



# Recent Advances of Imidazolin-2-iminato in Transition Metal Chemistry

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## Abstract

A new class of monoanionic nitrogen donor ligands imidazolin-2-iminato ( $\text{Im}^{\text{R}}\text{N}^-$ ) is produced from the reactivity of N-heterocyclic carbenes (NHCs) towards organic azides and is isolobally related to imido ligands ( $\text{RN}^{2-}$ ). The imidazolin-2-iminato ligands essentially can be derived by substituting alkyl or aryl group from imido moieties. The proton abstraction from imidazolin-2-imine results in the monoanionic imidazolin-2-iminato ligands that possesses the exocyclic nitrogen, which strongly favors the binding with electrophiles. The nucleophilicity of anionic nitrogen is markedly increased by the charge (positive) delocalization into the five-membered heterocyclic ring. Altering the N-substitutions could meet the necessities for kinetic stabilization of high valent reactive species. These ligands have been slowly cemented the status as a potential alternative for ubiquitous cyclopentadienyl ligand and continued receiving attention. These ligands have progressively accustomed as the ancillary ligands for early transition metals, rare earth elements, or early actinides affording pincer complexes or "pogo stick" type compounds. In this article, the present chemistry of transition metal elements bearing imidazolin-2-iminato/imine ligands is reviewed from the year 2015 to date.

**Keywords:** N-heterocyclic carbene; Catalysis; Polymerization; Metathesis; Transition metal; Hydroamination; Hydroboration.

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## 1. Introduction

Nitrogen, the third most electronegative element in the periodic table, is recognized as one of the most familiar donor heteroatoms in coordination chemistry. Notably, the coordination ability of carbon was established by following the first reports of N-heterocyclic carbene (NHC) independently by Öfele,<sup>[1]</sup> Wanzlick,<sup>[2]</sup> and Lappert.<sup>[3]</sup> Despite the significant advancement accomplished by these groups, the topic was not so appealing until the seminal report appeared on the first structural characterization of NHC by A. J. Arduengo III, which immediately turned out to be leading research areas in the field of organometallic and catalysis,<sup>[4-16]</sup> medicinal chemistry,<sup>[17-21]</sup> material science,<sup>[22-27]</sup> and organocatalysis.<sup>[28-29]</sup> NHCs received considerable attention due to the high thermal stability, ease of preparation, and nontoxic character.<sup>[30-32]</sup> Although NHCs were introduced as potential alternatives for phosphines in organometallic chemistry, they have been applied widely in diverse fields of

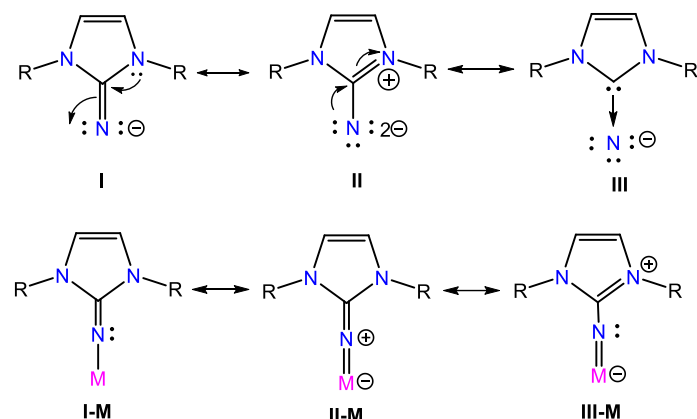
chemistry. One of such applications of NHCs is the synthesis of silylenes, a class of divalent silicon compound.<sup>[33-35]</sup> Recently silylenes have received considerable attention due to their potential applications in the field of catalysis.<sup>[36]</sup> For example, Cui and co-workers successfully employed bulky NHC (1,3-bis(*tert*-butyl)imidazol-2-ylidene) for the synthesis of cyclic silylenes via dehydrochlorination of cyclic diaminochlorosilanes.<sup>[37]</sup> This was the maiden report of metal-free cyclic silylenes synthesis under mild reaction conditions. The reactivity studies of silylenes were extensively explored towards carbonyls, imines, alkenes, and alkynes substrates. However, the low reactivity of nitrile is restricted further for this study. Cui and co-workers recently demonstrated the unique reactivity of NHC stabilized silylenes towards various unsaturated substrates. The NHC-stabilized silylene was successfully utilized for bis-silylation of nitriles to achieve highly regioselective corresponding trans-1,2-disilylimines.<sup>[38]</sup> The pivotal role of the imidazole ring to stabilize the positive charge<sup>[39-42]</sup> is the rationale for the high nucleophilicity of NHC.<sup>[43-44]</sup> Rational design by introducing exocyclic NH at 2-position of the NHC ring resulted in imidazolin-2-imine with higher nucleophilicity and basicity comparable to the parent NHC. The formation of a stable imidazolium center leads to a significant electron density dissemination from the heterocycle ring to the exocyclic

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Dedicated to Prof. Moris S. Eisen on the occasion of his 60<sup>th</sup> birthday.

nitrogen atom through the formation of the formally zwitterionic structure, demonstrated by conceivable canonical structures of the monoanionic imidazolin-2-iminato ligand **I** (Scheme 1).<sup>[45]</sup>

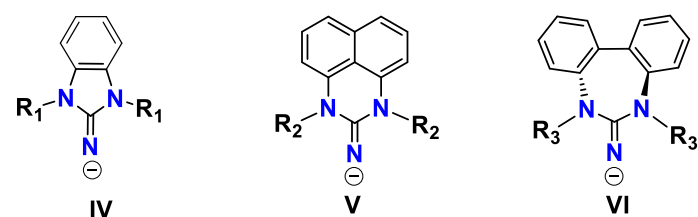


**Scheme 1.** The canonical form of the anionic imidazolin-2-iminato ligand, and model transition metal complexes.

The exocyclic nitrogen atom in canonical form **II** is carrying two formal charges, which enhance the electron-donating ability. Whereas partial N-heterocyclic carbene (NHC) character is displayed by form **III** (Scheme 1). Hence, imidazolin-2-iminato behaves as  $2\sigma$ ,  $4\pi$  electron donors,<sup>[46]</sup> resembling the cyclopentadienyl (Cp) ligand as both are 6 electrons donors and evident from the canonical structures (**I-III**) depicted in scheme 1. The metal complexes of imidazolin-2-iminato (**I-M**) showed significant metalla-2-aza-allene (**II-M**) or metal imide (**III-M**) character (Scheme 1). The canonical forms are revealed in the lengthening of  $C_{\text{ipso}}-N_{\text{exo}}$  bond distance and shortening of the  $M-N_{\text{exo}}$  distance. The linear C–N–M disposition identical to CCC allene is the manifestation of strong metal-nitrogen interaction. The imidazolin-2-iminato ( $\text{Im}^{\text{R}^{\text{N}}-}$ ) ligand, which is monoanionic, could be used for the synthesis of numerous transition metal complexes.<sup>[47-48]</sup> The steric and electronic parameters of the ligand can be tailored by altering the wingtip substituents on nitrogen atoms, which in turn affects the catalytic performance of the complexes and may be used to fine-tune the kinetic protection of the coordinated metal. The five-membered azole ring is featuring the more open coordination sphere by keeping away the 1,3-substituents from the metal center, critical for the polymerization of  $\alpha$ -olefins. During two decades,  $\text{Im}^{\text{R}^{\text{N}}-}/\text{Im}^{\text{R}^{\text{N}}}\text{NH}$  ligands have been explored thoroughly with the transition metal system owing to their unique structural motif of easily achievable flexible coordination modes by rational design. The design of a new class of ligand systems with identical electronic characteristics to imidazolin-2-imines is highly desired. The efforts are on to extend the members of the N-heterocyclic imine class either by introducing the phenyl ring at the backbone of the imidazole ring or extend its ring size (**IV-VI**) (Scheme 2).<sup>[49-51]</sup>

The synthesis, catalytic applications and the significance

of transition metal complexes containing imidazolin-2-iminato ligands in the field of homogeneous catalysis are briefly presented in this review. Catalytic applications, covered in the current review, are olefin polymerization, hydroamination, ring-opening metathesis (ROP), hydroboration, and metathesis reactions. All metal complexes were synthesized by utilizing N-silylated 2-iminoimidazolines, imidazolin-2-imine, and lithiated imidazolin-2-iminato. In general, N-silylated 2-iminoimidazolines and lithiated imidazolin-2-iminato were exploited in synthesizing metal complexes starting with halide metal precursors. The tunable steric and electronic features of imidazolin-2-iminato supported transition metal complexes and its impact on the catalytic efficiencies are briefly discussed. A related review of transition metal-containing imidazolin-2-iminato ligands was covered till 2014.<sup>[52]</sup> Thus, the recent progress of this field starting from 2015 to date is briefly documented in the current review. Further, the future scopes and possible structural modifications of the transition metal complexes bearing imidazolin-2-iminato/N-heterocyclic iminato moieties by altering ring size are also presented herein.<sup>[49-51]</sup>



**Scheme 2.** Schematic presentations of the new members of the N-heterocyclic iminato moiety.

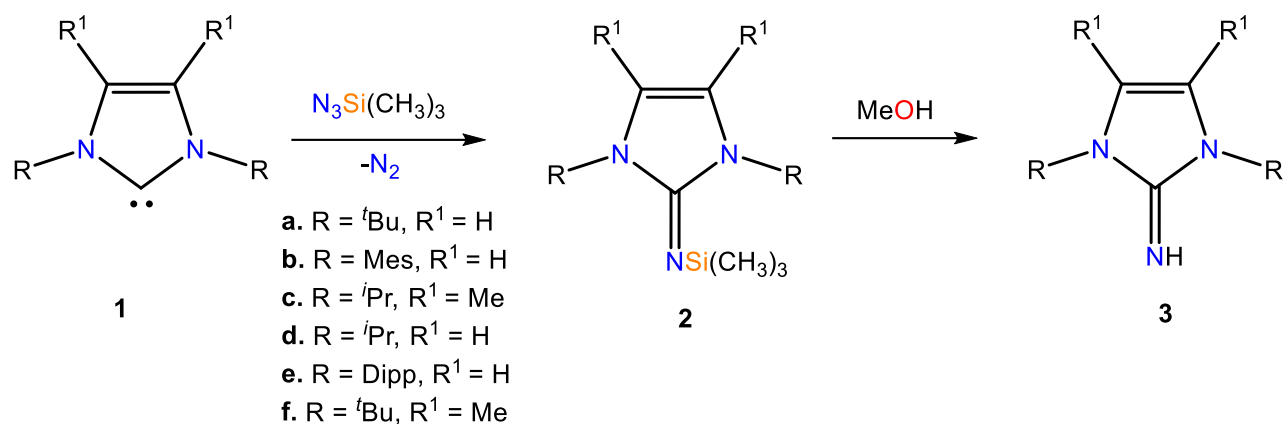
## 2. Synthesis of N-silylated 2-iminoimidazolines

Tamm *et al.* introduced the synthetic protocol of imidazolin-2-imine by the Staudinger reaction<sup>[53]</sup> of 1,3-di-*tert*-butyl imidazolin-2-ylidene **1a** with  $\text{N}_3\text{Si}(\text{CH}_3)_3$  in boiling toluene for 72 hours to afford the N-silylated 2-iminoimidazoline **2a** (Scheme 3). The formation of carbenes (**1a** and **1b**) was identified in  $^1\text{H}$  NMR as the appearance of two backbone NCH protons in high-field shifts of  $-0.74$  ppm (**1a**,  $\text{R}^1 = \text{H}$ ) and  $-0.72$  ppm (**1b**,  $\text{R}^1 = \text{H}$ ) upon the formation of corresponding imine **2a** and **2b**, respectively.<sup>[54]</sup>

The formation of **2c** from **1c** was confirmed by the low-field shift of the septet resonance of CH proton of the wingtip isopropyl group from 3.95 to 4.61 ppm. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicate the pseudo- $\text{C}_{2v}$  symmetry of **2** in solution. The detailed X-ray structure analysis of **2a** revealed that the exocyclic C–N bond distance of 1.275(3) Å is significantly shorter than the corresponding distance in 2-imino-1,3-dimethylimidazoline of 1.296(2) Å.<sup>[55]</sup>

## 3. Synthesis of 2-iminoimidazolines

Extensive applications of the N-silylated 2-iminoimidazolines



**Scheme 3.** Synthesis of N-silylated 2-iminoimidazolines (**2**) and 2-iminoimidazolines (**3**).

were not only limited to the synthesis of numerous transition metal complexes. Rather, the respective desilylated 2-iminoimidazolines were also exploited as valuable ligands for the advancement of organometallic chemistry of lanthanides and actinides. Initially, the syntheses of 2-iminoimidazolines were achieved by a multistep synthetic protocol starting from 2-aminoimidazole.<sup>[56]</sup> Later on, Tamm and co-workers developed a desilylation method that allowed a convenient access to 2-iminoimidazolines from N-silylated 2-iminoimidazolines with various N-substitutions (Scheme 3).

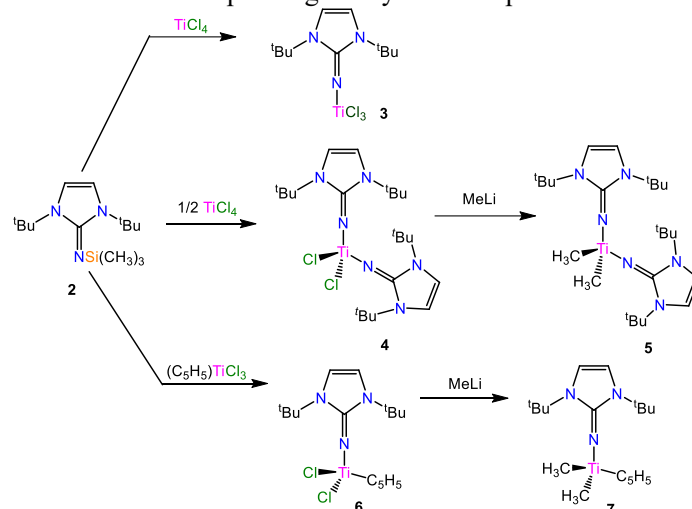
#### 4. Imidazolin-2-iminato transition-metal complexes

##### 4.1. Titanium complexes

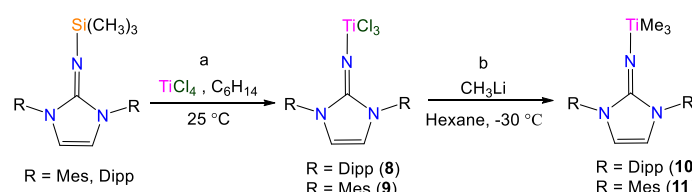
##### 4.1.1. Synthesis of titanium complex from N-silylated 2-iminoimidazolines

The reaction between N-silylated 2-iminoimidazolines and metal halide is one of the major synthetic protocols for preparing imidazolin-2-iminato metal complexes. The imidazolin-2-iminato titanium complexes were synthesized by following the identical synthetic protocol of complexation reaction of silylated iminophosphoranes with various metal halides to afford phosphoraneiminato complexes with the removal of trialkylsilyl halides.<sup>[57-58]</sup> The room temperature treatment of TiCl<sub>4</sub> in hexane with one and two equivalent of the imine resulted in the corresponding orange crystalline Ti(IV) complex **3** and **4**. Subsequent methylation of complex **4** with methyllithium afforded corresponding methylated complexes **5** in a moderate yield. The mixed imidazolin-2-iminato and cyclopentadienyl titanium complex **6** was also synthesized identically by the reaction of [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)TiCl<sub>3</sub>] with **2** (Scheme 4). The central metal ion in **6** is coordinated with two chloride ligands, one cyclopentadienyl, and one imidazolin-2-iminato ligand completing a pseudo-tetrahedral geometry. The complex **6** displayed a short Ti–N<sub>imine</sub> (1.765(3) Å) bond distance accredited to the efficient  $\pi$ -donation of imidazolin-2-iminato moiety. The Cl–Ti–Cl, Cl–Ti–N angles were found to be 102.10(3)° and 103.47(5)°, respectively. However, relatively longer Ti–N bond distance and significant deviation from the linearity of Ti–N–C angle in saturated imidazolidin-2-iminato titanium complex were observed.<sup>[59]</sup>

The treatment of **6** with methyllithium resulted in the formation of corresponding methylated compounds **7**.



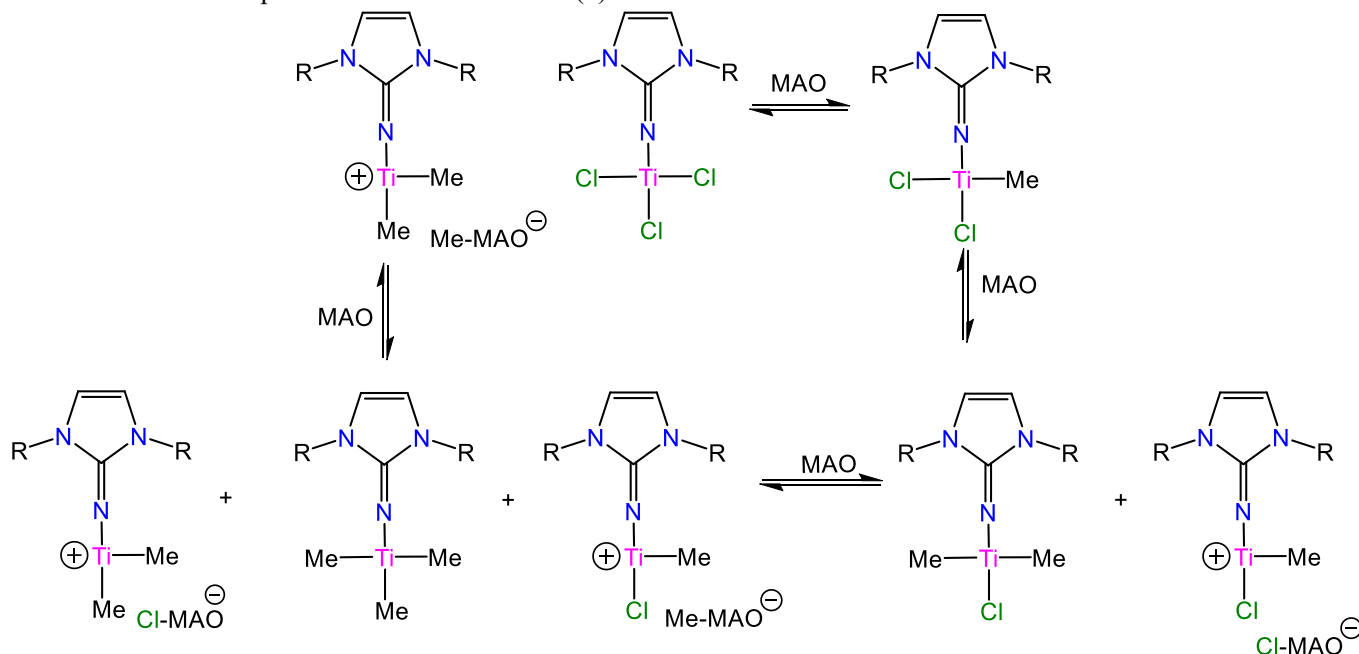
**Scheme 4.** Synthesis of imidazolin-2-iminato Ti complex by desilylation of N-silylated 2-iminoimidazoline.



**Scheme 5.** Synthesis of Ti complex with bulky imidazolin-2-iminato ligands.

Eisen and co-workers synthesized the Ti complexes **8** and **9** containing the bulky imidazolin-2-iminato ligands following the same aforementioned protocol (Scheme 5a).<sup>[60]</sup> Subsequent treatment with CH<sub>3</sub>Li at –30°C afforded the corresponding methylated complexes **10** and **11** (Scheme 5b). The central metal atom in **8** and **9** are coordinated with three chlorine atom and one imidazolin-2-iminato ligand exhibiting a tetrahedral geometry. The X-ray structure of **8** and **9** displayed short Ti–N<sub>imine</sub> bond distances (1.731(3) Å and 1.720(10) Å) and near-linear C–N–Ti bond angle (175.9(2)° and 172.4(9)°). These indicate the effective electron donation to the metal from

imidazolin-2-iminato moiety. Complexes **8** and **9** displayed a short Ti–N<sub>imine</sub> bond distance and a larger C–N–Ti bond angle compared to complex **6**. The X-ray studies of Im<sup>Dipp</sup>TiClMe<sub>2</sub> and Im<sup>Dipp</sup>NTiMe<sub>3</sub> (**10**) complexes showed that with the increase in the number of methyl groups in the complex, the Ti–N<sub>imine</sub> bond distance increases, and the C–N–Ti bond angle decreases. These bond parameters observed 1.762(4) Å –

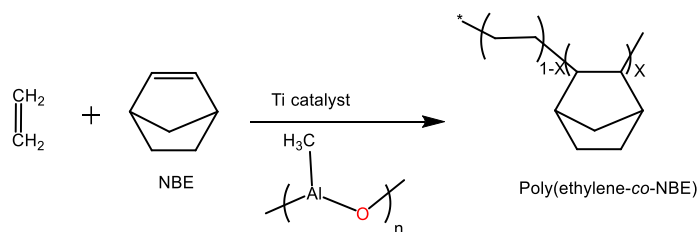


**Scheme 6.** Activation of Im<sup>Dipp</sup>NTiCl<sub>3</sub> by MAO.

However, the complexes of type L<sub>2</sub>TiX<sub>2</sub> (L = imidazolin-2-imide; X = Cl, CH<sub>3</sub>) were found to be active in the living polymerization of propylene<sup>[63]</sup> and motivated to employ the titanium complexes **8**, **9**, and corresponding methylated complexes **10**, **11** for polymerization reactions of ethylene with the combination of methylaluminumoxane (MAO) and trityltetrakis(pentafluorophenyl)-borate (TTPB). The PD of the obtained polymers at low ratios of MAO to **8** indicated the formation of more than one active species. The relatively higher Ti:Al ratios allowed the polymer formation with narrow PDs, attributed to the functioning of single-site catalysts. The molecular weight of the polymers varied with the amount of MAO used, and higher activity was achieved at Al:Ti = 100. The methylated complexes were synthesized to get a better insight into the nature of active species at low MAO concentrations. The highly active (Al:Ti = 20) Im<sup>Dipp</sup>NTiClMe<sub>2</sub> is assumed to be the first pre-catalyst intermediate formed with the reaction between Im<sup>Dipp</sup>NTiCl<sub>3</sub> and MAO. The activity decreases with the increase of MAO quantity. Surprisingly, the best catalytic activity was achieved with Im<sup>Mes</sup>NTiCl<sub>3</sub> (**9**) at a very low Al:Ti ratio of 8. The smaller cone angle was observed for **9** (173.8°) compared to other three complexes (i.e., Im<sup>Dipp</sup>NTiCl<sub>3</sub> = 259.0°, Im<sup>Dipp</sup>NTiClMe<sub>2</sub> = 257.3°, and Im<sup>Dipp</sup>NTiMe<sub>3</sub> = 248.7°). The smaller cone angle is the direct manifestation for the relative higher reactivity of

172.8(4)° in Im<sup>Dipp</sup>NTiClMe<sub>2</sub> and 1.792(3) Å – 171.9(3)° in Im<sup>Dipp</sup>NTiMe<sub>3</sub>. Initially, it was found that titanium complexes of the type CpTi(L)X<sub>2</sub> (L = imidazolin-2-imide; X = Cl, CH<sub>3</sub>) were highly active for the polymerization of ethylene and co-polymerization of ethylene with norbornene and 1-hexene.<sup>[61-62]</sup>

**9**. The small cone angle implies a greater availability space for the incoming monomer unit. The formation of four possible active species were presumed based on the experimental results obtained with Im<sup>Dipp</sup>NTiCl<sub>3</sub> and low amounts of MAO: [Im<sup>Dipp</sup>NTiClMe]<sup>+</sup>[Cl-MAO]<sup>-</sup>, [Im<sup>Dipp</sup>NTiClMe]<sup>+</sup>[Me-MAO]<sup>-</sup>, [Im<sup>Dipp</sup>NTiMe<sub>2</sub>]<sup>+</sup>[Cl-MAO]<sup>-</sup> and [Im<sup>Dipp</sup>NTiMe<sub>2</sub>]<sup>+</sup>[Me-MAO]<sup>-</sup>. It was also anticipated that the reaction between Im<sup>Dipp</sup>NTiClMe<sub>2</sub> with MAO might produce the complexes [Im<sup>Dipp</sup>NTiClMe]<sup>+</sup>[Me-MAO]<sup>-</sup>, [Im<sup>Dipp</sup>NTiMe<sub>2</sub>]<sup>+</sup>[Cl-MAO]<sup>-</sup>, and [Im<sup>Dipp</sup>NTiMe<sub>2</sub>]<sup>+</sup>[Me-MAO]<sup>-</sup>, while Im<sup>Dipp</sup>NTiMe<sub>3</sub> can generate only [Im<sup>Dipp</sup>NTiMe<sub>2</sub>]<sup>+</sup>[Me-MAO]<sup>-</sup> (**Scheme 6**).



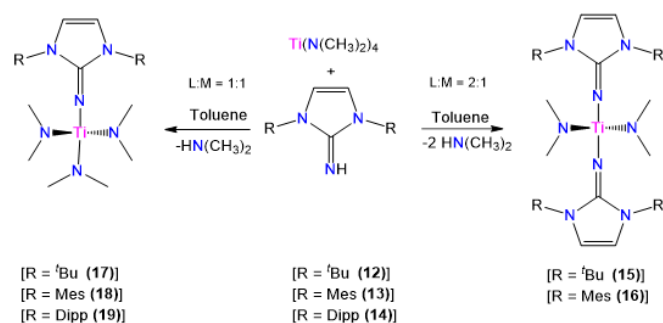
**Scheme 7.** Copolymerization of Ethylene/NBE by **6**.

Tamm and co-workers investigated the ethylene/1-hexene co-polymerization behavior of complex **6**.<sup>[64]</sup> The difference in catalytic behavior was investigated by replacing cyclopentadienyl ligand with tropidynyl ligand.<sup>[65]</sup> The co-polymerizations reactions of ethylene/norbornene have been explored by the half-titanocene complex comprising of

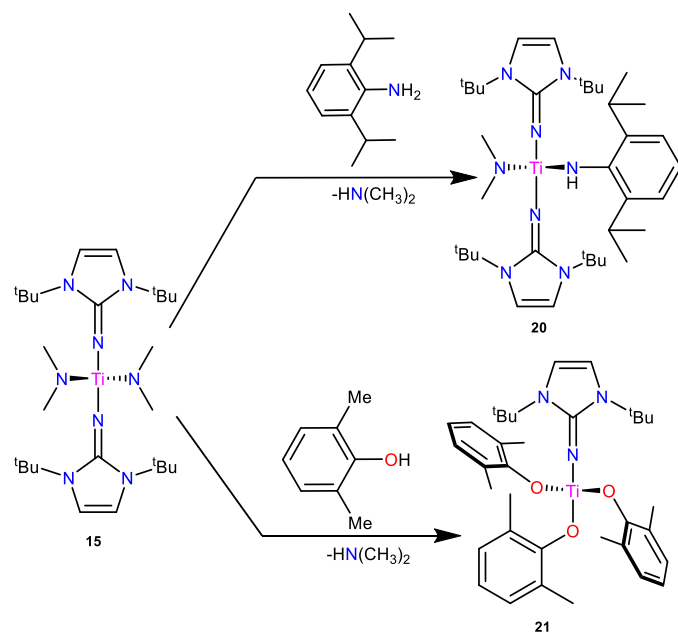
imidazolin-2-iminato ligands.<sup>[62]</sup> Complex **6** exhibited remarkable performance affording copolymers with a high molecular weight with uniform distributions (Scheme 7).

Based on the proven analogy between imidazolin-2-iminato and cyclopentadienyl ligands<sup>[52]</sup> and the excellent ability of Cp<sup>\*</sup>Ti(OAr)X<sub>2</sub> as pre-catalyst in the olefin polymerization reaction,<sup>[57]</sup> Eisen and co-workers synthesized numerous mixed imidazolin-2-iminato/aryl alkoxo Ti(IV) complexes. The complexes were prepared by treating different lithiated phenol with appropriate mono(imidazolin-2-iminato)titanium trichloride complexes, and the catalytic performances were subsequently examined towards the polymerization of ethylene, propylene, 1-hexene, and 1-octene.<sup>[66]</sup>

#### 4.1.2. Synthesis of titanium amido complex



**Scheme 8.** Synthesis of bis/mono-imidazolin-2-iminato titanium (IV) amido complexes **15-19**.



**Scheme 9.** Synthesis of **20** and **21**.

The 1:2 molar reaction between tetrakis(dimethylamido) titanium (IV) [Ti(N(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>] and imidazolin-2-imine (Im<sup>R</sup>NH) ligands [R = <sup>t</sup>Bu (**12**), Mes (**13**)] afforded bis-imidazolin-2-iminato titanium (IV) complexes **15** and **16** [*k*<sup>1</sup>-(Im<sup>R</sup>N)<sub>2</sub>Ti(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>] (R = <sup>t</sup>Bu, **15**; R = Mes, **16**) in high yields (Scheme 8). Similar reaction between metal and ligand

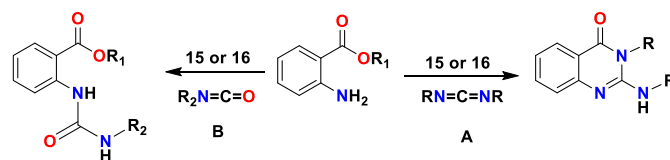
(**12-14**) maintaining 1:1 ratio afforded the mono-imidazolin-2-iminato titanium (IV) complexes **17-19** [R = <sup>t</sup>Bu (**17**), Mes (**18**), Dipp (**19**)].<sup>[67]</sup>

Subsequent treatment of **15** with 2,6-diisopropylamine (DippNH<sub>2</sub>) at 60°C afforded the corresponding mixed ligand titanium complex [*k*<sup>1</sup>-(Im<sup>tBu</sup>N)<sub>2</sub>Ti(NMe<sub>2</sub>)(HNDipp)] (**20**).<sup>[68]</sup> However, identical reaction conditions with 2,6-diphenyl phenol afforded mono-imidazolin-2-iminato Ti(IV) phenolate complex [*k*<sup>1</sup>-(Im<sup>tBu</sup>N)Ti(O-1,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>] (**21**) (Scheme 9).

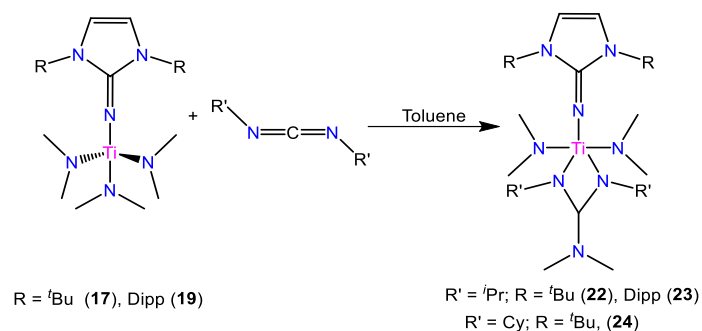
The Ti–N<sub>amide</sub> distances in complex **17** were slightly higher compared to complex **18** and **19**. The Ti–N<sub>iminato</sub> bond lengths in the complex **18** (1.851(1) Å) and **19** (1.853(1) Å) are comparable, however, these distances found slightly longer compared to complex **17**, presumably due to the positive inductive effect of tert-butyl groups enhanced the electron availability of ring N-atom of imidazolin-2-iminato moiety<sup>[50,52]</sup>. In complex **17** and **19**, the Im<sup>R</sup>N<sup>−</sup> moiety coordinated to the metal ion in a nearly linear fashion (Ti–N–C = 170.9° and 169.2(1)°, respectively), however, this angle significantly deviated from the linearity for the complex **18** (164.5(1)°). The Ti–N<sub>iminato</sub> bond lengths in all complexes are observed slightly shorter [1.847(2) Å and 1.858(2) Å for complex **16**; 1.8242(18) Å and 1.8334(17) Å for complex **20** and 1.7738(16) Å for **21**], compared to the previously reported complexes, indicating the strong 2σ, 4π-electron donation of imidazolin-2-iminato moiety.

#### 4.1.3. The cyclization of amino acid esters mediated by Ti complex

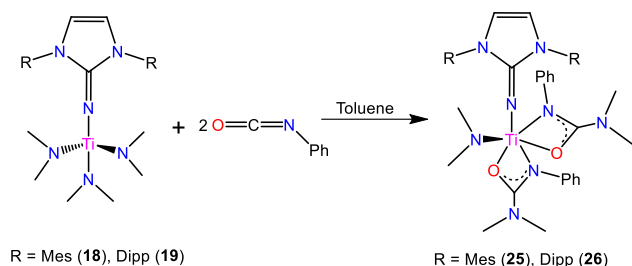
Quinazolinones, an imperative heterocyclic compound, have numerous biological applications<sup>[69-75]</sup> and are used as a synthon for various natural products.<sup>[76-78]</sup> It has been reported that quinazolinones can be synthesized by the reaction of halo benzoic acid and guanidine, catalyzed by CuI. However, this method becomes unfavorable due to the requirement of a large number of additives.<sup>[79]</sup> Panda and co-workers recently reported the hydroamination/cyclization of amino acid esters with carbodiimides and isocyanates to afford the corresponding quinazolinone and urea derivatives mediated by bis-imidazolin-2-iminato titanium(IV) amido complexes **15** or **16** (Scheme 10).<sup>[80]</sup>



**Scheme 10.** Catalytic cyclization (A) and guanylation (B) of amino acid esters with carbodiimides and isocyanates respectively.

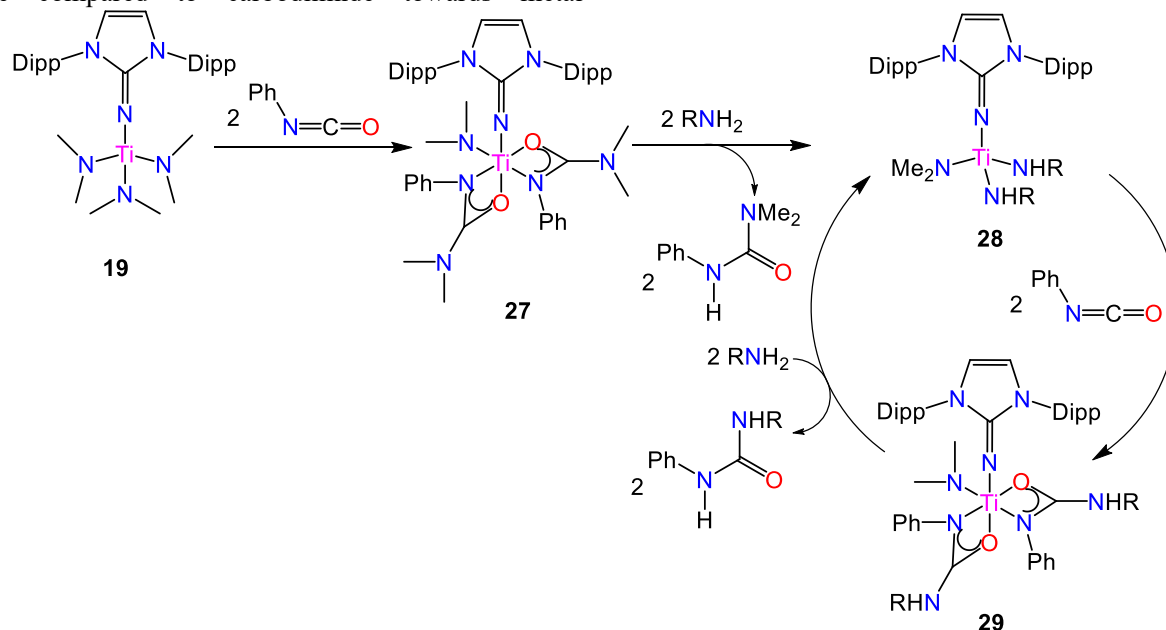


**Scheme 11.** Synthesis of titanium complexes **22**, **23** and **24**.



**Scheme 12.** Synthesis of Titanium complexes **25** and **26**.

The stoichiometric reaction between mono imidazolin-2-iminato titanium (IV) complexes (**17** and **19**) with N, N'-diisopropylcarbodiimide, and N, N'-dicyclohexylcarbodiimide afforded corresponding mono inserted titanium guanidinate complexes **22-24** in good yields (Scheme 11).<sup>[81]</sup> Further insertion products were not traced even in presence of excess carbodiimides, presumably attributed to the absence of free coordination sites on complex **24** and the lower electrophilicity of the sp-carbon of carbodiimide molecule. Exclusive formation of the bis-inserted compound as the sole reaction product upon the treatment of 1:1 or 1:2 molar ratio of the metal complex and PhNCO indicated the higher reactivity of isocyanate compared to carbodiimide towards metal



**Scheme 13.** A plausible mechanism for the catalytic addition of N-H bond to isocyanate by titanium precatalyst **19**.

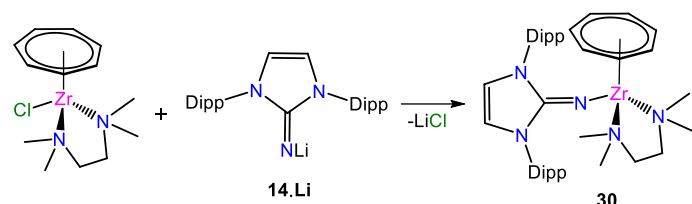
complexes **18** and **19**.

The complex **18** was exploited towards the catalytic addition of an amine to phenyl isocyanate and carbodiimide to afford corresponding urea and guanidine, respectively. The catalytic cycle started with the attack of metal coordinated NMe<sub>2</sub> of the pre-catalyst **19** to incoming phenyl isocyanate (PhNCO) to generate the complex **27** (Scheme 13). The second step involved the reaction between 2 equivalent incoming amines to form the corresponding titanium amido complex **28**. Subsequently, **28** was converted to ureate **29** upon the treatment of 2 equivalent PhNCO. The catalytic cycle terminated with the reaction between the two equivalent amines and **29** to eliminate urea and regenerate the active species **28**.

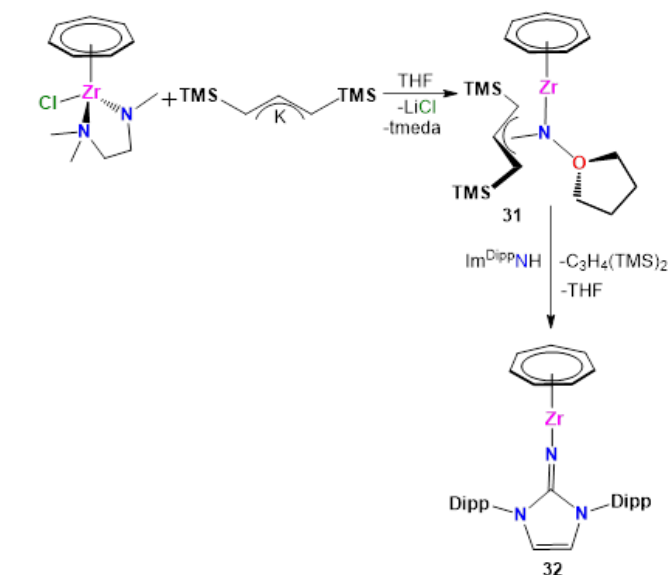
## 4.2. Zirconium Complex

Zirconium is the second most explored metal and has been used as a pre-catalyst for polymerization reactions. The Imidazolin-2-iminato is the ideal candidate for stabilizing high oxidation state metal and has been used as a spectator ligand for Zr(IV).<sup>[82]</sup> The Dipp substituted ligand (Im<sup>Dipp</sup>NH) was preferred for the study since its higher sterical encumbrance nature restricted the formation of the dinuclear complex and thus provided the stability of the mononuclear complex [(η<sup>7</sup>-C<sub>7</sub>H<sub>7</sub>)Zr(Im<sup>Dipp</sup>N)]. Tamm and co-workers used [(η<sup>7</sup>-C<sub>7</sub>H<sub>7</sub>)ZrCl(tmeda)] (tmeda = N,N,N',N'-tetramethylethylenediamine) as Zr metal precursor as it allowed for the smooth incorporation of pentadienyl,<sup>[83-85]</sup> cyclopentadienyl,<sup>[86]</sup> and phospholyl ligands.<sup>[87-89]</sup> The first Zr complex bearing imidazolin-2-iminato was synthesized by reacting lithium salt of **14** with [(η<sup>7</sup>-C<sub>7</sub>H<sub>7</sub>)ZrCl(tmeda)] (Scheme 14). The complex **30** exhibited slightly longer Zr–N bond distance (2.5136(14) and 2.5737(13) Å) than the starting material (2.477(2) / 2.519(2) Å).

In the  $^1\text{H}$  NMR spectrum, **30** exhibited a singlet at 4.82 ppm characteristics to  $\text{C}_7\text{H}_7$  ligand. The acid–base reaction between imidazolin-2-imine and rare-earth-metal neosilyl complexes found an expedient method for incorporation of imidazolin-2-iminato into the metal coordination sphere. The tmeda-free Zr complex  $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}\{\eta^3\text{-C}_3\text{H}_3(\text{TMS})_2\}(\text{THF})]$  (**31**) was synthesized by treating  $[(\eta^7\text{-C}_7\text{H}_7)\text{ZrCl}(\text{tmeda})]$  and  $\text{K}[\text{C}_3\text{H}_3(\text{TMS})_2]$  in THF. Subsequent treatment of **31** and **14** in 1:1 ratio afforded the  $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}(\text{Im}^{\text{Dipp}}\text{N})]$  (**32**) (Scheme 15), which acted as an initiator for the ring-opening polymerization of  $\epsilon$ -caprolactone (Scheme 16). Complex **32** displayed pogo stick geometry identical to  $[(\eta^8\text{-C}_8\text{H}_8)\text{Ti}(\text{NR})]$  complexes.<sup>[90]</sup> The reaction followed the coordination insertion mechanism, in which  $\epsilon$ -caprolactone was first coordinated to the metal. Subsequently, the nucleophilic attack of imidazolin-2-iminato to the carbon atom of the  $\text{C}=\text{O}$  group released the ring strain upon ring-opening. The presence of bulky Dipp substituents and cycloheptatrienyl ring in complex **32** inhibited the dimerization process.<sup>[91]</sup>



**Scheme 14.** Synthesis of complex  $[(\eta^7\text{-C}_7\text{H}_7)\text{Zr}(\text{Im}^{\text{Dipp}}\text{N})(\text{tmeda})]$  (**30**).

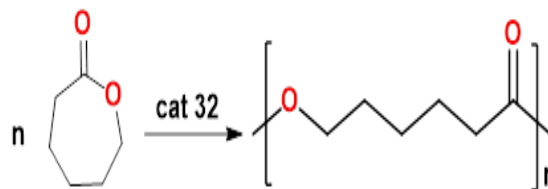


**Scheme 15.** Synthesis of **31** and **32**.

### 4.3. Hafnium complex

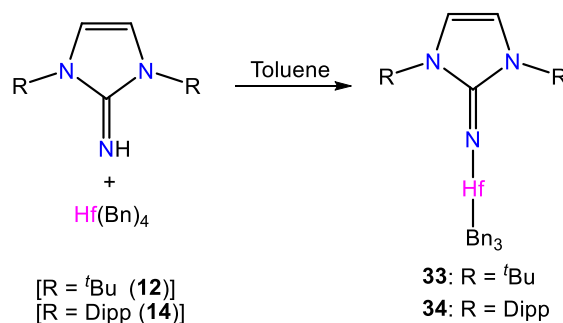
According to the recently maiden report, the Hf complex comprises of imidazolin-2-iminato moiety.<sup>[92]</sup> The uniqueness of Hf amongst the electrophilic group 4 is its highest oxophilicity and unusual small size due to lanthanide contraction.<sup>[93]</sup> The mono-(imidazolin-2-iminato)hafnium (IV) complexes **33–34** were prepared by reacting imidazolin-2-imine ligands (**12** and **14**) and hafnium-tetra benzyl complex

in equimolar ratios (Scheme 17). The Hf–N bond distance in complex **33** (1.924(6) Å) found slightly longer than complex **34** (1.911(5) Å). The near-linear disposition of Hf–N–C was observed in **33** (176.2(3)°) and **34** (172.2(3)°). The observed smaller cone angle for complex **33** (124°) compared to **34** (262°) implies the greater accessible space for incoming substrates to complex **33**.

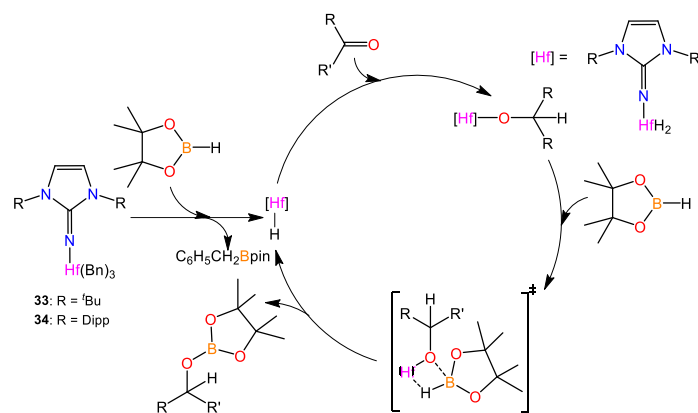


**Scheme 16.** Polymerization of  $\epsilon$ -CL using complex **32** as a catalyst.

The activities of Hf complexes **33** and **34** were investigated towards the hydroboration of a wide range of numerous aldehydes, ketones, and carbodiimides. The aldehyde containing electron-withdrawing groups proceeded at a faster rate than aldehydes with electron-donating groups. Both the complexes showed excellent chemoselectivity where the carbonyl group was selectively hydroborated, leaving other functionalities unchanged. A plausible mechanism was proposed for the carbonyl hydroboration reaction (Scheme 18).



**Scheme 17** Synthesis of mono imidazolin-2-iminato Hf (IV) complexes **33** and **34**.



**Scheme 18** Proposed mechanism for hydroboration of  $\text{C}=\text{O}$  promoted by the **33** and **34**.

The catalytic cycle for hydroboration of carbonyl substrates started with the generation of trihydride species by the rapid reaction between the hafnium pre-catalysts **33/34** and

HBpin. The second step involved the insertion of the incoming aldehyde/ketone substrates into one of the metal-hydride bonds to produce the hafnium alkoxide. Subsequently, metal alkoxide species reacted with another incoming HBpin to form the hydroborated products with the concomitant regeneration of active hydride species.

#### 4.4. Vanadium Complex

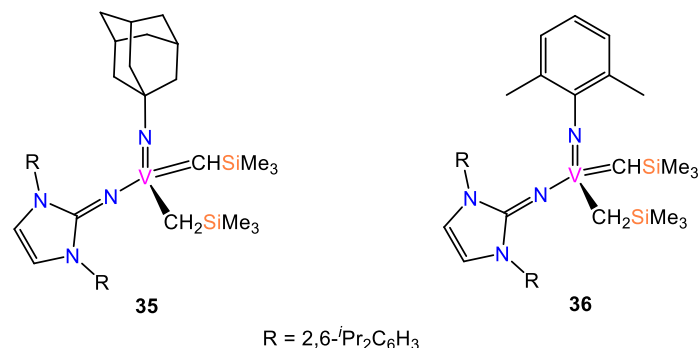
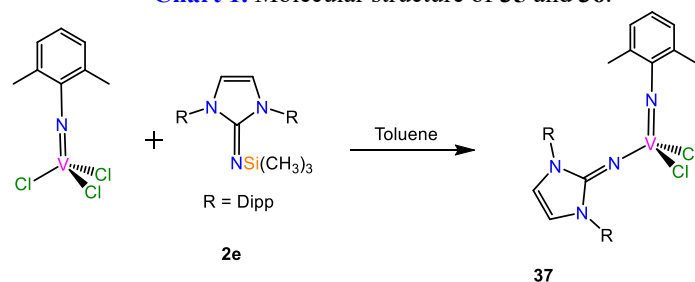
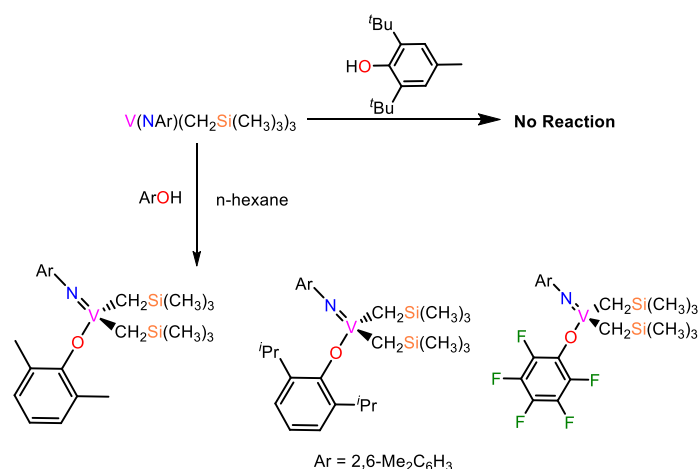


Chart 1. Molecular structure of **35** and **36**.



Scheme 19. Synthesis of **37**.

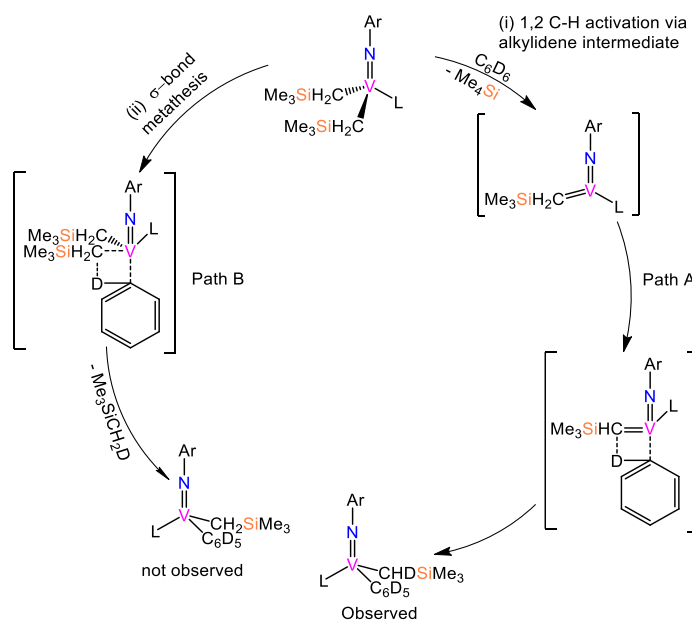


Scheme 20. Schematic presentation of reaction between (arylimido)vanadium(V) trialkyl and aryl alcohols.

Recently (Imido)vanadium(V) complexes received considerable attention due to their unique characteristics of resemblance to the popular olefin polymerization catalysts. Besides olefin polymerization reactions, (Imido)vanadium(V) complexes containing imidazolin-2-iminato (**35** and **36**) have been known as the promising candidates for ROMP of cyclic olefins (Chart 1).<sup>[94-97]</sup> Recently, Nomura *et al.* synthesized a series of (imido)vanadium(V) dichloride complexes containing imidazolin-2-iminato ligands. The (N-2,6-

Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) vanadium(V) dichloride complexes **37** bearing Im<sup>Dipp</sup>N ligand was synthesized by reacting V(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)Cl<sub>3</sub> with **2e** in toluene for six hours (Scheme 19).

The (Im<sup>Dipp</sup>N)(NAd)vanadium(V) dichloride (**38**) and (Im<sup>Dipp</sup>N)(NPh)vanadium(V) dichloride (**37**) were synthesized following similar reaction conditions by treating V(NAd)Cl<sub>3</sub> or V(NPh)Cl<sub>3</sub><sup>[98]</sup> with **2e**. All the complexes were employed as pre-catalysts for ethylene polymerization and ethylene/norbornene copolymerization using Et<sub>2</sub>AlCl as cocatalyst.<sup>[99]</sup> The calculated chemical shifts obtained by the GIAO-DFT method well agree with the experimental <sup>51</sup>V NMR chemical shifts value.<sup>[94]</sup> Various vanadium(V)-alkyls complexes were synthesized by reacting (arylimido)vanadium(V) trialkyl analogue, V(NAr)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub> (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and substituted phenols/alcohols in unimolar ratio. However similar reaction didn't proceed with bulky 2,6-*t*-Bu<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub>OH even with the use of excess amount (Scheme 20).



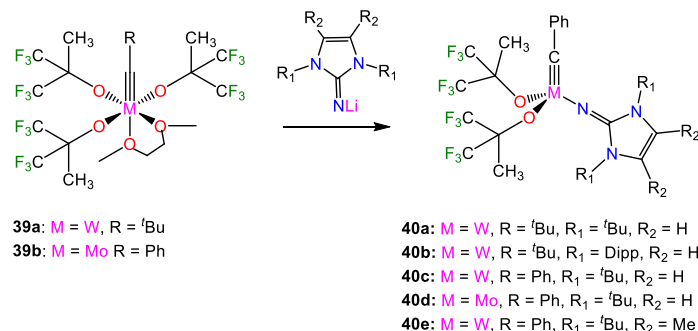
Scheme 21. The probable mechanism for the formation of the phenyl complexes.

Further, Nomura *et al.* studied 1,2-C-H/D activation of benzene/C<sub>6</sub>D<sub>6</sub> mediated by (arylimido)vanadium(V)-alkylidene complexes. Two possible mechanisms were suggested for the process: (1) 1,2 C-D activation; and (2)  $\sigma$ -bond metathesis (Scheme 21). The formation of CHDSiMe<sub>3</sub> was confirmed by the <sup>2</sup>H NMR spectrum ( $\delta$  = 2.10 ppm, d, J<sub>DH</sub> = 40 Hz). However, the nonexistence of CD<sub>2</sub>SiMe<sub>3</sub> and CH<sub>2</sub>SiMe<sub>3</sub> were confirmed by the <sup>2</sup>H NMR spectrum and <sup>1</sup>H NMR spectrum, respectively. The above data is strongly supportive of path A that involved the 1,2-C-D bond activation of C<sub>6</sub>D<sub>6</sub> via the vanadium(V)-alkylidene intermediate.

#### 4.5. Tungsten and molybdenum complexes

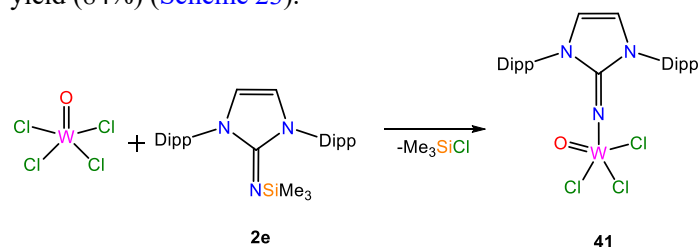
Alkene/alkyne metathesis has a substantial influence on modern petrochemical and polymer industries. High-oxidation-state tungsten and molybdenum complexes containing alkyldiene and alkyldiylne ligands are well known

to catalyze the olefin metathesis reactions.<sup>[100-104]</sup> For example, Tamm and co-workers contributed to this field by reporting first tungsten and molybdenum alkylidyne complexes bearing strongly electron-donating imidazolin-2-iminato ligands in combination with electron-withdrawing fluorinated alkoxides.<sup>[105-106]</sup> The reactions between the trialkoxides alkylidyne precursors **39** with lithium salt of imidazolin-2-imides at room temperature conveniently afforded the metal complexes **40** (Scheme 22). Most of the complexes (except **40b**) showed excellent activities for ring-closing alkyne metathesis (RCAM) and alkyne cross-metathesis (ACM) reactions.

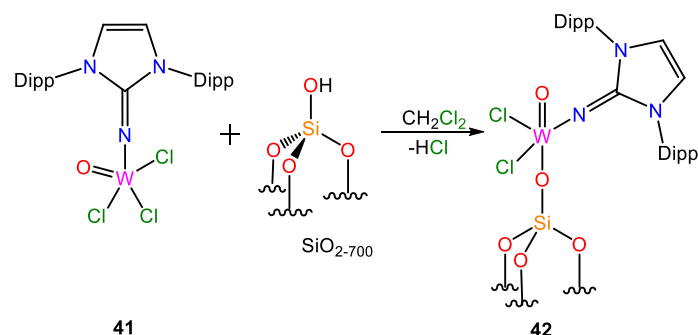


Scheme 22. Synthesis of **40**.

Recently, Basset and co-workers elaborately demonstrated a synthetic approach for the preparation of a functionalized silica-supported tungsten oxo complex [(≡Si-O)-W(=O)-(CH<sub>3</sub>)<sub>2</sub>-L], L = Im<sup>Dipp</sup>N.<sup>[107]</sup> The reaction between tungsten (VI) oxytetrachloride and 1 equivalent N-silylated 2-iminoimidazoline in dichloromethane under the refluxing condition afforded the rapid precipitation of complex Im<sup>Dipp</sup>NWOC<sub>3</sub> (**41**) as the orange crystalline solid in high yield (84%) (Scheme 23).



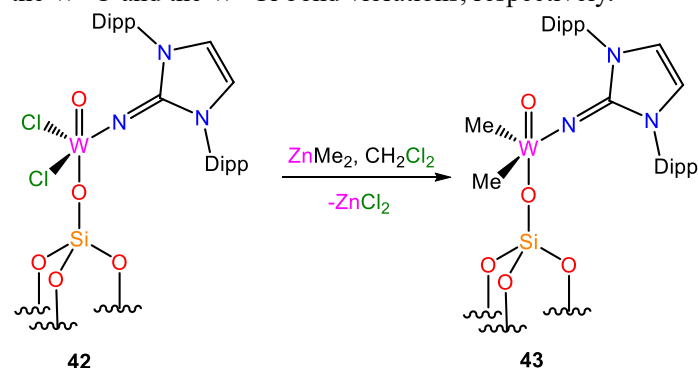
Scheme 23. Synthesis of Im<sup>Dipp</sup>NWOC<sub>3</sub> (**41**).



Scheme 24. Synthesis of [(≡Si-O)-W(=O)Cl<sub>2</sub>-Im<sup>Dipp</sup>N] (**42**).

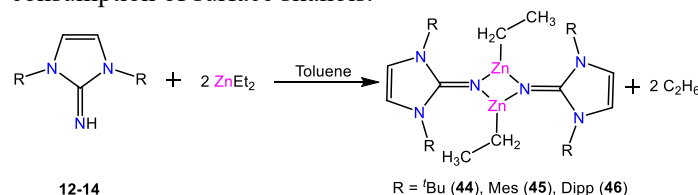
The pronounced shifting of backbone H of imidazolin-2-iminato ring in the downfield region of the <sup>1</sup>H NMR spectrum

confirmed the desilylation and coordination of the nitrogen to the metal center. The HSQC <sup>1</sup>H, <sup>13</sup>C correlation NMR spectra also support the structure of compound **41**. The W–N bond distance in **41** (1.782(5)) Å is consistent with other related tungsten complexes [Me<sub>3</sub>CCH=W(N<sup>Dipp</sup>)(OCCMe<sub>3</sub>)<sub>2</sub>]<sup>[108]</sup> (1.731(6), 1.748(6) Å) and [PhCH=W(N<sup>Dipp</sup>){OCMe(CF<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> (1.708(17) Å).<sup>[109]</sup> The W–Cl bond length (2.36 Å) is also compared with related bis(2,4,6-tribromophenoxy) tungsten(VI) oxochloride complex (2.3104(13)–2.3302(13) Å).<sup>[110]</sup> The W=O bond length in **41** (1.729(5) Å) is slightly larger than related tungsten complex W(O)(CH-*t*-Bu)[N(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(OHMT)(PMe<sub>2</sub>Ph) (1.710(2) Å, HMTO = 2,6-dimesityl phenoxide).<sup>[111]</sup> The characteristic stretching bands at 946 and 360 cm<sup>-1</sup> in Raman spectroscopy are attributed to the W=O and the W–Cl bond vibrations, respectively.



Scheme 25. Synthesis of [(≡Si-O)-W(=O)Me<sub>2</sub>-Im<sup>Dipp</sup>N] (**43**).

The surface compound [(≡Si-O)-W(=O)Cl<sub>2</sub>-Im<sup>Dipp</sup>N] (**42**) was synthesized by grafting of **41** on partially dehydroxylated silica at 700 °C (Scheme 24). The reaction was carried out under mild dynamic vacuum conditions to eliminate gaseous HCl produced during the reaction. The molecular complex **42** was collected as a light orange solid by washing with dichloromethane. The complete disappearance of the hydroxyl peak at 3745 cm<sup>-1</sup> in the IR spectra indicated the total consumption of surface silanols.



Scheme 26. Synthesis of Im<sup>R</sup>NZn complexes **44-46**.

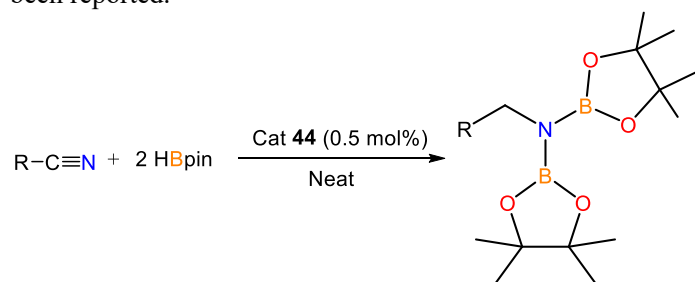
The compound **42** was further alkylated with ZnMe<sub>2</sub> to form [(≡Si-O)-W(=O)Me<sub>2</sub>-Im<sup>Dipp</sup>N] (**43**) (Scheme 25). A close look at the FT-IR spectrum of **43** revealed that a substantial shift for ν(C=N) band was observed to 1612 cm<sup>-1</sup> (vs. 1653 cm<sup>-1</sup> in **42**), which clearly indicated the alteration in the electronic environment around the central metal.

The catalytic utility of **42** was explored towards the metathesis of terminal olefins like propene and 1-hexene. Under the condition of temperature 150 °C, the metathesis reaction of propene produced an equilibrated mixture of

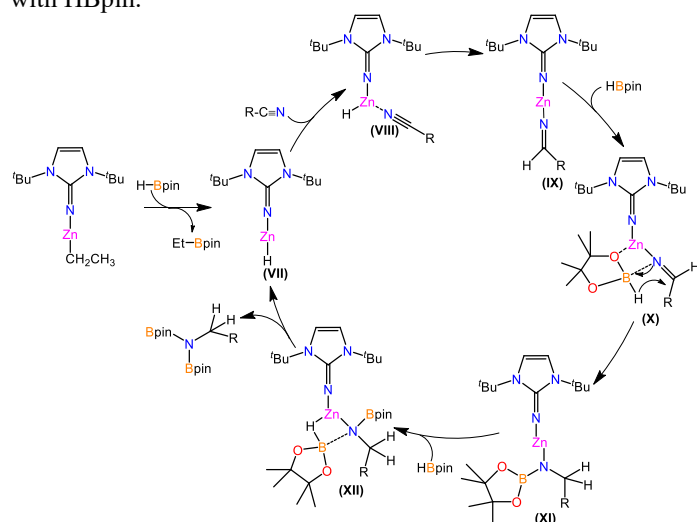
ethane/2-butenes with TON 1165. The tungsten complex **43** found to be more selective toward the formation of dec-5-ene than other tungsten-based catalysts.

#### 4.6. Zinc complex

In recent years, the first-row transition metal compounds have emerged as a homogeneous catalyst in the field of organometallic chemistry and catalysis, which were conventionally the realm of precious metal. Recently there is a growing interest in the potential replacement of precious metals with 3d metals, which are less environmentally harmful, low cost, and highly abundant. However, the performance of the base metal catalysts always lacked behind the noble metal catalysts. Therefore, suitably designed ligand systems might be an enabling methodology to enhance the aptitude of the base metal catalysts. Although the aptitude of organozinc compounds was established in numerous catalytic reactions like the Reformatskii reaction,<sup>[112-115]</sup> Negishi reaction,<sup>[116-118]</sup> Fukuyama reaction,<sup>[119-124]</sup> *etc.* it is still to explore catalytic borylation. Recently, Zn(II) complexes bearing different  $\text{Im}^{\text{R}^{\text{N}}}$  and analogous benzimidazolin-2-iminato ligands have been reported.<sup>[125-126]</sup>



**Scheme 27.** Organozinc (**44**) catalyzed hydroboration of nitriles with HBpin.

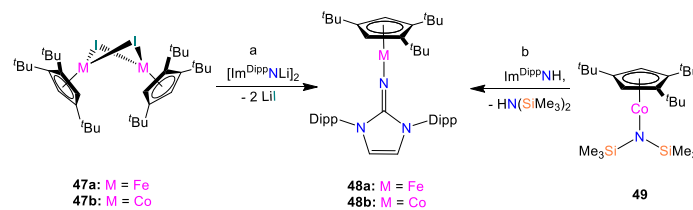


**Scheme 28.** The plausible mechanism for catalytic hydroboration of organic nitriles mediated by **44**.

The Zn complexes were conveniently synthesized by reacting diethylzinc ( $\text{ZnEt}_2$ ) with  $\text{Im}^{\text{R}^{\text{N}}}\text{NH}$  in equimolar ratios (**Scheme 26**). The  $^1\text{H}$  NMR spectra of **44** and **46** exhibit quartet signals at  $\delta_{\text{H}}$   $-0.71$  and  $-0.46$  ppm, which are attributed to methylene protons of respective complexes. In contrast,

complex **45** displayed two different quartet signals at  $\delta_{\text{H}}$   $0.02$  and  $-0.53$  ppm for each of the  $\text{CH}_2$  protons. The methyl protons of ethyl groups of the complexes **44** and **46** appeared as a triplet at  $\delta_{\text{H}}$   $1.58$  and  $1.26$  ppm, respectively. The molecular structure of **45** was confirmed by single-crystal X-ray diffraction analysis, which revealed that the geometry of central metal is distorted trigonal planar with the shortest Zn–N distance ( $1.974(2)$  Å) reported so far.<sup>[127-129]</sup> All the Zn complexes (**44-46**) were employed for catalytic hydroboration of different aliphatic and aromatic organic nitriles, and **44** amongst all was found most active in the series (**Scheme 27**). All the complexes displayed excellent tolerance for hydroborations of various electron-deficient and electron-rich organic nitriles and achieved desired diborylamine products within 12-24 h.

The compound **44** also exhibited chemoselectivity in the presence of other functionalities (nitro and ester). However, the use of 4-formylbenzonitrile and 4-acetylbenzonitrile resulted in hydroboration to both nitrile and aldehyde/ketone functionalities. A plausible reaction was proposed based on the experimental results (**Scheme 28**). The catalytic cycle started with the reaction between pre-catalyst **44** and HBpin to form the active metal hydride species (**VII**). Subsequently, incoming nitrile coordinated to metal to give species (**VIII**), followed by nitrile reduction, affording the Zn–iminium intermediate (**IX**). The next step involved the  $\sigma$ -bond metathesis between iminium intermediate and HBpin to yield a four-membered species (**X**), which underwent rearrangement to give monoboronate ester (**XI**). Afterward, the monoboronate ester reacted with the second molecule of incoming HBpin affording the species (**XII**), followed by the rearrangement of **VI** to the desired diborylamine product, along with regeneration of metal hydride species **VII**.



**Scheme 29.** Synthesis of **48**.

#### 4.7. Iron and cobalt complexes

In 2019, Walter and co-workers reported the synthesis and magnetic properties of monomeric half-sandwich imidazolin-2-iminato supported iron and cobalt complexes **48a** and **48b**, respectively.<sup>[130]</sup> The salt metathesis reaction between  $[\text{Cp}'\text{M}(\mu\text{-I})_2]$  ( $\text{M} = \text{Fe}, \text{Co}$ ;  $\text{Cp}' = \eta^5\text{-}1,2,4\text{-tri-}t\text{-butylcyclopentadienyl}$ ) (**47**) and  $[\text{Im}^{\text{Dipp}}\text{NLI}]_2$  afforded the iron (**48a**) and cobalt (**48b**) complexes in moderate yields (**Scheme 29a**). The alternate synthetic method of compound **48b** was achieved by reacting  $[\text{Cp}'\text{Co}\{\text{N}(\text{SiMe}_3)_2\}]$  (**49**) with  $\text{Im}^{\text{Dipp}}\text{NH}$  (**Scheme 29b**), which require high temperature compared to the previous process. The  $^{57}\text{Fe}$  Mossbauer spectroscopy and solid-state magnetic susceptibility data

confirmed that the central metal Fe(II) in **48a** adopted a high-spin ( $S = 2$ ) state. Whereas the cobalt complex **48b**, which is a rare example of a Co(II) system of not being a six coordinated species, displays a low-spin to high-spin spin-crossover (SCO) behavior. The complex **48a** exhibited pogo-stick geometry with the Fe–N<sub>imine</sub> bond length of 1.7885(13) Å and Fe–N–C bond angle of 171.45(8)°. The Co–N bond length and Co–N–C bond angle of complex **48b** are 1.721(4) Å and 173.1(3) Å respectively.

## 5. Conclusions and Outlook

In summary, we have covered recent trends in imidazolin-2-iminato supported transition metal complexes and their applications in metathesis, polymerization of ethylene/norbornene, RCAM, ROMP, etc. The catalytic activities of the compounds were shown to be tuned by wingtip alteration on N atom of imidazolin-2-iminato moieties. The titanium complexes **4** and **5** proved to be the highly active catalysts for the polymerization of propylene in the presence of MAO. Similarly, the titanium complexes **6** displayed an efficient activity in polymerization and co-polymerization of ethylene and ethylene/norbornene, respectively. The titanium complex Im<sup>Dipp</sup>NTiClMe<sub>2</sub> exhibited a unique reactivity in ethylene polymerization reaction featuring an extremely low Al:Ti ratio of 20. Interestingly, the Im<sup>Mes</sup>NTiCl<sub>3</sub> (**9**) complex displayed the best catalytic activity so far reported for ethylene polymerization with MAO at a very low Al:Ti ratio of 8. So overall, the imidazolin-2-iminato supported titanium complexes showed efficient catalytic activity and selectivity compared to other transition metal complexes. The zirconium complex **32** served as an efficient catalyst in ROP reactions. The hafnium complexes **33** and **34** exhibited excellent chemoselective reactivity in the hydroboration reaction. Similarly, the tungsten complex **39** also displayed enormous activities in RCAM and ACM reactions. The zinc complex **43** displayed efficient catalytic activity in the hydroboration of numerous aromatic and aliphatic nitriles. The (imido)vanadium(V) alkylidene complexes containing the imidazolidin-2-iminato ligand V(CHSiMe<sub>3</sub>)-(NR)(X)(PMe<sub>3</sub>) (where R = Ph, X = 1,3-(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>N)<sub>2</sub>C=N)) exhibited very high catalytic activities of ring-opening metathesis polymerization (ROMP) of norbornene (NBE) and achieved 7070 turnovers within 5 minutes at 80 °C. Thus, this compound could be utilized as a promising thermally robust olefin metathesis catalyst. Similarly, **37** proven to be an effective complex to activate C<sub>6</sub>H<sub>6</sub> or C<sub>6</sub>D<sub>6</sub> via 1, 2-C-H/1,2-C-D activation. Thus this complex could be utilized further to activate polynuclear hydrocarbon or aromatic heterocyclic compounds. In the future, imidazolin-2-iminato ligands will continue their way to produce compounds that are green and sustainable. Despite the recent advancement of imidazolin-2-iminato ligands in transition metals chemistry, documented in the current review, however, the effects of the ring expansion of N-heterocycle from 5 to 6/7 in the catalytic performance of the resulted complexes need to be explored. The N-heterocyclic carbene (NHC) has already been a recognized

candidate as a metal-free catalyst system.<sup>[131]</sup> Nevertheless, the proficiency of more nucleophilic imidazolin-2-iminato is yet to investigate for this application. We also believe that the transition metal catalysts bearing N-heterocyclic iminato ligand can be used to perform a few important transformations of recent demand. For instance, the catalytic aptitude of these complexes and newly synthesized complexes might be explored for the generation of H<sub>2</sub> and O<sub>2</sub> via water splitting reactions and for efficient C-capture processes.

## Acknowledgment

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## Support information

Not applicable

## Conflict of Interest

There are no conflicts to declare.

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