyl Functional Groups.

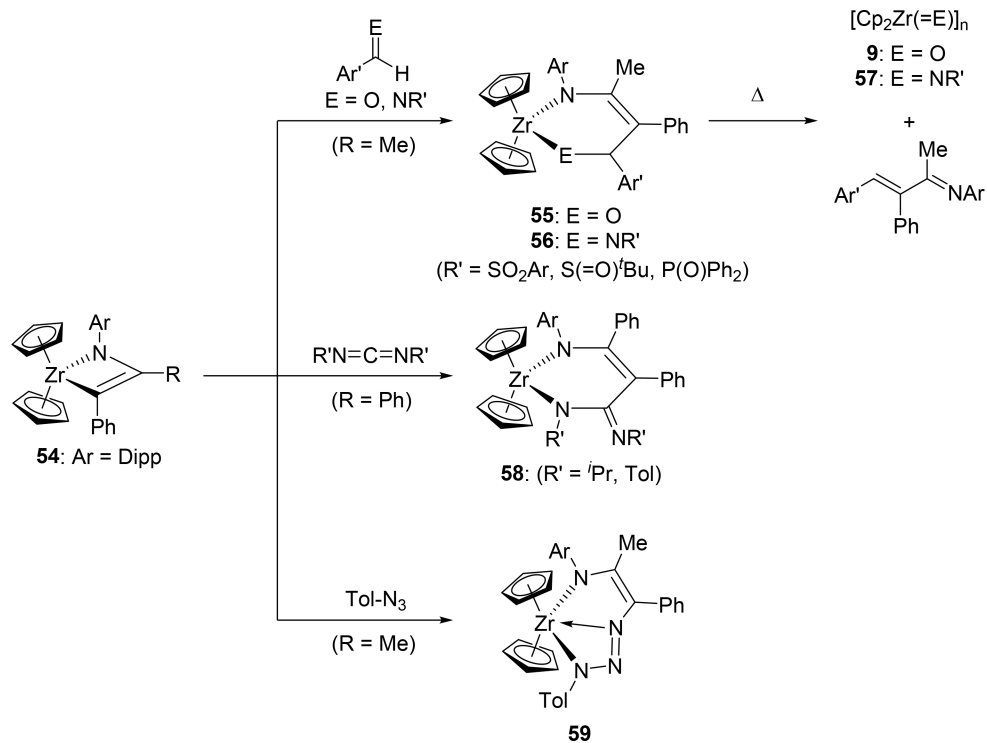


Scheme 7.
Proposed Mechanism for Complex **41** Formation

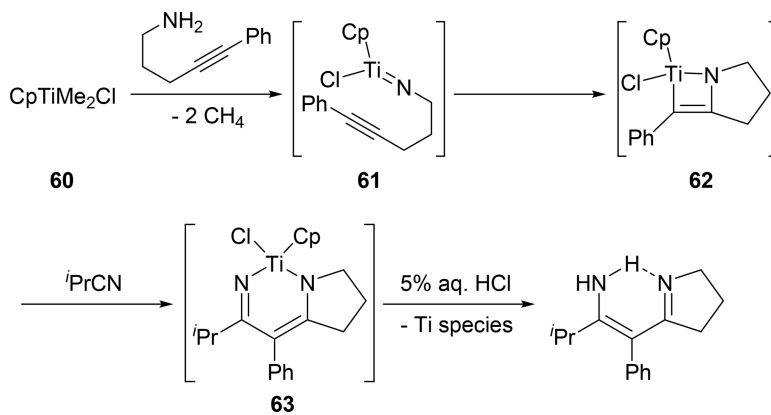
**Scheme 8.**Formation of **50** through Photolysis of Imido-azido Complex **49**

**Scheme 9.**

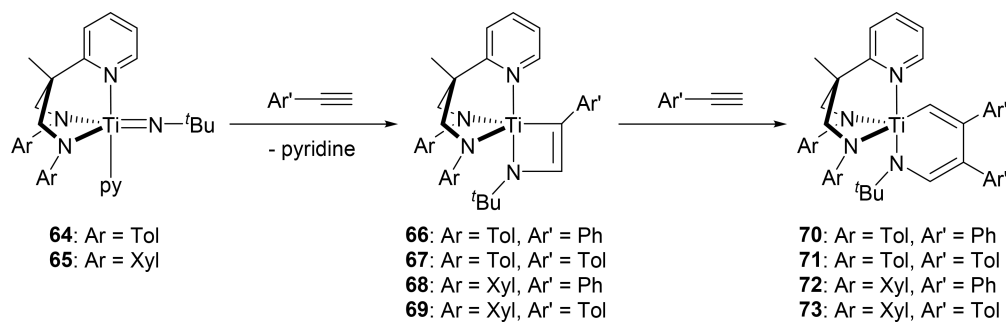
Formation of a Niobium-Imine Complex **53** from Defluorination of α,α,α -trifluorotoluene



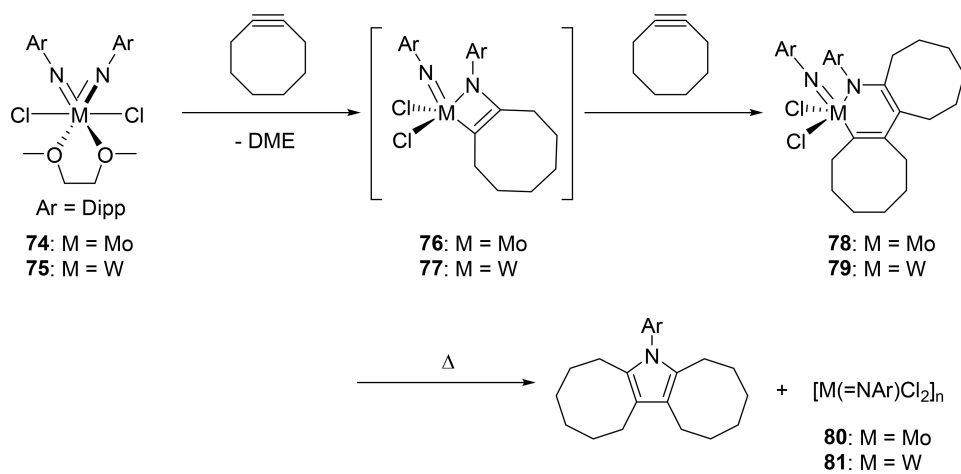
Scheme 10.
 Insertion Reactions of Aldehydes, Imines, Carbodiimides, and Organic Azides into
 Azazirconacyclobutene **54**



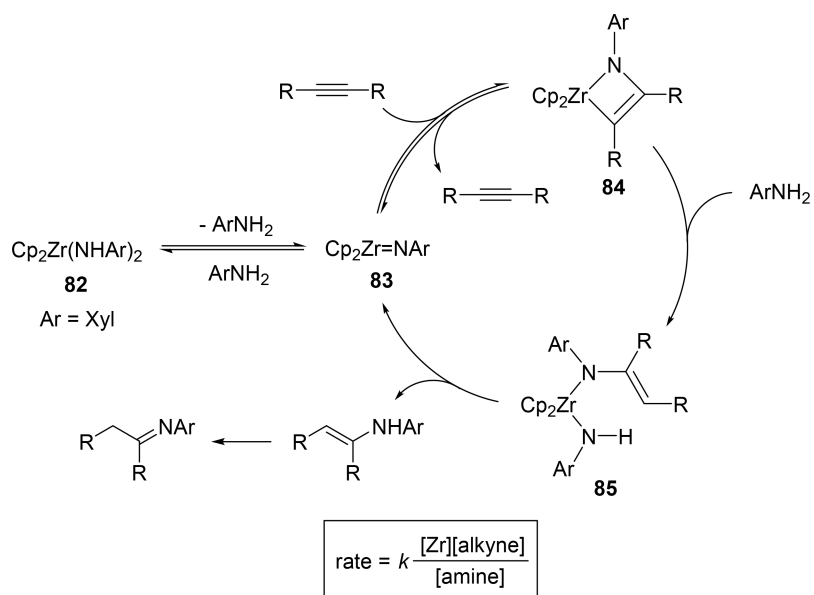
Scheme 11.
Insertion Reaction of Isobutyronitrile into Azatitanacyclobutene **62**

**Scheme 12.**

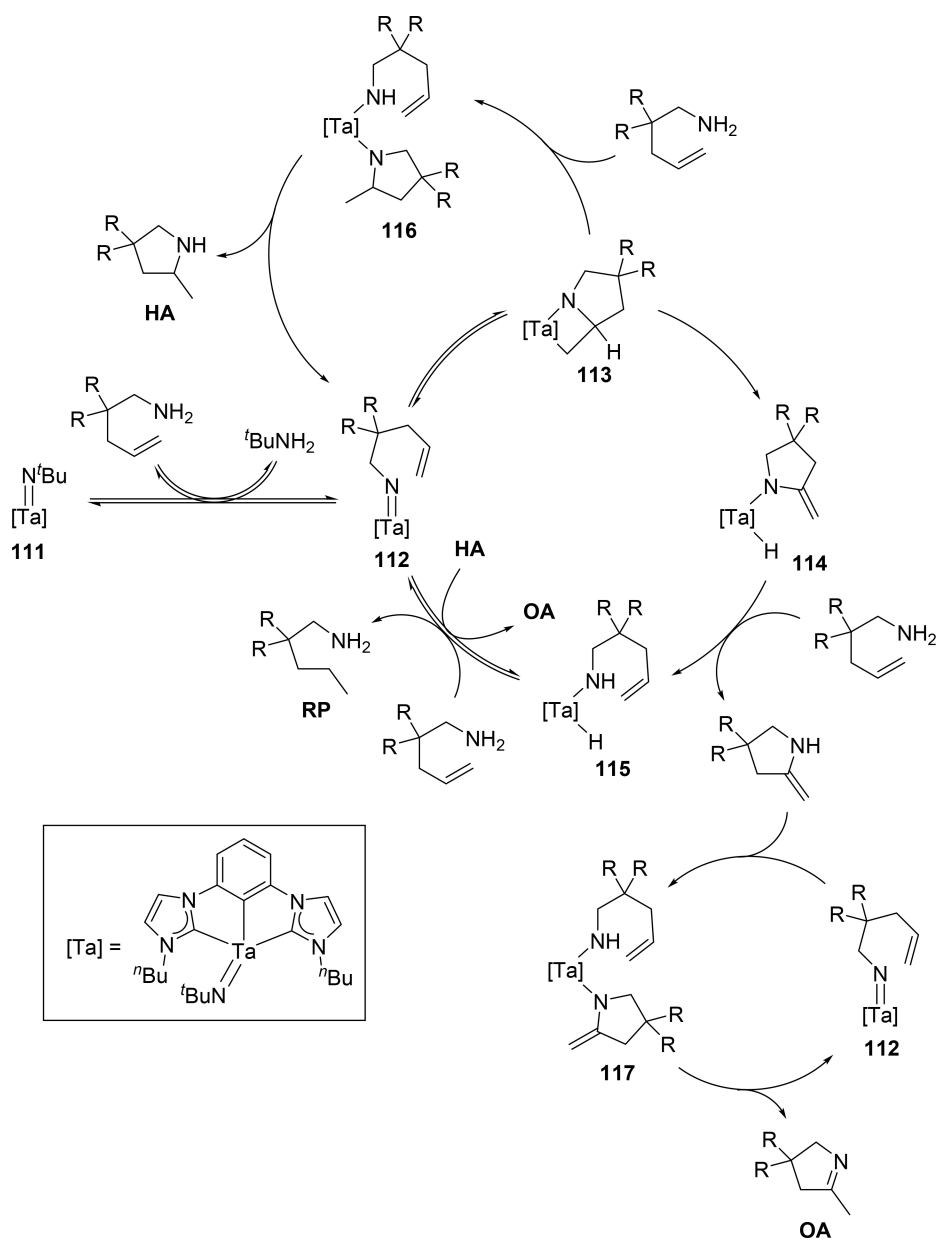
Formation of Azametallacyclohexadiene Complexes through [2+2] Cycloaddition followed by Arylacetylene Insertion



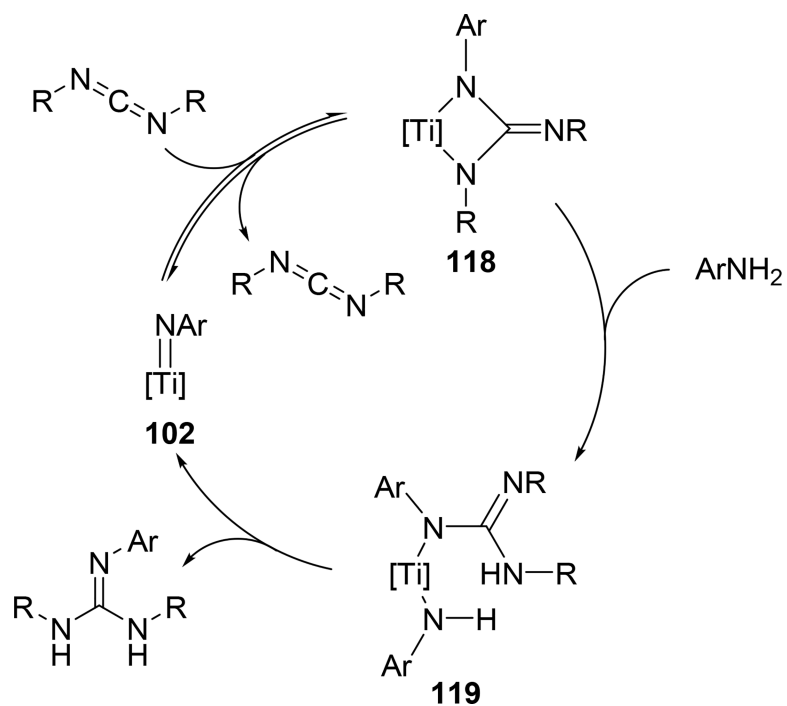
Scheme 13.
 Formation of Six-Membered Azametallacyclohexadienes **74** and **75** via Four-Membered Azametallacyclobutenes **76** and **77** and Reductive Elimination of Pyrrole Derivative



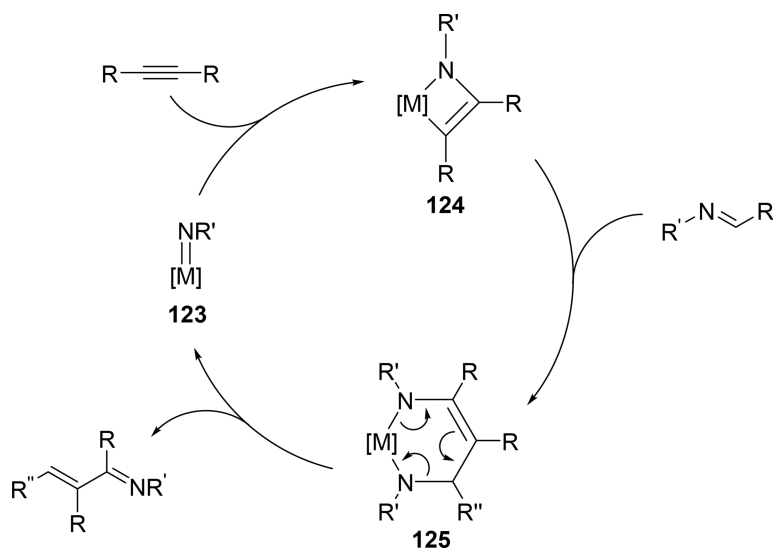
Scheme 14.
Proposed Mechanism for Zr-Catalyzed Hydroamination of Alkynes



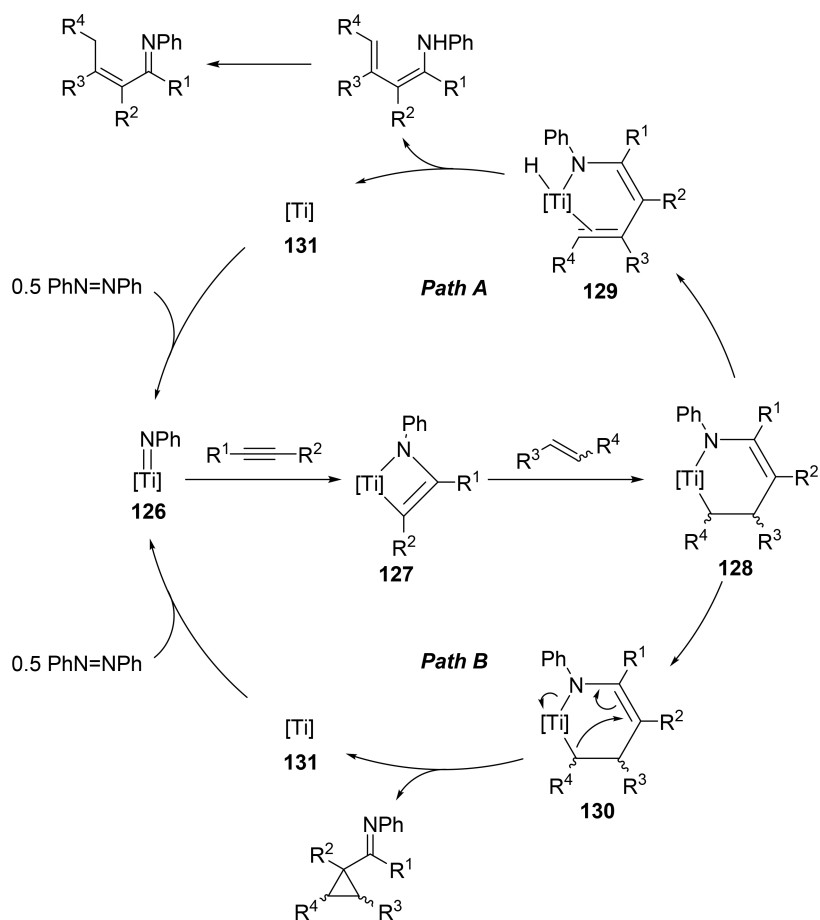
Scheme 15.
Proposed Mechanism for Ta-Catalyzed Oxidative Amination



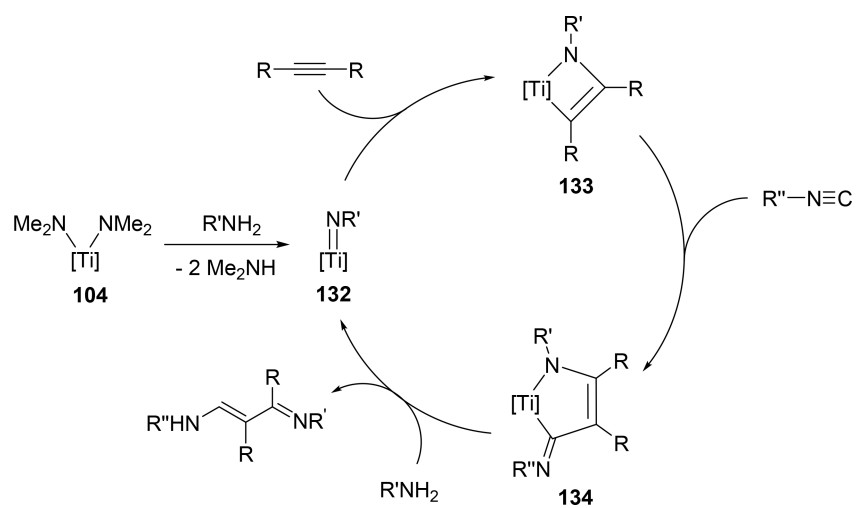
Scheme 16.
Proposed Reaction Mechanism for Ti-Catalyzed Guanylation of Amines



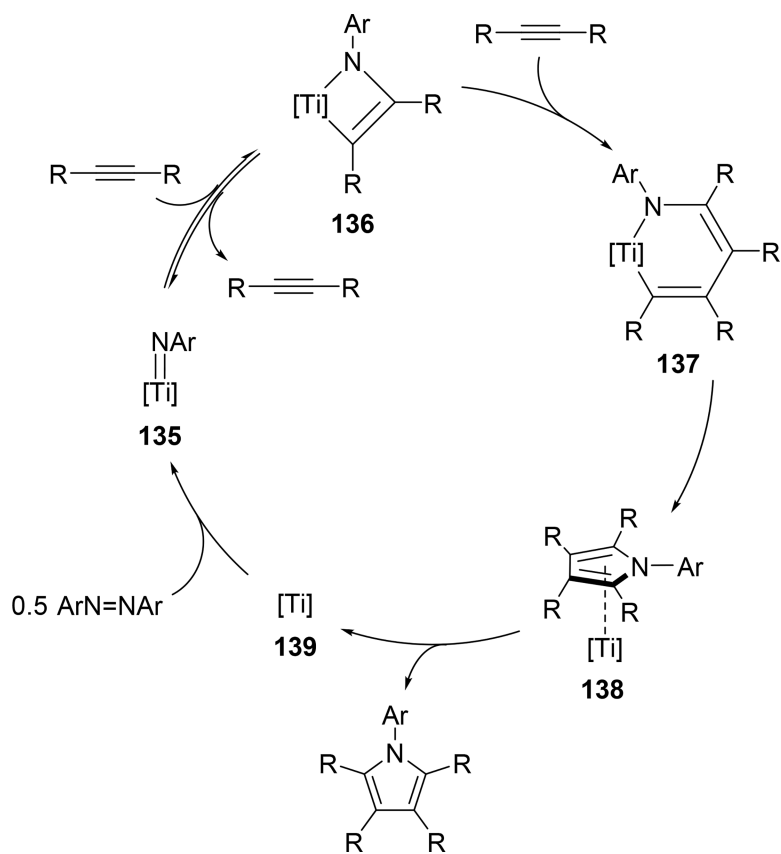
Scheme 17.
Proposed Mechanism for Carboamination of Alkynes with Aldimines



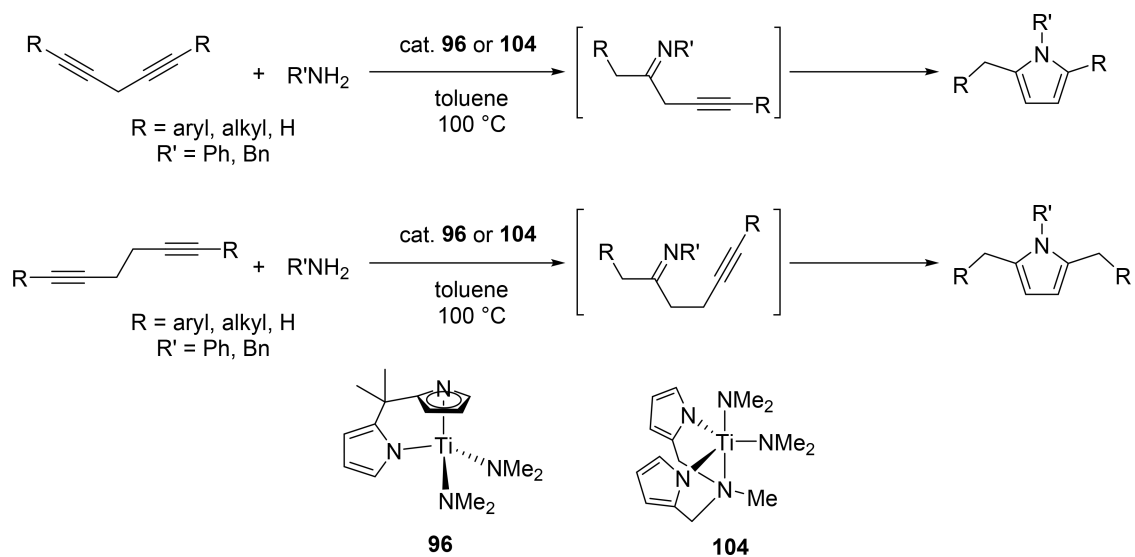
Scheme 18.
Proposed Mechanism for Ti-Catalyzed Carboamination of Alkynes with Alkenes and Azobenzenes



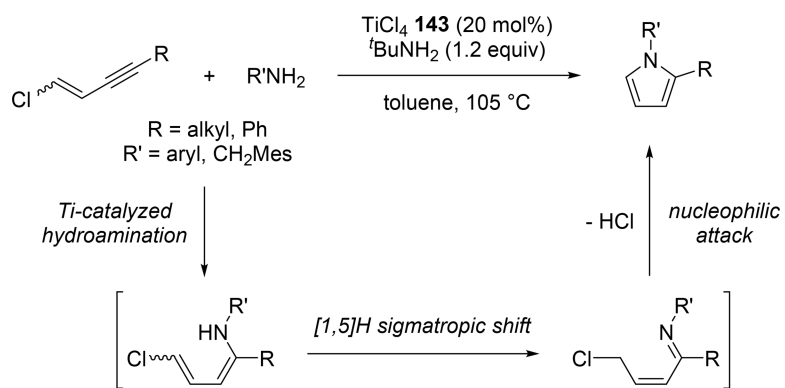
Scheme 19.
Proposed Mechanism for Titanium-Catalyzed Iminoamination of Alkynes



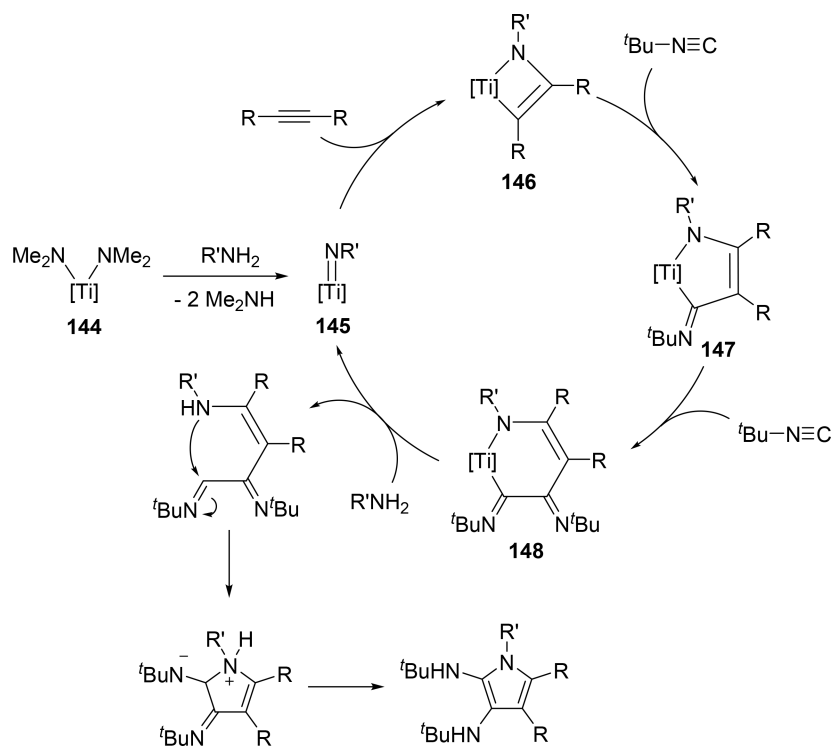
Scheme 20.
Proposed Mechanism for Ti-Catalyzed [2+2+1] Pyrrole Formation from Alkynes and Azobenzenes



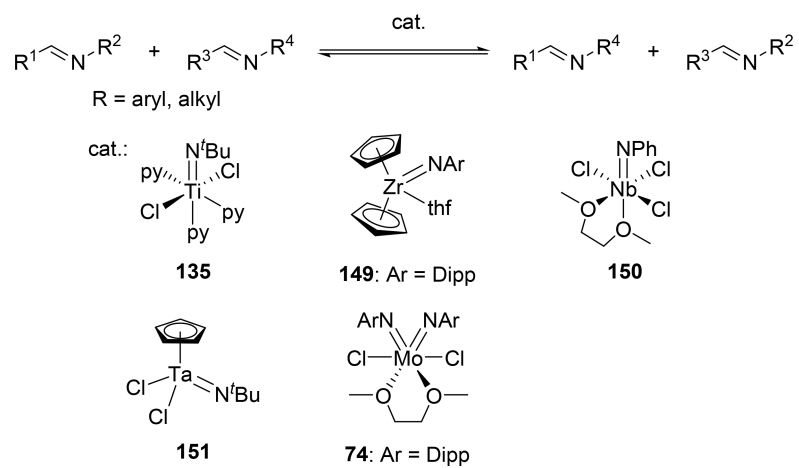
Scheme 21.
Catalytic Pyrrole Formation from Diynes and Amines by Titanium Catalysts



Scheme 22.
Catalytic Pyrrole Formation by Hydroamination of Chloroenynes

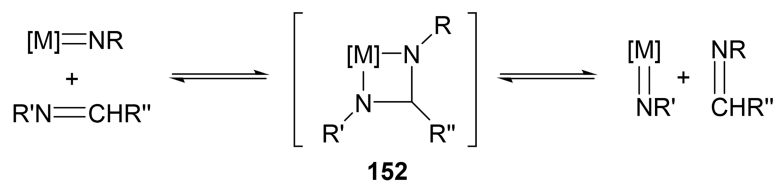


Scheme 23.
Proposed Mechanism of the Ti-Catalyzed Four-Component Coupling Giving 2,3-Diamino Pyrroles

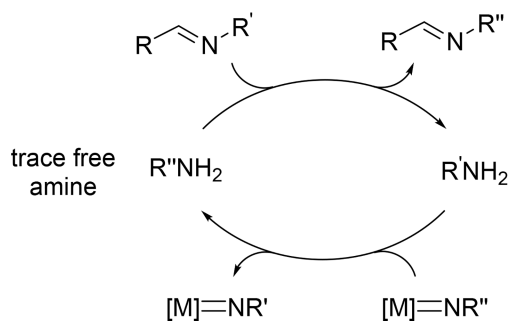


Scheme 24.
Catalytic Imine Metathesis by Early Transition Metal Catalysts

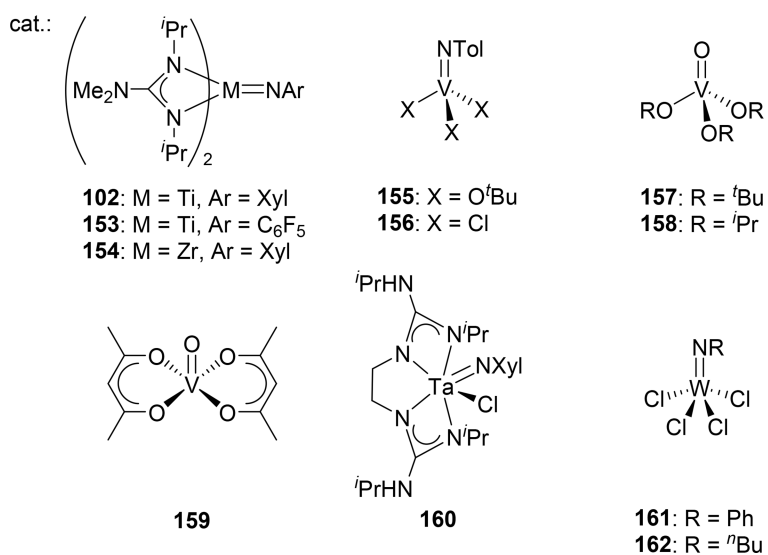
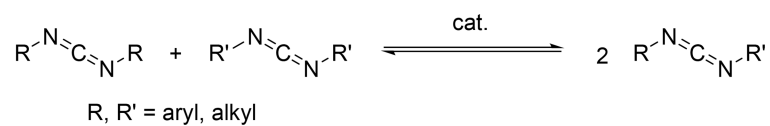
(a) Chauvin-type mechanism



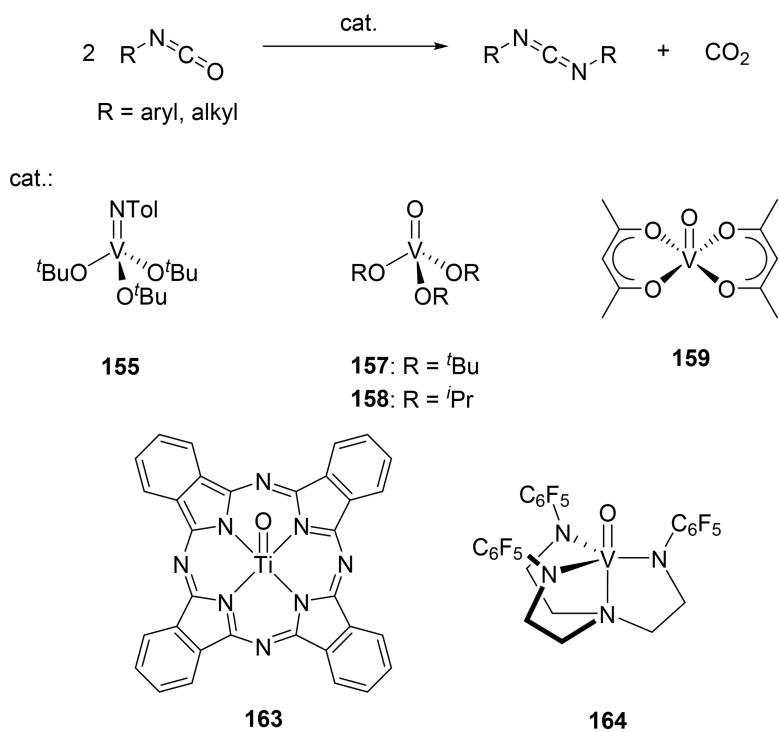
(b) Amine-mediated mechanism

**Scheme 25.**

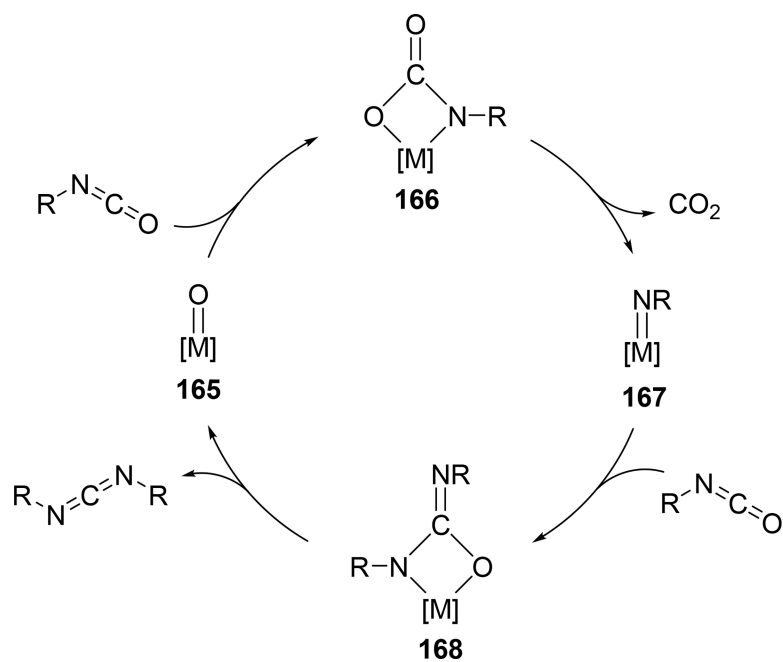
Two Proposed Mechanisms for Catalytic Imine Metathesis



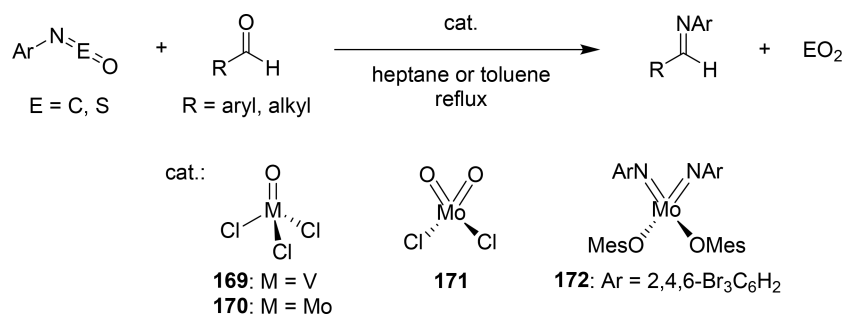
Scheme 26.
Catalytic Carbodiimide Metathesis by Early Transition Metal Catalysts



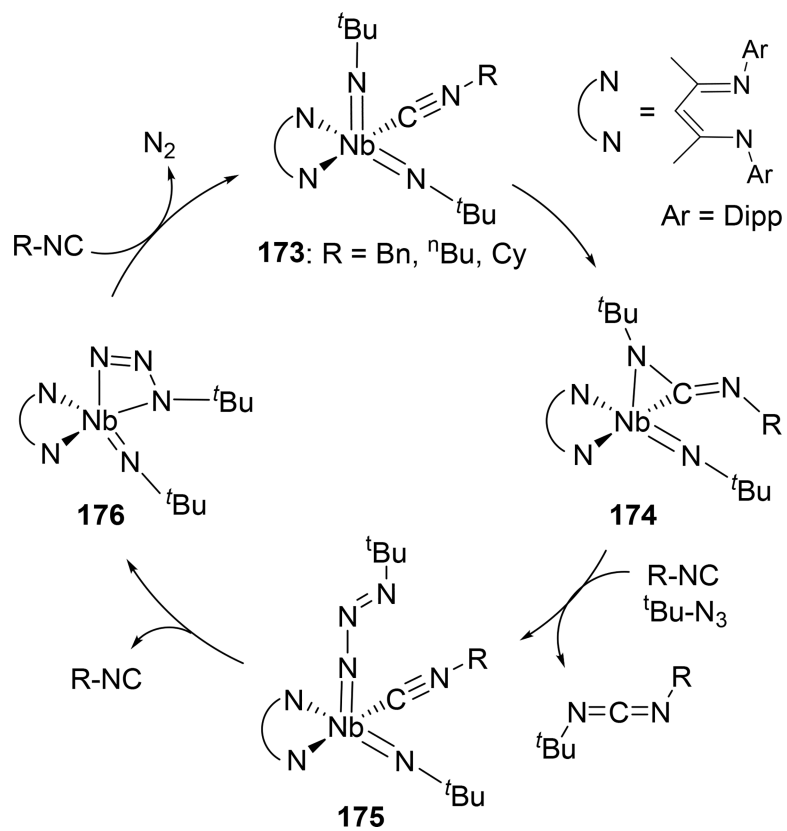
Scheme 27.
Catalytic Isocyanate Condensation to Give Carbodiimides



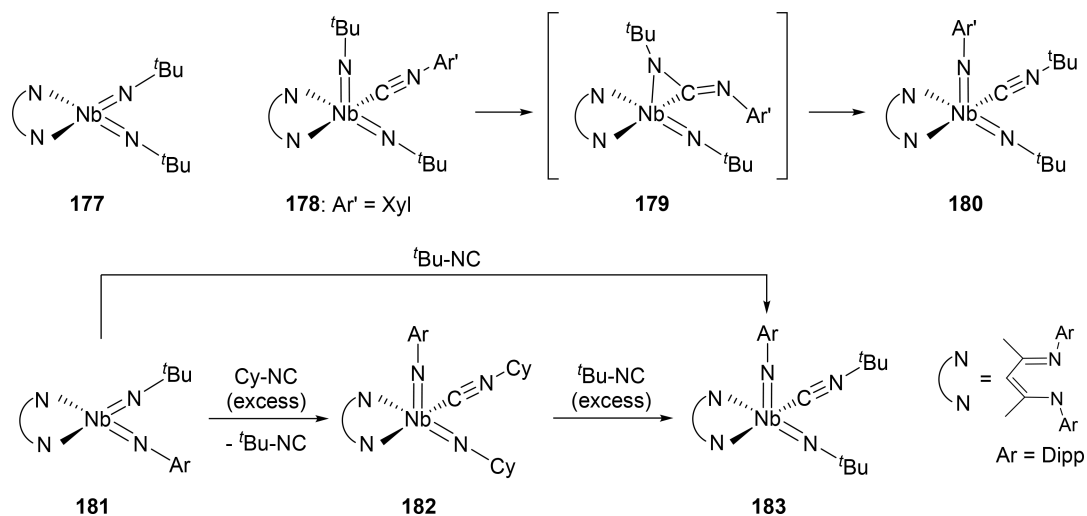
Scheme 28.
Proposed Mechanism for Isocyanate Condensation to Give Carbodiimides



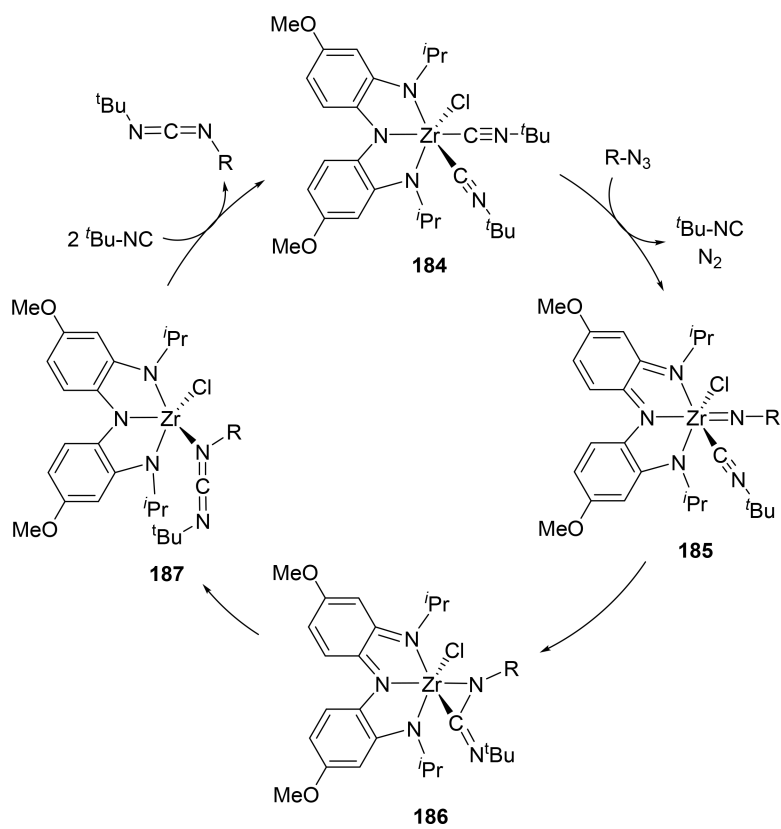
Scheme 29.
Catalytic Isocyanate or *N*-sulfonylimine Condensation with Aldehydes to Produce Imines



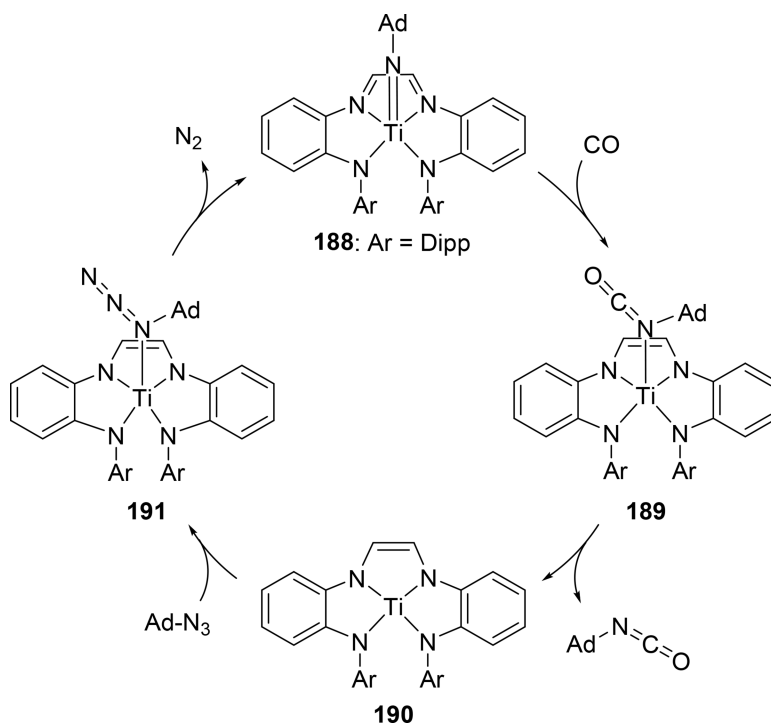
Scheme 30.
Catalytic Nitrene Metathesis to form Carbodiimides



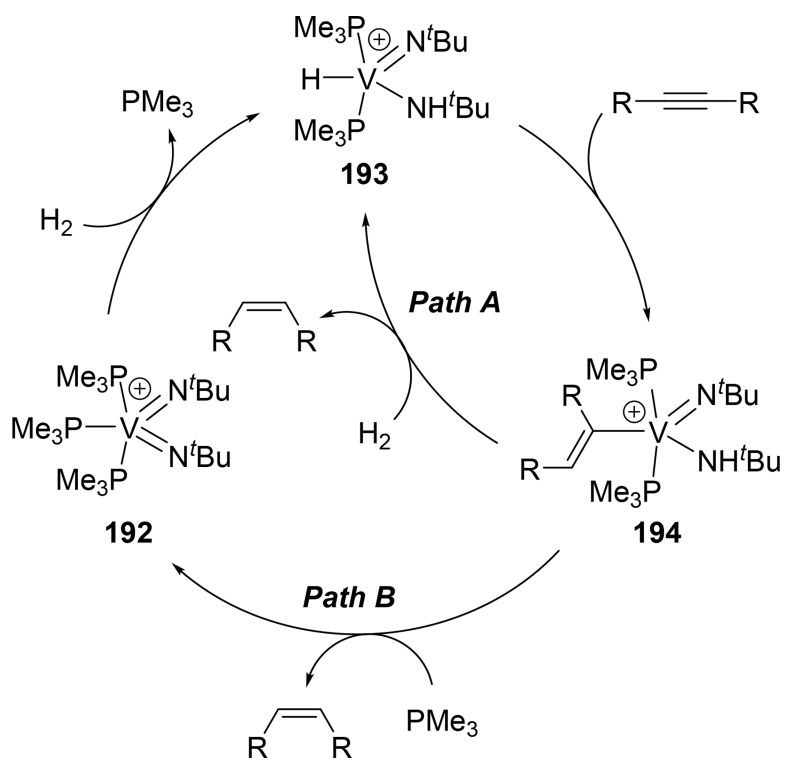
Scheme 31.
Imine Metathesis Reactions of Niobium Bis(imido) Complexes



Scheme 32.
Catalytic Carbodiimide Formation Utilizing a Redox-active Ligand on Zirconium



Scheme 33.
Catalytic Isocyanate Formation by Direct Addition of CO to an Imido Group

**Scheme 34.**

Proposed Mechanism for Catalytic *Z*-Selective Semihydrogenation of Alkynes by the Cationic Vanadium Imido Catalyst $[V(=N^tBu)_2(PMe_3)_3][Al(pftb)_4]$ (pftb = perfluoro-*tert*-butoxide) (**192**).