N-Heterocyclic Carbene (NHC) Complexes of Group 4 Transition Metals

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N-Heterocyclic carbene (NHC) complexes of group 4 transition metals

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Since the discovery of a stable *N*-heterocyclic carbene (NHC), the use of NHCs in chemistry has developed rapidly over the past two decades. These interesting compounds are predominantly employed in organometallic chemistry as ligands for various metal centers, and as organocatalysts for a variety of transformations. In particular, the NHC transition metal complexes have received a widespread attention, and a significant progress has been made in the development of group 4 NHC-complexes in the last few years. These group 4 NHC-complexes are of interest because of their unique structural properties, and their potential application in organic transformations and catalysis. This review covers the superior design strategies for NHC ligands to stabilize early transition metals and well-defined group 4 metal complexes with mono- and multi-dentate NHC ligands. In this context, four types of NHC-complexes, *i.e.*, carbon-functionalized NHCs, nitrogen-functionalized NHCs, oxygen-functionalized NHCs and nitrogen/oxygen-functionalized unsymmetric NHCs, are described. In addition, the use of group 4 NHC-complexes as catalysts in olefin (co)polymerization, ring-opening polymerization of *rac*-lactide, copolymerization of epoxides and CO_2, as well as hydroamination/cyclization of aminoalkenes, is presented. Furthermore, limitations and challenges are discussed.

1. Introduction

Since the isolation and characterization of the first stable *N*-heterocyclic carbene (NHC), namely **IAd** (Fig. 1a) by Arduego and co-workers in 1991,[1] tremendous advances have been made in this area. Many different NHCs with various ring sizes, heteroatoms, ring backbones and *N*-substituents have been prepared.[2] Among these, the five-membered NHCs with adjacent σ-electron-withdrawing and π-electron-donating nitrogen atoms (Fig.1b) next to the carbene carbon atom, are typical representatives of remarkably stable NHCs.[3] In its ground-state the lone pair of the carbene carbon atom is situated in the plane of the heterocyclic ring. This nucleophilic characteristic makes NHCs good σ-donors, so they can bind to a wide range of metallic and non-metallic species,[4-6] and are also used in organocatalysis.[7] A concise overview of the properties and broad application of NHCs was recently summaried.[8]

<Figure 1 here>

Since the first example of metal-NHC (M-NHC) complex appeared in the literature, NHCs have become ubiquitous ligands for transition metal complexes because of their strong σ-donating but poor π-accepting capabilities,[9-12] and nowadays they rival phosphines as ancillary ligands in the organometallic chemistry including the early transition and f-block metals despite their soft character.[3,13]

However, the NHC complexes of group 4 transition metals (Ti, Zr and Hf) in high oxidation states are considerably less developed despite the great potential of this class of molecules. Mono- and bis-NHC adducts {$M(NHC)_nCl_4$} (M = Ti, Zr, Hf; n = 1, 2) were reported in 1994[14] and 1995[15], respectively. These results show that such nucleophilic NHCs have sufficiently flexible electronic structure to accommodate metal species ranging from electron-rich fragments, e.g. metal carbonyls, to more electropositive Lewis acids such as metal halides and metal oxides. However, research in this area is scanty after that and no progress was made in the following seven years. This is mainly due to the dissociation of the soft NHC ligand from the electron deficient metal center, which makes it difficult to study the early transition metal NHC complexes. Until 2002, this research area began to recover and then received a significant interest.[16,17] In particular, in the last few years, a significant progress has been made in the development of group 4 NHC-complexes and these complexes have successfully been applied as promising catalysts in polymerizations and organic transformations.

This review will summarize the progress in the synthesis and catalytic activity of group 4 NHC-metal complexes, and is organized by ligand and catalytic reaction types. However, main group, f-block and other d-transition metal NHC complexes are not included in this review because several excellent reviews have covered their synthesis and reactivity in recent years.[3,9,10,18-23]

2. NHC ligands for group 4 complexes

2.1 Design strategies for NHC ligands

In general, all NHC fragments reported in group 4 metal compounds carry the unique five-membered ring backbone, namely imidazol-2-ylidene or imidazolin-2-yliene. This ubiquity is due to their strong donor properties, which are enhanced by the diversity of two substituents on nitrogen atoms that provide for some tunability of stereo/electronic effects (Fig. 1). Monodentate NHC ligands ($\mathbf{L}^1$-$\mathbf{L}^7$, Fig. 2) with less steric R groups (e.g. Me, Et) bound to the nitrogen atoms usually favor dimerization to olefins (the Wanzlick equilibrium).[24] Traditionally, this problem was solved by use of two bulky substituents (e.g. Mes, Dipp) adjacent to the carbene carbon ($\mathbf{L}^8$-$\mathbf{L}^9$, Fig. 2).[25-30] Nonetheless, the formed group 4 NHC complexes are sensitive to air and moisture.

<Figures 2-4 here>

A practical means for directing metal-NHC interactions is the covalent tethering of coordinating functional groups to the NHC ligand system (Fig. 3). In recent years, some NHC hybrid ligands have been successfully developed as auxiliary ligands to stabilize group 4 metals. The functional substituents of NHCs fall into three categories. The carbon-coordinated arms (Fig. 4a) comprise of both σ-donors (NHC[31] and phenyl[32,33]) and π-electron donors (cyclopentadienyl,[34] indenyl[35,36] and fluorenyl[35,36]), while nitrogen-containing functional groups (pyridine,[37,38] imino,[39] amino[40-43], Fig. 4b) and oxygen-functionalized substituents (alkoxy,[44-47] aryloxy[48-63], Fig. 4c) tend to follow the same σ-binding mode. With the help of these functional side arms, the NHC moiety is held in proximity of the group 4 metal center by one or more covalent tethers. This strategy allowed chemists to prepare more suitable NHC derivatives for early transition metals. In particular, some robust and air-stable group 4 complexes have been readily prepared from NHC-containing multidentate ligands.[61] Moreover, a novel nitrogen/oxygen functionalized unsymmetrical tridentate dianionic NHCs precursor $[H(\mathbf{L}^{31})Br]$ was reported, in which the imidazolyl unit always rearranges to the benzimidazolyl moiety ($\mathbf{L}^{32}$) in the synthesis of titanium and zirconium complexes (Fig. 4d).[64,65]

2.2 Approaches to group 4 NHC complexes

NHC-silver(I) complexes[66] are well established NHC transfer reagents for the preparation of the late transition metal NHC complexes.[9-12] However, this approach has not been established for group 4 metals.[19-21,23] The NHC-Ag(I) halides adopt a variety of different coordination environments including in the solid state mononuclear complexes with either one or two carbenes coordinated, dinuclear and tetranuclear complexes containing halide bridges, polymeric and in solution existing an equilibrium between the Ag(NHC)X and cationic $[Ag(NHC)_2]^+$ complex.[67] In addition, the nature of the acceptor metal complex determines whether NHC or halide transfer occurs.[68] For example, treatment of $(1,3\text{-}R_2\text{-}C_3H_2N_2)AgCl$ with 2 equiv of $TiCl_4$ or $CpZrCl_3$ in CH_2Cl_2 did not yield the expected group 4 NHC-complexes, instead, the chloride transfer occurred leading to the formation of the salts $[(1,3\text{-}R_2\text{-}C_3H_2N_2)_2Ag][(MCl_2R')_2(\mu_2\text{-}Cl)_3]$ with accompanying precipitation of AgCl (Scheme 1), indicating that in the case of the group 4 transition metal Lewis acids, the high chlorophilicity of the d^0 metal center together with the large solvation/lattice enthalpy of the ionic products formed favor chloride transfer rather than the transmetallation of the NHC observed for the soft Lewis acidic, late transition metal centers.[68]

<Schemes 1-2 here>

Excitingly, several methods have been developed for the preparation of group 4 NHC complexes (Scheme 2). Strong bases, such as NaH/KO^{t}Bu, $M[N(SiMe_3)_2)]$ (M = Na, K) or *n*-BuLi can be used for the preparation of free NHC ligands (Path A to C, Scheme 2). For example, neutral *bis*-NHC pyridine ligand $\mathbf{L}^{17}$ (Fig. 4b) could be easily prepared at low temperature in good yield with $K[N(SiMe_3)_2]$.[37] Unfortunately, most NHCs or their salts M-NHC cannot be isolated due to their rather poor stability. For example, the sodium derivative of *bis*-aryloxy NHC ligand $(\mathbf{L}^{25})^{2-}$ (Fig. 4c) generated at -78 ^{o}C, but degraded to *bis*-aryloxide imidazole at room temperature *via* 1,2-migration.[48,49] However, group 4 NHC complexes can be formed *in situ* by reaction of group 4 metal sources with the NHC ligand at low temperature.

Another approach to group 4 NHC complexes is amine, toluene or alcohol elimination by reactions of imidizalium salts with metal precursors such as $M(NR_2)_4$, $MCl_2(NR_2)_4$, $M(CH_2Ph)_4$, $M(O^iPr)_4$ and $MCl(O^iPr)_3$ (M = Ti, Zr, Hf) (Path D-F, Scheme 2).

Thus, a number of group 4 NHC complexes have been prepared *via* above mentioned approaches, which are comprehensively listed in Table 1, for which the literatures were reviewed to November, 2014.

<Table 1 here>

3. Well-defined group 4 NHC complexes

3.1 Monodentate NHC complexes

The reactions of isolated free NHCs $\mathbf{L^1}$-$\mathbf{L^4}$ (Fig. 2) with $MCl_4(thf)_2$ (M = Ti, Zr, Hf) yielded the bis-NHC metal complexes *trans*-$[M(\mathbf{L^{1-4}})_2Cl_4]$ (**1**-**7**, Scheme 3).[14,17] In the solid state, the two NHC ligands are *trans*-positioned in a pseudo-octahedral coordination geometry at the metal center, and the two five-membered heterocycles are arranged coplanar and bisect the Cl-M-Cl angles. However, DFT calculations reveal that the two NHCs rapidly rotate in solution because of the low energy barriers of 2.5-3.8 kcal mol^{-1}.

<Scheme 3 here>

Similarly, mono-NHC adducts $[(\mathbf{L})TiCl_4]$ (**L** = $\mathbf{L^5}$ (**8**), $\mathbf{L^6}$ (**9**), $\mathbf{L^7}$ (**10**)) can be formed by treatment of $TiCl_4$ with free tetramethyl-NHCs ($\mathbf{L^{5-7}}$, Fig. 2) in good yields.[15] The dinuclear complex $\{[(\mathbf{L^7})TiCl_3]_2(\mu\text{-}O)\}$(**11**) was obtained by careful hydrolysis of **10** and included two penta-coordinated titanium fragments connected by a near linear oxygen bridge. This presented the first example of structurally authenticated group 4 metal NHC complexes.

<Scheme 4 here>

As a two-electron donor, NHC can be used to stabilize the group 4 alkyl metallocene cations that are very active species or precursors for Ziegler-Natta catalysts. For example, treatment of $[Cp_2TiCH_3(thf)][BPh_4]$ or $[Cp_2ZrCH_3][CH_3B(C_6F_5)_3]$ with $\mathbf{L^2}$ (Fig. 2) at ambient temperature resulted in the formation of the NHC methyl titanocene cation complexes $[Cp_2TiCH_3(\mathbf{L^2})][BPh_4]$ (**12**) and $[Cp_2ZrCH_3(\mathbf{L^2})][CH_3B(C_6F_5)_3]$ (**13**) (Scheme 4).[16] The crystal structural parameters of **12** showed that NHC ligand $\mathbf{L^2}$ [$Ti\text{-}C_{carbene}$ = 2.289(2) Å] was indeed bonded to titanium, in which the NHC ring lies in a plane (not perpendicular) of the bent metallocene moiety (Fig. 5). Furthermore, the DFT calculations reveal that the NHCs serve as pure σ-donor ligands in these group 4 metal complexes.

<Figure 5 here>

Treatment of $[(\eta^7\text{-}C_7H_7)M(\eta^5\text{-}C_5H_5)]$ (M = Zr, Hf) with three different two-electron donor ligands, NHC ligand $\mathbf{L^5}$ (Fig. 2), PMe_3 and isocyanides (^{t}BuNC and XyNC) resulted in the formation of the adducts $[(\eta^7\text{-}C_7H_7)M(\eta^5\text{-}C_5H_5)(\mathbf{L})]$ (M = Zr, Hf) (Scheme 5).[69,70] The crystal structural parameters showed that the NHC is strongly σ-coordinated to the metal forming complexes $[(\eta^7\text{-}C_7H_7)M(\eta^5\text{-}C_5H_5)(\mathbf{L^5})]$ (M = Zr (**14**), Hf (**15**)) and adopt an “in plane” arrangement (also see Fig. 5), while PMe_3 coordinates more weakly to the metal centers. This was also supported by DFT calculations revealing that the NHC-adduct is more stable than PMe_3 adduct as shown by the formation enthalpies of $\Delta H^o(Zr\text{–}\mathbf{L^5})$ = -56.3 kJ mol^{-1} and $\Delta H^o(Zr\text{–}PMe_3)$ = -2.3 kJ mol^{-1}, respectively.[69]

<Scheme 6 here>

It is well kown that fluoro compounds behave more differently than the heavier halides.[71] Ti(IV) fluoride complexes *trans*-$[TiF_4(\mathbf{L})_2]$ (**L** = $\mathbf{L^5}$ (**16**), $\mathbf{L^7}$ (**17**)) can be prepared from the readily available tetramethyl-NHCs and TiF_4 in THF (Scheme 6).[72] Reaction of **16** with $AlMe_3$ leads to ligand transfer from the Ti(IV) to the Al(III) center (Scheme 6). In addition, complex **16** was a versatile precursor for the preparation of the Ti(IV) fluoride NHC complexes $[\{TiF_2(\mathbf{L^5})(NEt_2)\}_2(\mu\text{-}F)_2]$ (**18**) and $\{[TiF_4(\mathbf{L^5})_2]\text{-}(NacNacLi)\}$ (**19**), while complex **17** degraded in solution at room temperature, giving $[H(\mathbf{L^7})][TiF_5(\mathbf{L^7})]$ (**20**), indicating that the bulky substituents cannot give a more stable fluoride NHC complex. Although the crystals of complexes **18** and **20** were thermally stable, they always afforded a mixture in solution, which were detected by ^{1}H and ^{19}F NMR spectroscopy. Moreover, the relative basicities of NHCs and other donor ligands THF, pyridine, DMSO, H_2O as well as Cl^- and F^- toward the Ti(IV) pentafluoride anion were established by NMR and confirmed by DFT calculations. The NHC ligand is more basic than the other mentioned donor molecules and the chloride anion, while less basic than the fluoride anion.

<Scheme 7 here>

It has been shown that imidazolium salts react with chromocene or nickelocene to form the NHC complexes *via* cyclopentadiene elimination.[25,26] However, the amine elimination reaction between imidazolium salt (**L**^{8})·HCl and amido metal precursor $Ti(NMe_2)_4$ or $[Ti(=NR)(NMe_2)_2]_2$ results in the incomplete conversions for the expected NHC complexes $[(\mathbf{L}^8)TiCl_2(NMe_2)_2]$ (**21**)[27] and $[(\mathbf{L}^8)Ti(=NR)Cl_2(NHMe_2)]$ (**22a-e**),[28] respectively (Scheme 7) and some byproducts such as $[(\mathbf{L}^8)_2Ti^{III}Cl_2(NMe_2)]$, $[(\mathbf{L}^8)_2Ti(=NR)Cl_2]$ and $[(\mathbf{L}^8)Ti(=NR)Cl(NHR)(NHMe_2)]$ were also isolated.[28] However, direct addition of NHC to the above mentioned metal precursors is the preferable approach to titanium NHC complexes **21**, **22a-e** and $[(\mathbf{L}^8)Ti(=NR)Cl_2(Py)]$ (**23a, d, e**) (Scheme 7).[28] Moreover, in complex **23** the displacement of the NHC ligand with strong donors such as pyridine or phosphine was not observed. Similarly, several monodentated NHC group 4 metal complexes such as $[(\mathbf{L}^8)_2Ti(=NR)Cl_2]$ (**24**), $[(\mathbf{L}^8)Ti(=NR)(NHR)Cl(NHMe_2)]$ (**25**) (for **24** and **25**, R = 2,6-Cl_2-(C_6H_3)), $[(\mathbf{L}^9)Ti(NMe_2)_2Cl_2]$ (**26**), $[(\mathbf{L}^9)_2Ti^{III}Cl_3]$ (**27**), $[(\mathbf{L}^8)_2ZrCl_4]$ (**28**), $[(\mathbf{L}^8)M(NMe_2)_2Cl_2]$ (M = Zr (**29**); Hf (**30**)) and $[(\mathbf{L}^8)Zr(=N\text{-}Dipp)(NHMe_2)Cl_2]$ (**31**) were prepared.[29,30]

<Table 2 here>

<Figure 6 here>

The X-ray crystal structural analyses of Ti and Zr complexes **21**, **26**, **27** and **29** with bulky ligand **L**^{8} or **L**^{9}, revealed that the environment around metal is a distorted-trigonal-bipyramidal geometry, in which the NMe_2 groups and the NHC ligand occupy the equatorial sites (Table 2). Most importantly, the structural parameters demonstrated the presence of $Cl\cdots C_{NHC}$ interactions. The close $Cl\cdots C_{NHC}$ distances (the average values is from 3.061Å to 3.264Å) are much shorter than the sum of the van der Waals radii (3.65 A for Cl···C),[73] and the averaged $Cl–Ti–C_{NHC}$ angles are 81.82(9)°- 83.34(12)°.[27] Furthermore, the interaction (e.g. for complex **21**) between the chloride lone pairs and the formally vacant C(2p) orbital on the carbene ligand can be discerned by DFT studies, as illustrated with the HOMO-8, in which the chloride lone pairs and the carbenic 2p orbital of the NHC overlap (Fig. 6).[27]

3.2 Carbon-functionalized NHC complexes

3.2.1 *Bis*-NHCs

<Scheme 8 here>

<Figure 7 here>

Deprotonation of the *N,N*'-bisborane-protected bisimidazole 1,1'-bis(3-borane-4,5-dimethylimidazolyl)methane $H_2(\mathbf{L}^{10})$, followed by reaction with Cp_2MCl_2 resulted in the formation of the NHC complexes $[MCp_2(\mathbf{L}^{10})]$ (M = Ti (**32**), Zr (**33**); Scheme 8).[31] X-ray structure analysis showed that there is a 3c-2e interaction (B2-H2A-Zr) in zirconium complex **33** (Fig.7). This interaction is non-fluxional in solution at 20 °C, because two signals are observed in ^{11}B NMR spectrum. The NHC-Zr complex **33** has an 18-electron structure, in contrast, the NHC-Ti complex **32** has 16 valence electrons, which is responsible for the poor stability.

3.2.2 Phenylene *bis*-NHCs

In recent years, Hollis and co-workers prepared a series of group 4 pincer NHC complexes *via* activation of an aryl C-H bond.[32,33,74,75] Reaction of phenylene-bridged bis(imidazolium) salt $[H_3(\mathbf{L}^{11})]I_2$ with 2.5 equiv of $Zr(NMe_2)_4$ yielded a mixture of Zr pincer complexes $[Zr(\mathbf{L}^{11})(NMe_2)_2I)]$ (**34**) and $[Zr(\mathbf{L}^{11})(NMe_2)I_2)]$ (**35**). Complex **34** was isolated as a solid from the reaction mixture, but also 9% of the diiodo mono-amido complex **35** was formed as the byproduct (Scheme 9).[32] When an excess of MeI (ca 200 equiv) was added to this reaction solution at ambient temperature, a triiodide complex $[Zr(\mathbf{L}^{11})I_3]$ (**36**) was isolated in 87% yield. To obtain diiodo product **35** in high yield, high temperature (150-160 °C) and a stoichiometric reaction between Zr precursor and $[H_3(\mathbf{L}^{11})]I_2$ are required.[74] This approach worked well for the preparation of both Zr complex **35** and Hf complex $[Hf(\mathbf{L}^{11})(NMe_2)I_2)]$ (**37**).[75] Similarly, the NHC-Zr complex $[Zr(\mathbf{L}^{12})(NMe_2)_3]$ (**38**) was obtained from the saturated NHC precursor $[H_3(\mathbf{L}^{12})][BPh_4]_2$.[32] Although CCC-NHC Zr pincer complexes can be generated *in situ*, importantly, they can act as transmetallation reagents with an appropriate Rh source to yield CCC-NHC Rh pincer complexes.[32]

<Schemes 9-10 here>

Furthermore, the above amine elimination approach has been extended to titanium chemistry.[33] For example, reaction of an excess amount of $Ti(NMe_2)_4$ with the dihalide salts $[H_3(\mathbf{L^{11}})]X_2$ (X = I, Cl) yielded the complexes $[Ti(\mathbf{L^{11}})(NMe_2)_2X]$ (X = I (**39**-I), Cl (**39**-Cl)) (Scheme 10). Recrystallization of **39**-I in CH_2Cl_2 afforded the trichloro titanium complex $[Ti(\mathbf{L^{11}})Cl_3]$ (**40**) due to a dimethylamido/halide exchange, while reaction of complex **39**-I with TMSCl gave a mixture of **40** and $[Ti(\mathbf{L^{11}})Cl_2I]$ (**41**). An efficient synthesis of **40** was accomplished by the reaction of **39**-Cl with TMSCl. The stoichiometric reaction of the dichloro salt $[H_3(\mathbf{L^{11}})]Cl_2$ with $Ti(NMe_2)_4$ yielded dichloro complex $[Ti(\mathbf{L^{11}})(NMe_2)Cl_2]$ (**42**), while reaction of **42** with CH_2Cl_2 or $[Ti(NMe_2)_3Cl]$ gave the monochloro titanium complex **39**-Cl.

3.2.3 Indenyl, fluorenyl and Cp connected NHCs

In recent years, Danopoulos and co-workers prepared a series of group 4 NHC constrained-geometry complexes (CGC) with the ligands containing both indenyl or fluorenyl and NHC species (Scheme 11 and 12).[35,36] Reaction of potassium fluorenyl NHC ligand $K(\mathbf{L^{13}})$ with $Ti(NMe_2)_2Cl_2$ in benzene gave, after filtration and crystallization, the yellow-brown, paramagnetic Ti(III) complex $[Ti(\mathbf{L^{13}})(NMe_2)Cl]$ (**43**) in low yields (ca. 25%) (Scheme 11).[35] The ligand ($\mathbf{L^{13}}$) was proposed to act as a reducing agent during the reaction, which is supported by the isolation of a spiro imidazolium salt (Scheme 11) from the supernatant solution by fractional crystallization.

<Schemes 11-12 here>

The Ti(III) complex $[Ti(\mathbf{L^{14}})Cl_2]$ (**44**) could be obtained by the salt metathesis reaction between potassium indenyl NHC ligand $K(\mathbf{L^{14}})$ and $TiCl_3(THF)_3$ in 50% yield (Scheme 12).[36] Similarly, reaction of the potassium indenyl NHC ligand $K(\mathbf{L^{14}})$ with $[Ti(N^tBu)Cl_2(py)_3]$ or $[ZrCl_4(THT)_2]$ (THT = tetrahydrothiophene) in THF yielded titanium (IV) complexes $[Ti(\mathbf{L^{14}})(=N^tBu)Cl]$ (**45**; **45a** and **45b**) and zirconium (IV) complexes $[Zr(\mathbf{L^{14}})Cl_3]$ (**46**; **46a** and **46b**), respectively, in good yields. In contrast to the fluorenyl ligand system, no reducing complex was observed, presumably due to the electronic effect.

X-ray diffraction analyses reveal that both the Ti (III) and Ti(IV) complexes (**43**, **44**, **45a** and **45b**) adopt a distorted-tetrahedral-geometry, while in zirconium complex **46a** the metal is coordinated in a distorted piano-stool geometry, assuming that the fluorenyl and indenyl group occupy one coordination site defined by the centroid of the five-membered ring. In contrast to the indenyl NHC titanium complexes, the zirconium analogs partially degrade in hydrocarbon solvents, and exhibit complicated ^1H NMR spectra recorded in polar non-coordinating reagents (such as CD_2Cl_2, C_6D_5Cl).

<Scheme 13 here>

The amine-elimination reaction of imidazolium iodide $[H(\mathbf{L^{15}})]I$ with $Ti(NEt_2)_4$ led to the formation of an ionic NHC complex $[Ti(\mathbf{L^{15}})(NEt_2)_2]I$ (**47a**), in which a η^5-Cp and an NHC unit were linked by an 1,2-ethylidene bridge to form a novel chelating ligand system (Scheme 13). However, under similar reaction conditions, treatment of $[H(\mathbf{L^{15}})]I$ with $Zr(NEt_2)_4$ results in a mixture of an ionic complex $[Zr(\mathbf{L^{15}})(NEt_2)_2]I$ (**47b**) and a neutral complex $[Zr(\mathbf{L^{15}})(NEt_2)I_2]$ (**48**) (the ratio is 2:3) (Scheme 13).[34] X-ray structural analyses further confirmed that in **47a** the Ti is tetra-coordinated and no coordinative interaction exists with the iodide anion, while in **48** the Zr center is penta-coordinated.

3.3 Nitrogen-functionalized NHCs complexes

3.3.1 Imino NHCs

In recent years, Lavoie and co-workers reported a series of NHC late transition metal complexes with a stable aryl-substituted acyclic imino-NHC ligand ($\mathbf{L^{16}}$) (Fig. 4b).[76,77] In their studies, the free NHC ligand $\mathbf{L^{16}}$ could be successfully isolated in 91% yield from the reaction of the imidazolium salt $[H(\mathbf{L^{16}})][BF_4]$ with sodium bis(trimethylsilyl)amide (NaHMDS).[39] In the ligand $\mathbf{L^{16}}$, the imine group adopts a *Z*-conformation in the solid state, while a 5:2 equilibrium mixture of *E* and *Z* isomers was observed in $CDCl_3$ by a 1D NOESY NMR spectroscopy.

<Scheme 14 here>

Treatment of 1 equiv of $\mathbf{L^{16}}$ with $MCl_4(THF)_2$ (M = Ti, Zr, Hf) or $TiCl_3(THF)_3$ in THF gave the NHC complexes $[M(\mathbf{L^{16}})Cl_4]$ (M

= Ti (**49**), Zr (**50**), Hf (**51**)) and [Ti^{III}(**L^{16}**)(THF)Cl$_3$] (**52**-THF), respectively (Scheme 14).[39] A decrease in the C=N stretching frequency ($\nu_{C=N}$ 1604-1609 cm^{-1}) compared to the free ligand ($\nu_{C=N}$ 1662 cm^{-1}), indicates coordination of the imine nitrogen to the mental center. Moreover, the X-ray analyses showed that these complexes exhibit a distorted-octahedral geometry around the group 4 mental center.

3.3.2 Pyridylene *bis*-NHCs

<Scheme 15 here>

Late-transition-metal complexes with bis(imino)pyridine ligands are stable and effective catalysts in olefin polymerization.[78,79] Bis(carbene)pyridines such as the type 2,6-bis(1-(alkyl/aryl) imidazol-2-ylidene)pyridine can also stabilize the transition metals (Fe, Ti, Cr etc.).[37] For example, using [TiCl$_3$(THF)$_3$], a highly air and moisture sensitive purple titanium (III) complex [Ti^{III}(**L^{17}**)Cl$_3$] (**53**) was obtained (Scheme 15). However, the Ti-NHC bonds in imido Ti(IV) analogue [Ti(**L^{17}**)(=N^{t}Bu)Cl$_2$] (**54**) is relatively inert to a variety of reagents (Scheme 15).[38] The octahedral titanium center is coordinated by the "pincer" ligand in a usual way, two *trans*-chlorides and one *tert*-butylimido or chloride group. The Ti–C bond lengths in Ti(IV) complex **54** are in the range of 2.281(6)-2.286(6) Å, slightly longer than those found in Ti(III) complex **53** (2.191(5)-2.211(5) Å).

3.3.3 Amino NHCs

<Schemes 16-17 here>

In 2006, Arnold and co-workers prepared a series of titanium(IV) amido-tethered NHC complexes [Ti(**L^{18}**)(O^{i}Pr)$_{(3-x)}$Br$_x$] (x = 0 (**55**), 1 (**56**), 2 (**57**)) and {Ti(**L^{18}**)[(C$_3$N$_2$H$_3$)^{t}Bu](O^{i}Pr)$_2$}Br (**58**) by reaction of [Ti(O^{i}Pr)$_3$Cl] with [Li(**L^{18}**)] or lithium bromide stabilized NHC [Li(**L^{18}**)·nLiBr] (n = 1, 2) in moderate yields (Scheme 16).[40] X-ray diffraction analyses revealed that complexes **56** and **58** are much closer to a square-based pyramid (sbp) than a trigonal bipyramid (tbp), consistent with a minimum of interelectron repulsion in five-coordinate d^0 metal complex (Scheme 17). This notable bending of the coordinated oxygen and chlorine atoms *cis* (and perpendicular) to the plane of the NHC fragment has been recently perceived as a pseudo-back-bonding interaction between metal and the carbene p orbital.[27,72] However, inspection of a space-filling model and DFT calculation of the bond order do not support this conclusion. The bending was found to be a consequence of repulsive interactions between lone pairs on the adjacent donors, and no specific interaction between NHC and *cis* σ-donors was observed.

<Scheme 18 here>

<Figure 8 here>

At room temperature, treatment of Zr(CH$_2$Ph)$_4$ with 1 equiv of the amino linked NHCs [H(**L$^{18\text{-}19}$**)] gave the NHC complexes {Zr[H(**L**)]Bz$_4$} (**L** = **L^{18}** (**59**), **L^{19}** (**60**)). The complexes **59** and **60** were unstable and degraded to complexes {Zr[η^2-N,C-(C$_3$N$_2$H$_2$)-R][η^3-(C$_2$N)-^{t}Bu]Bz$_2$} (R = ^{t}Bu (**61**), Mes (**62**)) and {Zr(**L^{19}**)Bz$_3$} (**63**) (Scheme 18).[41] Complex **62** possesses η^2-N,C-imidazolyl carbene (Zr-C1 = 2.228(3) Å, Zr-N1 = 2.167(2) Å), η^3-azaallyl (Zr-C13 = 2.657(3) Å, Zr-C14 = 2.557(3) Å, Zr-N3 = 2.137(2) Å), η^2-benzyl (Zr-C19 = 2.251(3) Å, Zr-C$_{ipso}$ = 2.775(3) Å) and η^1-benzyl fragments around the zirconium atom (Fig. 8). Complex {Zr(**L^{19}**)Bz$_3$} (**63**) consists of a five-coordinate Zr center bearing a bidentate amide-carbene and three η^1-benzyl ligands with an unexpected β-agostic interaction (Zr-C*= 2.7052(19) Å and Zr-H^a = 2.4549(2) Å in Scheme 18) associated with the methylene carbon adjacent to the amide, suggesting that C-H activation precedes C-N bond cleavage to form **62**. On the basis of these observations, a plausible reaction pathway of intermediate **63*** was proposed in Scheme 18, which would engage in an intramolecular C-H activation at the β-position (β to the Zr atom) *via* a six-electron rearrangement in a metallacyclic ring, followed by the subsequent C-N cleavage to afford the η^3-azaallyl and η^2-N,C-imidazolyl functionalities.

3.3.4 *Bis*-amino NHCs

<Scheme 19 here>

In recent years, Fryzuk and co-workers constructed a kind of dianionic *bis*-amido NHC tridentate ligand (**L$^{20\text{-}21}$**)$^{2-}$ (Fig. 4b) by flanking NHC with two amido groups. With the help of two pendants, the carbene donor has been forced to bind to Zr(IV) and Hf(IV) by virtue of its position in the chelate array.[42,43] Amine elimination reaction between the NHC precursors [H$_2$(**L$^{20\text{-}21}$**)] and [M(NR$_2$)$_4$] afforded *bis*-amido NHC metal complexes

$[Zr(\mathbf{L^{20}})(NEt_2)_2]$ (**64**) and $[M(\mathbf{L^{21}})(NMe_2)_2]$ (M = Zr (**65**), Hf (**66**)). These complexes could be further quantitatively converted to the dichloro derivatives $[Zr(\mathbf{L^{20}})Cl_2(THF)_n]$ (n = 0 (**67**), n = 1 (**67**-THF)) and $[M(\mathbf{L^{21}})Cl_2]$ (M = Zr (**68**), Hf (**69**)) by treatment with an excess of Me_3SiCl (Scheme 19). In addition, reaction of dichloride compounds **68** and **69** with Grignard reagents proceeded smoothly to afford dialkyl products $[Zr(\mathbf{L^{21}})R'_2]$ (R' = Me (**71**), Bz (**72**), ^{i}Bu (**75**)) and $[Hf(\mathbf{L^{21}})R'_2]$ (R' = Me (**73**), Bz (**74**), Et (**76**)) exclusively.[43] For the alkyl product $[Zr(\mathbf{L^{20}})(CH_2SiMe_3)_2]$ (**70**), direct $SiMe_4$ elimination between $[H_2(\mathbf{L^{20}})]$ and $[Zr(CH_2SiMe_3)_4]$ leads to a better yield than that derived from the reaction of dichloride **67** with $LiCH_2SiMe_3$.[42] The X-ray diffraction analyses revealed a distorted trigonal-bipyramidal geometry around the Zr or Hf metal in alkyl compounds **70** and **75**. The two chlorides in **67**-THF are a mutually *cis* disposition, with the tridentate ligand $(\mathbf{L^{20}})^{2-}$ in a meridional orientation to generate a pseudo-octahedral arrangement around the central Zr atom.

3.4 Oxygen-functionalized NHCs complexes

3.4.1 Alkoxy NHCs

<Scheme 20 here>

<Figure 9 here>

In 2005, Arnold and co-workers reported an anionic NHC hybrid ligand $(\mathbf{L^{22}})^-$ with an alkoxy tether. By the pendant functional group, the soft NHC may be bound more strongly to an electropositive metal. As expected, treatment of $[TiCl(O^iPr)_3]$ with 1 equiv of alkoxide-NHC $[K(\mathbf{L^{22}})]_n$[80] gave the colorless NHC titanium alkoxide $[Ti(\mathbf{L^{22}})(O^iPr)_3]$ (**77**). Complex **77** is remarkably air stable, and may be sublimed in good yield (10^{-3} mbar, 80 °C) (Scheme 20).[44] When a toluene solution of **77** was treated with elemental potassium at 70 °C for 16 h, the only isolable product was a bimetallic, mixed valent potassium-titanium complex $[Ti^{III}(\mathbf{L^{22}})_2\{^iPrOSiMe_2O\}\text{-}K_2OTi^{IV}(O^iPr)_4]_2$ (**78**) in a rather poor yield (5%).[45] Siloxane cleavage was suggested to be mediated by the titanium (III) in the reductive process. Moreover, the reaction of $[TiCl_3(THF)_3]$ with 3 equiv of $[K(\mathbf{L^{22}})]_n$ afforded the homoleptic, octahedral Ti(III) complex $[Ti^{III}(\mathbf{L^{22}})_3]$ (**79**) in moderate yield, which is shown to form as a *mer*-isomer by the single-crystal X-ray diffraction analysis (Fig.9).[46] To find whether there is a π interaction in the Ti-C_{NHC} bond of the d^1 titanium(III) complex **79**, the isostructural d^0 yttrium complex $[Y(\mathbf{L^{22}})_3]$ was prepared. Experimentally, the metal radius-corrected Ti-C_{NHC} distance is shorter than the Y-C_{NHC} distance, suggesting a π-bonding contribution to the d^1 complex; however, the DFT studies suggested that the shorter σ bond might due to the more polarized Ti(III) cation.[45]

<Scheme 21 here>

Moreover, treatment of a similar alkoxy NHC precursor $[H_2(\mathbf{L^{23}})]I$ containing a cyclopentene bridge with 1 equiv of $KN(SiMe_3)_2$, followed by reaction with 1 equiv of $Zr(NEt_2)_4$ gave the NHC complex $[Zr(\mathbf{L^{23}})_2(NEt_2)_2]$ (**80**) (Scheme 21).[47] Complex **80** is an efficient catalyst in the polymerization of ethylene and propylene, which will be described below.

3.4.2 Aryloxy NHCs

<Scheme 22 here>
<Figure 10 here>

In 2004, Grubbs and co-workers prepared an aryloxy NHC ligand $(\mathbf{L^{24}})^-$, which features a chelating aryloxy moiety appended to one of the NHC nitrogen atoms. Such "Sal-like" NHC ligand was found to easily form robust organometallic fragments with late metals such as Ni and Pd.[55] Recently, they prepared group 4 metal complexes $[M(\mathbf{L^{24}})_2Cl_2]$ (M = Ti (**81**), Zr (**82**)) (Scheme 22),[56] that are useful initiators for ethylene polymerization. The ^{1}H NMR spectra of these two compounds are broad and complicated, suggestive of the hindered C-N and C-aryl rotation around the Dipp and Ad groups of ligand $\mathbf{L^{24}}$.[56] X-ray crystal diffraction analysis confirmed the sterically congested *cis*-octahedral environment at the metal center (Fig.10). The aryloxy moieties are typically coordinated equatorially, while the NHCs are axial. Such coordination mode is different from that reported for the bis-ligated salicylaldimine complexes of Ti[81] and Zr[82].

3.4.3 *Bis*-aryloxy NHCs

The *bis*-aryloxy NHC ligand precursor, bis-phenol imidazolium salt $[H_3(\mathbf{L^{25}})]Br$, was obtained by a stepwise alkylation of imidazole.[48,49,51-53] Although $[H_3(\mathbf{L^{25}})]Br$ can readily be deprotonated by $NaN(SiMe_3)_2$, the formed sodium salt $Na_2(\mathbf{L^{25}})$ is unstable and degrades to 1,2-disubstituted imidazol $Na_2(\mathbf{L^{25}})$* *via* an 1,2-benzyl migration at room temperature (Scheme 23). Similar migration also occurs for the mono-aryloxy NHC system, and the rate of migration is faster for aryloxy than for alkyl.[50] However, $[Na_2(\mathbf{L}^{25})]$ is stable at low temperature, thus, a series of titanium and zirconium NHC complexes were prepared *in situ*. Moreover, in solution most of them are stable even at elevated temperatures in an inert atmosphere (Schemes 23 and 24).

<Schemes 23-24 here>

The small size of the titanium renders mono-ligand substitution straightforward to give the halide titanium (IV) complexes $[Ti(\mathbf{L}^{25})(THF)X_2]$ (X = Cl (**83**), Br (**84**)), of which **84** can be reduced to a green Ti(III)-NHC complex $[Ti^{III}(\mathbf{L}^{25})(THF)_2Br]$ (**85**).[48,51] While the larger size of the zirconium results in the formation of $[Zr(\mathbf{L}^{25})(THF)Cl_2]$ (**86**), which was contaminated with a little of bis-ligated zirconium complex $[Zr(\mathbf{L}^{25})_2]$ (**87**), however, these two complexes can be easily separated by fractional crystallisation.[49] In addition, the bis-ligated titanium complex $[Ti(\mathbf{L}^{25})_2]$ (**88**) was prepared *in situ* by treatment of $TiCl_4(THF)_2$ with 2 equiv of $Na_2(\mathbf{L}^{25})$.[52]

Treatment of complexes **83** and **86** with Grignard or group 1 alkyl reagents gave complexes $[Ti(\mathbf{L}^{25})R_2]$ (R = Me (**89**), R = Bz (**90**)) and $[Zr(\mathbf{L}^{25})R_2]$ (R = Bz (**91**), CH_2TMS (**92**)) (Scheme 24).[48,49] Oxygen-bridged titanium dimers $\{[Ti(\mathbf{L}^{25})Br]_2(\mu\text{-}O)\}$ (**93**) and $\{[Ti(\mathbf{L}^{25})]_2(\mu\text{-}O)_2\}$ (**94**) were obtained by partially hydrolysis of **84** and **90** in THF and diethyl ether.[52] A rare macrocyclic hexa-zirconium(IV) complex $[Zr(\mathbf{L}^{25})(OSiMe_3)(k^2\text{-}[N^\wedge O])]_6$ ($k^2\text{-}[N^\wedge O] = 3,5\text{-}{}^tBu_2\text{-}2\text{-}O^-\text{-}C_6H_2\text{-}CH_2\text{-}(C_3N_2H_3)$) (**95**) was derived from mononuclear complex **86** by salt metathesis reaction with $NaOSiMe_3$ in the presence of a linker [N^O] at room temperature.[53] Moreover, the amine-elimination of $[Zr(NMe_2)_4]$ with $[H_3(\mathbf{L}^{25\text{-}26})]Br$ in THF affords the tethered NHC Zr complexes $[Zr(\mathbf{L})(NMe_2)Br(THF)]$ ($\mathbf{L} = \mathbf{L}^{25}$ (**96**), $\mathbf{L}^{26}$ (**97**)).[54]

<Figure 11 here>

For the halide metal complexes (**83**, **85** and **86**) and bis-ligated species (**87** and **88**), titanium or zirconium adopt a distorted octahedral geometry coordination environment, while dialkyl compounds (**89**, **90**, **91**) display a distorted trigonal bipyramidal mode. Notably, the meridionally coordinated tridentate ligand ($\mathbf{L}^{25}$) adopts exclusively the *transoid* conformation (*S*-shape) in mononuclear complexes, whereas the rare *cisoid* conformation (*U*-Shape)[52] is observed in the oxygen-bridged dinuclear complexes (**93** and **94**) (Fig.11). Moreover, ^1H NMR spectroscopy suggests that the *bis*-aryloxy NHC ligand is fluxional at room temperature.[48,49]

<Scheme 25 here>

Another rigid bis-aryloxy NHC ligand $(\mathbf{L}^{27})^{2-}$ with a saturated NHC moiety was prepared by Bellemin-Laponnaz and co-workers.[57] Reaction of $[H_3(\mathbf{L}^{27})]Cl$ with 0.5 equiv of MCl_4 (M = Ti, Zr, Hf) in the presence of NEt_3 (to trap the generated HCl) yielded the homoleptic bis-ligated NHC complexes $[M(\mathbf{L}^{27})_2]$ (M = Ti (**98**), Zr (**99**), Hf (**100**)) (Scheme 25).[57,61] Salt metathesis reaction of $[Li_2(\mathbf{L}^{27})]$ with $ZrCl_4(THF)_2$ *in situ* afforded the complex $[Zr(\mathbf{L}^{27})Cl_2(THF)]$ (**101**-THF) as an air stable colorless solid in moderate yield.[58]

<Schemes 26-27 here>

Moreover, alcohol elimination is also a suitable route for the preparation of bis-/mono-chloride group 4 metal complexes (Scheme 26). For example, treatment of the imidazolium salt $[H_3(\mathbf{L}^{27})]Cl$ with alkoxide Ti(IV) precursor $[TiCl(O^iPr)_3]$ in THF afforded quantitatively the dichloride complex $[Ti(\mathbf{L}^{27})Cl_2(THF)]$ (**102**-THF).[57] The mixed chloro/isopropoxide derivatives $[M(\mathbf{L}^{27})(O^iPr)Cl(THF)]$ (M = Ti (**103**-THF),[57] Zr (**104**-THF),[59] Hf (**105**-THF)[60]) could be quantitatively prepared in a similar manner by using $[M(O^iPr)_4]$ or $[M(O^iPr)_4(HO^iPr)]$ as the metal alkoxide precursors. The bis-isopropoxide titanium compound $[Ti(\mathbf{L}^{27})(O^iPr)_2]$ (**106**) can be prepared *via* salt metathesis reaction of **103**-THF with 1 equiv of LiO^iPr.[57] The alkoxide/chloride exchange reaction of **104**-THF or **105**-THF with Me_3SiCl affords the dichloride complexes $[M(\mathbf{L}^{27})Cl_2(THF)]$ (M = Zr (**101**-THF), Hf (**107**-THF)).[60] The penta-coordinated THF-free complex $[Ti(\mathbf{L}^{27})Cl_2]$ (**102**) was achieved *via* an alcohol elimination reaction in a non-coordinating solvent CH_2Cl_2.[57] While an imidazolium zwitterionic intermediate $\{Ti[H(\mathbf{L}^{27})]Cl_2(O^iPr)\}$ (**102***) was formed together with complex **102** in a 2:1 ratio. The pure kinetic product **102*** could not be isolated, but it readily converts to the thermodynamic product **102** at 90 °C in toluene.

The amine elimination reaction of $[H_3(\mathbf{L}^{27})]Cl$ with $M(NMe_2)_4$ in THF or CH_2Cl_2 resulted in the formation of the group 4 metal amido NHC complexes $[M(\mathbf{L}^{27})(NMe_2)Cl(THF)]$ (M = Ti (**108**-THF), Zr (**109**-THF)), and $[Zr(\mathbf{L}^{27})(NMe_2)Cl(NHMe_2)]$ (**109**-

$NHMe_2$) (Scheme 27).[57,60] However, lower conversion was observed than that in the case of alcohol elimination. Toluene elimination from [H_3(**L**^{27})]Cl with 1 equiv of [Zr(CH_2Ph)$_4$] in toluene at -78 °C yielded the chloride/benzyl complexes [M(**L**^{27})(CH_2Ph)Cl] (M = Zr (**110**), Hf (**111**)), which can be convert to the dibenzyl complexes [M(**L**^{27})(CH_2Ph)$_2$] (M = Zr (**112**), Hf (**113**)) by treatment with 1 equiv of $PhCH_2MgCl$ (Scheme 27).[58,60]

<Figure 12 here>

Compound **100** is stable in non-coordinating solvents such as dichloromethane and toluene, but it is quite reactive in the presence of THF. For example, it readily quantitatively forms a hepta-coordinated THF adduct {Zr(η^5-[O^N^C^N^O])Cl(THF)} (**114**-THF), as determined by X-ray crystallography (Fig. 12).[58] The η^5-*O*,*N*,*C*,*N*,*O*-pentadentate trianionic ligand, consists of a central η^3-*N*,*C*,*N* chelating 2-imidazolidinyl anionic unit that is flanked on each side by an aryloxy group; this binding mode makes the [Zr(ONCNO)] chelate severely distorted from planarity. The ^{13}C NMR spectrum supported the formation of **114**-THF with the presence of an extra resonance at δ 100.8 ppm for N*C*(CH_2Ph)N carbon atom compared to **100** with a characteristic $C_{carbene}$ signal at δ 205.8 ppm. Moreover, reaction of [H_3(**L**^{27})]Cl with Zr(CH_2Ph)$_4$ in THF cleanly gave the complex **114**-THF in a quantitative yield. This unexpected reaction was described as a Lewis base assisted benzyl migration from the zirconium center to the $C_{carbene}$ of **L**^{27}; this migration clearly illustrates the nucleophilic nature of the NHC moiety within the planar [Zr(**L**^{27})] chelate in complex **100**. To gain more insight into the pathway, the calculations for the model compounds of **100*** and **114*** were carried out at the DFT level.[58] The calculated energy difference (ΔE = -4.4 kcal/mol) suggested that species **100*** can readily form its **100***-THF adduct in the presence of THF. Moreover, compound **114***-THF is energetically favored compared to all isomers of species **100***-THF. Furthermore, the barrier energy for the rearrangement of **100***-THF to the thermodynamic product **114***-THF is about ΔG = 25.2 kcal/mol (ΔE = 23.6 kcal/mol).

<Scheme 28 here>

In 2014, Zi and co-workers prepared a series of chiral group 4 NHC complexes [M(**L**$^{28\text{-}30}$)(NR_2)X(THF)] (X = Ti, Zr, Hf; R = Me, Et; **115**-**127**) in good yields by amine elimination reaction of M(NR_2)$_4$ with 1 equiv of the imidazolium salt [H_3(**L**$^{28\text{-}30}$)]X (X = Br, Cl) in THF (Scheme 28).[63] These complexes are sensitive to moisture but stable in an inert atmosphere. X-ray diffraction analyses showed that all M^{4+} ions feature a similar distorted-octahedral ligand environment.

3.5 Nitrogen/Oxygen-functionalized unsymmetrical NHC complexes

<Scheme 29 here>

In recent years, Despagnet-Ayoub and co-workers prepared anilino/aryloxy tethered NHC precursors [H_3(**L**^{31})]Cl (Scheme 29).[64,65] Unfortunately, this imidazolium salt is unstable and rearranges slowly in solution (7 days at room temperature or 15 min at 90 °C, in THF) to a more stable benzimidazolium species [H_3(**L**^{32})]Cl. Attempt to form a dichloride complex [Zr(**L**^{31})Cl_2] failed but an aryloxy-anilino-NHC complex [Zr(**L**^{32}) $_2$] (**128**) (Scheme 29) was isolated.[64] While Ti(NMe_2)$_2Cl_2$ was used as a metal source, it afforded a zwitterionic complex **129**, in which NHC ligand **L**^{31} rearranged to a bidentate (N,O) ligand and coordinated to Ti with an open uncoordinated iminium group.[65] This arrangement probably involves an nucleophilic attack at the imidazolium carbon either by an amide ligand or by a liberated amine, followed by ring opening of the N-heterocycle. Compound **129** could slowly rearrange (overnight at 50 °C) to a new species {Ti[H(**L**^{32})]Cl_3($NHMe_2$)} (**130**), which could be also prepared by the reaction of $TiCl_2(NMe_2)_2$ with [H_3(**L**^{32})]Cl. However, in contrast to [H_3(**L**^{27})]Cl,[60] the [H_3(**L**^{31})]Cl resulted in the complex [Zr(η^4-[N^N^N^O])Bz_2] (**131**) when it was treated with [Zr(CH_2Ph)$_4$] and $PhCH_2MgCl$, in which a benzyl group migrated to the carbene carbon, converting the heterocycle to a imidazolidine.[65]

4. Catalytic activity of group 4 metal NHC complexes

4.1 Oligomerization/Polymerization/Coplymerization of olefins

<Scheme 30 here>

Group 4 meal catalysts play a very important role in the coordination polymerization of olefins (Scheme 30). The Ziegler-Natta, metallocene and FI catalysts are fairly representative examples.[83-85] In addition, the spatial configuration of the metal centers can be controlled by auxiliary ligands so that they could afford a wide variety of polymers. In this context, group 4 NHC complexes are active for the oligomerization/polymerization/coplymerization of olefins.

The group 4 NHC complexes *trans*-[M($\mathbf{L^{2\text{-}4}}$)$_2$Cl$_4$] (**4**-**7**, Scheme 3) with two monodentate NHC ligands were tested in ethylene polymerization.[17] With the co-catalyst methylalumoxane (MAO, Al/Zr = 1650-2200), zirconium complexes **4**, **6** and **7** showed moderate activity for this transformation (56-75 kg·mol^{-1}Zr·bar^{-1}·h^{-1}; 2 bar ethylene pressure, toluene, 5-90^{o}C), while hafnium complex **5** exhibited a poor catalytic activity (1 kg·mol^{-1}Zr·bar^{-1}·h^{-1}) under similar reaction conditions. Moreover, the obtained polyethylenes (PEs) are linear polymers with the melting point of 126-130 ^{o}C.

The group 4 imino-NHC complexes [M($\mathbf{L^{16}}$)Cl$_4$] (M = Ti (**49**), Zr (**50**), Hf (**51**); Scheme 14)[39] are also active catalysts for the ethylene polymerization in the presence of co-catalyst MAO (1000 equiv). In this case, Zr complex **50** (140 Kg PE·mol^{-1}Zr·h^{-1}) was more active than its Ti homologue **49** (40 Kg PE·mol^{-1}Ti·h^{-1}), while Hf compound **51** did not yield polymers. Moreover, no oligomers were generated, and the polyethylenes (PEs) produced by **49**/MAO and **50**/MAO were linear polymers with the maximum melting temperatures of 134.0 and 135.9 ^{o}C, respectively.

The titanium NHC complex [Ti^{III}($\mathbf{L^{17}}$)Cl$_3$] (**53**, Scheme 15), bearing a pyridylene *bis*-NHC ligand, showed a high activity in ethylene polymerization (791 kg·mol^{-1}Ti·bar^{-1}·h^{-1} or 28195 h^{-1}) in the presence of co-catalyst MAO.[37] However, when other co-catalysts such as dried MAO (DMAO), co-MAO (10% ^{i}Bu) or Et$_2$AlCl are used, its catalytic activity is reduced. The produced PEs showed a high molecular weight (> 2×10^{6} g mol^{-1}) and melting point (141^{o}C), which is in line with linear high-density polyethylenes (HDPEs).

In the presence of co-catalyst MAO, the alkoxy NHC Zr complex [Zr($\mathbf{L^{23}}$)(NEt$_2$)$_2$] (**80**, Scheme 21)[47] could homopolymerize ethylene and propylene. The obtained linear PEs have high molecular weight (M_w = 6.7-37 × 10^{5} g mol^{-1}) and broad PDI (1.6-3.4), while the produced polypropylenes (PPs) are highly isotactic accompanying with an atactic fraction (30% w/w). The authors concluded that there are more than one catalytic site because its alkylated complex [Zr($\mathbf{L^{23}}$)(CH$_3$)$_2$] has several possible diastero-isomers. DFT calculations in both gas phase and benzene solution revealed that the highly C_2-symmetrical enantiomer *C*-*SSSS*-Δ with a *cis*-methyl group and a *trans*-NHC moiety was responsible for the olefins polymerization, especially for the formation of isotactic PP.

The “Sal-like” aryloxy-NHC group 4 complexes [M($\mathbf{L^{24}}$)$_2$Cl$_2$] (M = Ti (**81**), Zr (**82**); Scheme 22) showed moderate activities (131-761 kg polymer·mol^{-1}M·h^{-1}) for ethylene polymerization and copolymerization with norbornene or 1-octene under the desired conditions (1000-1500 equiv of MAO, 120-400 psi of ethylene, 1746-6360 equiv of co-monomer).[56] The two bulky Dipp groups were hypothesized to be sterically to hinder the fast association of olefin monomer, which is responsible for its inactivity in propylene polymerization.

The *bis*-aryloxy NHC titanium complexes [Ti^{IV}($\mathbf{L^{25}}$)(THF)X$_2$] (X = Cl (**83**), Br (**84**); Scheme 23), [Ti^{III}($\mathbf{L^{25}}$)(THF)$_2$Br] (**85**, Scheme 23), {[Ti($\mathbf{L^{25}}$)Br]$_2$(μ^2-O)} (**93**) and {[Ti($\mathbf{L^{25}}$)]$_2$(μ^2-O)$_2$} (**94**) showed different catalytic activity for the ethylene polymerization in the presence of co-catalyst MAO.[48,51,52] Mononuclear complexes **83**-**85** exhibited similar catalytic activity due to their similar structures (up to ca. 90 kg PE·mol^{-1}Ti·h^{-1}·atm^{-1}) at low ethylene pressure (50 psig).[48,51,52] The average molecular weights (M_n) of the obtained polymer are very low (< 3830 g mol^{-1}). The ^{13}C NMR spectrum of the polyethylene produced by **83** revealed its linear microstructure, and no methyl or long-chain branches were observed. In addition, no resonances of terminal (P-CH=CH$_2$, vinyl end group) and internal (PCH=CH-CH$_3$, 2 olefin types) double bonds (P means polymer) were observed by NMR spectroscopy. In contrast to mononuclear complex **83**,[48] the binuclear complexes **93** and **94** showed a very low activity for the polymerization of ethylene. The catalytic activity in the polymerization of ethylene decreases in the order of **83** > **93** > **94**. Although the relationship between the conformation (*cisoid* or *transoid*) of the *bis*-aryloxy NHC ligand and the activity in polymerization reactions could not be concluded, it seems that the co-catalyst MAO plays an important role in this catalytic transformation, because the ground-state conformation of the pro-catalysts is largely irrelevant to that generated by the reaction with co-catalyst MAO.

<Scheme 31 here>

The catalytic activity of the dibenzyl NHC group 4 complexes [M($\mathbf{L^{27}}$)(CH_2Ph)$_2$] (M = Zr (**112**), Hf (**113**); Scheme 27) and their cationic derivatives [M($\mathbf{L^{27}}$)(CH_2Ph)(NMe_2Ph)][B(C_6F_5)$_4$] (M = Zr (**132**), Hf (**133**); Scheme 31) has been examined for the polymerization of 1-hexene.[60] Complexes **112** and **113** did not initiate the polymerization of 1-hexene in the presence of 1 equiv of co-catalyst B(C_6F_5)$_3$. While in the presence of [Ph_3C][B(C_6F_5)$_4$], zirconium complex **112** could oligomerize 1-hexene (250 equiv 1-hexene per h) to afford oligomers containing dimers to heptamers in a molar ratio of 5/22/25/28/16/4. In contrast, the anilinium cation Zr species **132** showed a 100% conversion of 250 equiv monomer within 5h, but the produced oligo(1-hexene) has only three different chain length with the molar ratio of 77/16/7 for trimer, tetramer and pentamer, respectively. The high regioselectivity (>99%) might arise from the β-elimination from 1,2-enchained cationic Zr centers. However, for hafnium, both **113**/[Ph_3C][B(C_6F_5)$_4$] and **133** showed a very slow polymerization under similar reaction conditions.

4.2 Ring-opening polymerization of *rac*-lactide

The biodegradable polylactide (PLA) is an attractive polymeric material prepared from the ring-opening polymerization (ROP) of lactide in a controlled and stereoselective manner.[86] The subject of numerous investigations mainly focused on the development of novel ancillary ligands and their complexes during the last decades.[87,88] The well-defined group 4 metal complexes have been investigated as active initiators for lactide ROP due to their oxophilic nature.[89]

<Scheme 32 here>

In 2006, Arnold and co-workers found that the alkoxide titanium NHC complex [Ti($\mathbf{L^{22}}$)(OPr^i)$_3$] (**77**, Scheme 20) is an active bifunctional catalyst for the lactide polymerization.[44] In this transformation, the MALDI mass spectrometry suggested that the NHC moiety was involved in the initiation stage. In the absence of initiators such as benzyl alcohol, the Ti–NHC species **77** could initiate the polymerization of *rac*-lactide (LA/[NHC-Ti] = 100/5, CH_2Cl_2, 24 h, room temperature) in a controlled fashion to afford PLA (M_w = 3600 g·mol^{-1}, PDI = 1.05) in 65% yield. The polymerization was proposed to be initiated by the nucleophilic attack of the hemilabile NHC on the metal-coordinated LA, followed by coordination insertion polymerization of the remaining monomers (Scheme 32). Thus, Lewis acidic metals and labilized NHC have a synergistic effect on the ROP polymerization.

<Scheme 33 here>

Recently, Bellemin-Laponnaz and co-workers found that group 4 NHC complexes [M($\mathbf{L^{27}}$)(O^iPr)Cl(THF)] (M = Ti (**103**-THF), Zr (**104**-THF); Scheme 26) and [Ti($\mathbf{L^{27}}$)(O^iPr)$_2$] (**106**, Scheme 26) could initiate a controlled ROP of *rac*-LA under various conditions to produce PLA with OR-ester end.[57,59] Therefore the NHC moiety was ruled out in the ROP initiation step. The titanium complex **106** showed a poor catalytic activity because of the steric hindrance around the metal center. In contrast, the mono(alkoxide) titanium complex **103**-THF displayed a well-controlled ROP mode under the given conditions ([LA]/Ti = 100, toluene, 90 °C, 15 h) to afford PLA (M_n = 9800 g·mol^{-1}, PDI = 1.08) in 89% conversion. In addition, its Zr analogue [Zr($\mathbf{L^{27}}$)(O^iPr)Cl(THF)] (**104**-THF) promoted a more controlled and hetero-selective ROP process of *rac*-LA at room temperature. The chain-length-controlled, narrowly dispersed and heterotactic PLAs were obtained in 84-95% conversion (Scheme 33a). Most significantly, such high level of control could be well maintained in 83-92% conversion under an immortal manner in the presence of benzyl alcohol (Scheme 33b).[59] Moreover, an external alcohol source served as a chain transfer agent, suggesting a chain end control mechanism. Furthermore, a sequential ROP of trimethylene carbonate (TMC) and then *rac*-LA afforded highly heterotactic PLA-b-PTMC block co-polymers (Scheme 33c). This provided a promising method for the synthesis of the stereoregular co-polymeric biomaterials.

Chiral group 4 metal NHC complexes [M($\mathbf{L^{28\text{-}30}}$)($NR_2$)X(THF)] (X = Ti, Zr, Hf; R = Me, Et; X = Cl, Br, **115-127**; Scheme 28) are also active catalysts for the polymerization of *rac*-lactide in the presence of isopropanol.[63] In toluene Zr and Hf complexes showed a more rapid polymerization (90-100% conversion) than the Ti derivatives (30-70% conversion), due to the different size of the metal ions. However, in coordinating solvents such as THF, the conversion significantly decreased to 45-64% for the Zr and Hf catalysts, due to competitive monomer-solvent coordination to the metal ion. The obtained polylactides are heterotactic, but the P_r values are moderate (0.66-0.74).

4.3 Copolymerization of epoxides and CO_2

As an abundant, inexpensive, and nontoxic raw material, carbon dioxide has been used as a monomer to co-polymerization with epoxides to afford biodegradable co-polymers poly(cyclohexene carbonate) (PCHC). In recent years, a number of di- and trivalent metal complexes supported by a wide variety of auxiliary ligands have been investigated in the manufacturing of the polycarbonates.[91]

Examples of co-polymerization of CO_2 and epoxides initiated by group 4 complexes are very rare. One is promoted by a salen-like ligand supported Ti(IV) complex, which was developed by Nozaki and co-workers in 2011;[92] the other is initiated by *bis*-aryloxy NHC Ti(IV) complexes [Ti($\mathbf{L^{27}}$)X_2] (X = Cl (**102**), O^iPr (**106**); Scheme 26) and [Ti($\mathbf{L^{27}}$)(O^iPr)Cl(THF)] (**103**-THF, Scheme 26), which was recently reported by Roux and co-workers.[62] Although the catalytic activity is not comparable to those initiated by cobalt and chromium salen catalysts, less toxic titanium provides an attractive alternative for this transformation.

<Table 3 here>

When the copolymerization of cyclohexene oxide (CHO) with CO_2 ([CHO]/[Ti] = 2500; CO_2 = 10 bar) was carried out at 60 °C for 24 h, these neutral titanium complexes only gave homopolymer poly(cyclohexene oxide) (PCHO) in low yield (up to 15%). However, with the addition of co-catalyst such as bis(triphenylphosphine)iminium chloride or nitrite [$Ph_3P{=}N{=}PPh_3$]X (X = Cl, NO_2), alternating copolymers PCHCs were obtained in 12-44% yields (Table 3), and the best catalytic activity (44% TOF) was achieved by complex **103**-THF in the presence of the co-catalyst [$Ph_3P{=}N{=}PPh_3$]Cl ([PNP]Cl). For this transformation, [$Ph_3P{=}N{=}PPh_3$]X is required, although the [$Ph_3P{=}N{=}PPh_3$]$^+$ cation shows only weak interactions with the titanium ion because of steric hindrance, it increases the electron density on metal center of the formed putative six-coordinate titanium intermediate. All copolymers exhibited highly alternating structures (carbonate linkage: >99%), which was determined by ^1H NMR spectroscopy.

4.4 Hydroamination/cyclization of aminoalkenes

<Schemes 34-35 here>

Hydroamination/cyclization, defined as the catalytic intramolecular addition of an N-H bond into an unsaturated C-C bond, is a fundamentally important process that can offer an atom-efficient pathway to nitrogen-containing heterocyclic compounds.[93] During the past decades, a number of group 4 catalysts for hydroamination have been developed due to their enhanced stability and functional group tolerance together with the low cost and toxicity. For example, the group 4 NHC complexes [M($\mathbf{L^{11}}$)(NMe_2)I_2] (M = Zr (**35**), Hf (**37**); Scheme 9) and [Ti($\mathbf{L^{11}}$)(NMe_2)$_2$X] (X = I (**39**-I), Cl (**39**-Cl); Scheme 10) are efficient catalysts for the hydroamination/cyclization of primary aminoalkenes,[33,74,75] while the zirconium complexes [Zr(**L**)(NMe_2)Br(THF)] (**L** = $\mathbf{L^{25}}$ (**96**) $\mathbf{L^{26}}$ (**97**)) showed no reactivity under the similar catalytic conditions.[54] A possible mechanism (Scheme 34) suggested that the group 4 metal imido intermediate was the active species in this catalytic transformation, followed by a [2+2] cycloaddition with the olefin and subsequent protonation of the azametallacyclobutane with another incoming substrates. However, to overcome the high reaction barriers, high temperature (up to 160 °C) is required. For example, Zr complex **35** did not show any catalytic activity at 80 °C, however, at 160 °C, the Zr catalyst **35** outperformed the Hf catalyst **37**, while both were more efficient than their Ti analogues **39**-I and **39**-Cl. The best conversion (>98%) can be achieved by **35** within 50 min. In addition, the nature of the substrate affected this transformation (Scheme 35). For example, a substrate with *gem*-dialkyl leaded to high yields of the cyclic product. Moreover, spiro-pyrrolidine compounds were also achieved. While mono- and unsubstituted primary aminoalkene substrates reacted much slower or not at all. 1,1-Disubstituted substrates with a methyl group adjacent to the terminal olefin rapidly formed pyrrolidine products containing a quaternary carbon center, while internal olefins and secondary amines did not undergo cyclization. A six-membered ring was readily formed, whereas seven-membered analogues were not.

5. Conclusions and perspective

Group 4 NHC-complexes can be prepared either by coordination of free NHCs to suitable metal complex or by alcohol or amine or alkane elimination from NHC precursors (imidazolium salts). These complexes have successfully been applied as promising catalysts in polymerizations and organic transformations. Furthermore, research in this area helped us to understand the bonding and reactivity of group 4 complexes; and therefore it closes the gap in our knowledge of early and late transition NHC complexes.

Although the recent effort has focused on the synthesis and reactivity of the group 4 NHC complexes and a significant progress has been made, compared to their late transition metal counterparts, the number of group 4 metal NHC complexes is still limited. Most of the group 4 metal NHC complexes, especially those containing monodentate NHC ligands are air and moisture sensitive, which requires an inert synthetic atmosphere. To overcome facile dissociation of the soft NHCs from the hard metal ions, functional groups such as amido and alkoxy have been introduced on the NHC to act as covalent tethers, which strengthen the metal-NHC interactions. Even so, NHC complexes of group 4 metals are still less developed compared with the late transition metals. Moreover, even in the group 4 NHC complexes, the hafnium NHC complexes are scarcely reported, and very limited progress has been made for group 4 NHC complexes with chiral NHC ligands.[63,94] Nevertheless, group 4 NHC complexes have shown some promises in homo- and co-polymerization of olefins (ethylene and 1-hexene), the ring-opening polymerization of *rac*-lactide and copolymerization of epoxides and CO_2, and the hydroamination/cyclization of primary aminoalkenes. However, the development of new, highly active group 4 NHC complexes especially chiral ones is still a challenge, and the use of group 4 NHC complexes in polymerization of conjugated olefins, small molecule transformations and (asymmetric) organic synthesis, has yet to be reported. Moreover, heterogeneous catalytic system with polymer-supported group 4 NHC catalysts, remains elusive. There is no doubt, with the right ancillary NHC ligands, this perspective will eventually become true.

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Notes and references

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Table 1 Well defined NHC complexes of group 4 transition metals

Complex	M-C$_{carbene}$ [Å]	^{13}C [ppm] (solvent)	Methods of characterization	ref
Momodentate NHC Complexes				
Ti(**L^1**)$_2$Cl$_4$ (**1**)		180.7 (CD$_3$CN)	EA, ^{1}H, ^{13}C NMR	14
Zr(**L^1**)$_2$Cl$_4$ (**2**)		178.2 (CD$_3$CN)	EA, ^{1}H, ^{13}C NMR	14
Hf(**L^1**)$_2$Cl$_4$ (**3**)		176.2 (CD$_3$CN)	EA, ^{1}H, ^{13}C NMR	14
Zr(**L^2**)$_2$Cl$_4$ (**4**)	2.432(3)	181.8 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	17
Hf(**L^2**)$_2$Cl$_4$ (**5**)	2.401(2)	189.1 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	17
Zr(**L^3**)$_2$Cl$_4$ (**6**)	2.456(3)	183.5 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	17
Zr(**L^4**)$_2$Cl$_4$ (**7**)	2.448(3)	185.4 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, MS, X-Ray	17
Ti(**L^5**)Cl$_4$ (**8**)		186.7 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR	15
Ti(**L^6**)Cl$_4$ (**9**)		185.5 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR	15
Ti(**L^7**)Cl$_4$ (**10**)		185.2 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR	15
[Ti(**L^7**)Cl$_3$]$_2$(μ-O)](**11**)	2.194(7) 2.202(7)		X-ray	15
[Cp$_2$TiMe(**L^2**)][BPh$_4$] (**12**)	2.289(2)	178.2 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C, ^{11}B NMR, IR, HRMS, X-Ray	16
[Cp$_2$ZrMe(**L^2**)][CH$_3$B(C$_6$F$_5$)$_3$] (**13**)		178.0 (CD$_2$Cl$_2$)	^{1}H, ^{13}C, ^{11}B, ^{19}F NMR, IR, HRMS	16
[(η^7-C$_7$H$_7$)Zr(η^5-C$_5$H$_5$)(**L^5**)] (**14**)	2.445(2)	191.2 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, EI-MS, X-Ray	69
[(η^7-C$_7$H$_7$)Hf(η^5-C$_5$H$_5$)(**L^5**)] (**15**)	2.394(2)	192.6 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, X-Ray	70
trans-[TiF$_4$(**L^5**)$_2$] (**16**)	2.255(4)	181.9 (CDCl$_3$)	EA,^{1}H,^{13}C, ^{19}F NMR, EI-MS, X-Ray	72
trans-[TiF$_4$(**L^7**)$_2$] (**17**)	2.2781(12) 2.2812(12)	184.3 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C, ^{19}F NMR, EI-MS, X-Ray	72
[{TiF$_2$(**L^5**)(NEt$_2$)}$_2$(μ-F)$_2$] (**18**)	2.2367(9)	N.O.^{a} (C$_6$D$_6$)	EA, ^{1}H, ^{13}C, ^{19}F NMR, EI-MS, X-Ray	72
{[TiF$_4$(**L^5**)$_2$](NacNacLi)} (**19**)		181.8 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C, ^{19}F NMR, EI-MS	72
[H(**L^7**)][TiF$_5$(**L^7**)] (**20**)	2.310(3)	207.6 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C, ^{19}F NMR, EI-MS, X-ray	72
[(**L^8**)TiCl$_2$(NMe$_2$)$_2$] (**21**)	2.313(5) 2.316(10)	194.0 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	27^b
[(**L^8**)Ti(=N-Dipp)Cl$_2$(NHMe$_2$)] (**22a**)	2.277(4)	191.1 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	28
[(**L^8**)Ti(=N-SiPh$_3$)Cl$_2$(NHMe$_2$)] (**22b**)		190.8 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR	28
[(**L^8**)Ti(=N-Ad)Cl$_2$(NHMe$_2$)] (**22c**)			EA, ^{1}H NMR, IR	28
[(**L^8**)Ti(=N-2,6-Cl$_2$C$_6$H$_3$)Cl$_2$(NHMe$_2$)] (**22d**)	2.263(5)	191.4 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	28
[(**L^8**)Ti(=N-^{t}Bu)Cl$_2$(NHMe$_2$)] (**22e**)	2.297(3)	191.6 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	28
[(**L^8**)Ti(=N-Dipp)Cl$_2$Py] (**23a**)		192.6 (C$_6$D$_6$)	^{1}H, ^{13}C NMR	28
[(**L^8**)Ti(=N-2,6-Cl$_2$C$_6$H$_3$)Cl$_2$Py] (**23d**)		191.8 (C$_6$D$_6$)	^{1}H, ^{13}C NMR	28
[(**L^8**)Ti(=N-^{t}Bu)Cl$_2$Py] (**23e**)		191.6 (C$_6$D$_6$)	^{1}H, ^{13}C NMR	28

[($\mathbf{L}^{8}$)$_2$Ti(=NR)Cl$_2$] (**24**) (R = 2,6-Cl$_2$C$_6$H$_3$)	2.315(2) 2.307(2)	192.8 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	28
[($\mathbf{L}^{8}$)Ti(=NR)(NHR)Cl(NHMe$_2$)] (**25**) (R = 2,6-Cl$_2$C$_6$H$_3$)	2.290(6)	191.8 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	28
[($\mathbf{L}^{9}$)Ti(NMe$_2$)$_2$Cl$_2$] (**26**)	2.313(3)	195.2 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	30
[($\mathbf{L}^{9}$)$_2$Ti$^{\mathrm{III}}$Cl$_3$] (**27**)	2.336(4)		EA, IR, EPR, X-ray	30
[($\mathbf{L}^{8}$)$_2$ZrCl$_4$] (**28**)	2.453(4) 2.471(4)	Poor solubility	EA, ^{1}H NMR, IR, X-ray	29
[($\mathbf{L}^{8}$)Zr(NMe$_2$)$_2$Cl$_2$] (**29**)	2.435(3)	192.4 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	29
[($\mathbf{L}^{8}$)Hf(NMe$_2$)$_2$Cl$_2$] (**30**)		204.0 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR	29
[($\mathbf{L}^{8}$)Zr(=N-Dipp)(NHMe$_2$)Cl$_2$] (**31**)	2.425(3)	190.8 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	29
Carbon-functionalized NHC complexes				
[TiCp$_2$($\mathbf{L}^{10}$)] (**32**)	2.210(5) 2.215(5)	N. O.^{a} (DMSO-d^6)	^{1}H, ^{13}C, ^{11}B NMR, EI-MS, X-ray	31
[ZrCp$_2$($\mathbf{L}^{10}$)] (**33**)	2.383(1) 2.299(1)	173.6 (DMSO-d^6)	^{1}H, ^{13}C, ^{11}B NMR, EI-MS, X-ray	31
[Zr($\mathbf{L}^{11}$)(NMe$_2$)$_2$I)] (**34**)	2.4256(10) 2.3990(11)	188.9 (CD$_2$Cl$_2$)	^{1}H, ^{13}C NMR, X-ray	32
[Zr($\mathbf{L}^{11}$)(NMe$_2$)I$_2$)] (**35**)	2.367(3) 2.362(3)	193.7 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, X-ray	73
[Zr($\mathbf{L}^{11}$)I$_3$] (**36**)	2.334(3) 2.335(3)	195.5 (C$_6$D$_6$)	^{1}H, ^{13}C NMR, X-ray	32
[Hf($\mathbf{L}^{11}$)(NMe$_2$)I$_2$)] (**37**)	2.34(3) 2.35(3)	201.0 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, X-ray	74
[Zr($\mathbf{L}^{12}$)(NMe$_2$)$_3$] (**38**)		211.8 (CD$_2$Cl$_2$)	^{1}H, ^{13}C NMR	32
[Ti($\mathbf{L}^{11}$)(NMe$_2$)$_2$I] (**39**-I)		190.5 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR	32
[Ti($\mathbf{L}^{11}$)(NMe$_2$)$_2$Cl] (**39**-Cl)		190.5 (CD$_2$Cl$_2$)	^{1}H, ^{13}C NMR	32
[Ti($\mathbf{L}^{11}$)Cl$_3$] (**40**)	2.2192(10) 2.2115(10)	194.5 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, X-ray	32
[Ti($\mathbf{L}^{11}$)Cl$_2$I] (**41**)		201.8, 197.1 (CD$_2$Cl$_2$)^c	EA, ^{1}H, ^{13}C NMR, X-ray	32
[Ti($\mathbf{L}^{11}$)(NMe$_2$)Cl$_2$] (**42**)	2.2406(14) 2.2172(14)	196.4 (CD$_2$Cl$_2$)	^{1}H, ^{13}C NMR, X-ray	30
[Ti$^{\mathrm{III}}$($\mathbf{L}^{13}$)(NMe$_2$)Cl] (**43**)	2.221(2)		EA, X-ray	35
[Ti($\mathbf{L}^{14}$)Cl$_2$] (**44**)	2.196(5)		EA, X-ray	36
[Ti($\mathbf{L}^{14}$)(=N^{t}Bu)Cl] (n = 1, **45a**)	2.227(4)	196.7 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, X-ray	36
[Ti($\mathbf{L}^{14}$)(=N^{t}Bu)Cl] (n = 2, **45b**)	2.226(2)	N.O. (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, X-ray	36
[Zr($\mathbf{L}^{14}$)Cl$_3$] (n = 1, **46a**)	2.441(9)	N.O. (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, X-ray	36
[Zr($\mathbf{L}^{14}$)Cl$_3$] (n = 2, **46b**)		190.1 (C$_6$D$_5$Cl)	EA, ^{1}H, ^{13}C NMR	36
[Ti($\mathbf{L}^{15}$)(NEt$_2$)$_2$]I (**47a**)	2.218(4)	185.3 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, X-ray	34
[Zr($\mathbf{L}^{15}$)(NEt$_2$)$_2$]I (**47b**)		182.7 (CDCl$_3$)	^{1}H, ^{13}C NMR	34
[Zr($\mathbf{L}^{15}$)(NEt$_2$)I$_2$] (**48**)	2.440(3)	187.8 (CDCl$_3$)	EA, ^{1}H, ^{13}C NMR, MS, X-ray	34
Nitrogen-functionalized NHC complexes				

[Ti(**L**^{16})Cl$_4$] (**49**)	2.167(5)	197.4 (CDCl$_3$)	EA, ^{1}H, ^{13}C NMR, X-ray	39
[Zr(**L**^{16})Cl$_4$] (**50**)	2.297(17)	195.3 (CDCl$_3$)	EA, ^{1}H, ^{13}C NMR, FT-IR, HR-MS, X-ray	39
[Hf(**L**^{16})Cl$_4$] (**51**)		201.6 (CDCl$_3$)	EA, ^{1}H, ^{13}C NMR, FT-IR	39
[Ti^{III}(**L**^{16})(THF)Cl$_3$] (**52**-THF)	2.178(3)		EA, X-ray	39
[Ti^{III}(**L**^{17})Cl$_3$] (**53**)	2.191(5) 2.211(5)		EA, ^{1}H NMR, MS(FAB), X-ray	37
[Ti(**L**^{17})(=N^{t}Bu)Cl$_2$] (**54**)	2.281(6) 2.286(6)	200.7 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, IR, X-ray	38
[Ti(**L**^{18})(O^{i}Pr)$_3$] (**55**)		205.6（C$_6$D$_6$）	^{1}H, ^{13}C NMR	40
[Ti(**L**^{18})(O^{i}Pr)$_2$Br] (**56**)	2.252(3) 2.256(3) 2.241(6)	187.6（C$_6$D$_6$）	EA, ^{1}H, ^{13}C NMR, X-ray	40
[Ti(**L**^{18})(O^{i}Pr)Br$_2$] (**57**)		N. D.^{d}（Py-d^5）	EA, ^{1}H NMR	40
{Ti(**L**^{18})[(C$_3$N$_2$H$_3$)^{t}Bu](O^{i}Pr)$_2$}Br (**58**)	2.221(6)	N. D.^{d}（C$_6$D$_6$）	^{1}H NMR, X-Ray	40
{Zr[H(**L**^{18})]Bz$_4$} (**59**)	2.2710(18)	193.4 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, X-ray	41
{Zr[H(**L**^{19})]Bz$_4$} (**60**)	2.420(2)		^{1}H NMR, X-ray	41
{Zr[η^2-*N*,*C*-(C$_3$N$_2$H$_2$)-^{t}Bu][η^3-(C$_2$N)-^{t}Bu]Bz$_2$} (**61**)			^{1}H NMR	41
{Zr[η^2-*N*,*C*-(C$_3$N$_2$H$_2$)-Mes][η^3-(C$_2$N)-^{t}Bu]Bz$_2$} (**62**)	2.228(3)	198.0 (CD$_2$Cl$_2$)	EA, ^{1}H, ^{13}C NMR, X-ray	41
{Zr(**L**^{19})Bz$_3$} (**63**)	2.451(2)	195.4 (CD$_2$Cl$_2$)	^{1}H, ^{13}C NMR, X-ray	41
[Zr(**L**^{20})(NEt$_2$)$_2$](**64**)		188.8（C$_6$D$_6$）	EA, ^{1}H, ^{13}C NMR, EI-MS	42
[Zr(**L**^{21})(NMe$_2$)$_2$](**65**)		190.9（C$_6$D$_6$）	EA, ^{1}H, ^{13}C NMR	43
[Hf(**L**^{21})(NMe$_2$)$_2$](**66**)		195.7（C$_6$D$_6$）	EA, ^{1}H, ^{13}C NMR	43
[Zr(**L**^{20})Cl$_2$(Py)](**67**-Py)			EA. EI-MS	42
[Zr(**L**^{20})Cl$_2$(THF)](**67**-THF)	2.391(5)	181.0（C$_6$D$_6$）	EA, ^{1}H, ^{13}C NMR	42
[Zr(**L**^{21})Cl$_2$](**68**)		192.3 (C$_5$D$_5$N)	EA, ^{1}H, ^{13}C NMR	43
[Hf(**L**^{21})Cl$_2$](**69**)		198.2 (C$_5$D$_5$N)	EA, ^{1}H, ^{13}C NMR	43
[Zr(**L**^{20})(CH$_2$TMS)$_2$] (**70**)	2.415(3)	186.8（C$_6$D$_6$）	EA, ^{1}H, ^{13}C NMR, EI-MS, X-ray	42
[Zr(**L**^{21})Me$_2$] (**71**)		189.8 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR	43
[Zr(**L**^{21})Bz$_2$] (**72**)		190.1 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR	43
[Hf(**L**^{21})Me$_2$] (**73**)		196.1 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR	43
[Hf(**L**^{21})Bz$_2$] (**74**)		196.5 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR	43
[Hf(**L**^{21})(^{i}Bu)$_2$] (**75**)	2.385(3)	194.9 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR, X-ray	43
[Hf(**L**^{21})Et$_2$] (**76**)		196.4 (C$_6$D$_6$)	EA, ^{1}H, ^{13}C NMR	43
Oxygen-functionalized NHC complexes				
[Ti(**L**^{22})(O^{i}Pr)$_3$] (**77**)	2.293(2)	189.5 (C$_6$D$_6$) 190.5 (C$_5$D$_5$N)	^{1}H, ^{13}C NMR, X-ray	44
[Ti^{III}(**L**^{22})$_2${^{i}PrOSiMe$_2$O}-K$_2$OTi^{IV}(O^{i}Pr)$_4$]$_2$ (**78**)	2.308(3) 2.306(4)		EA, ^{29}Si NMR, X-ray	45
[Ti^{III}(**L**^{22})$_3$](**79**)	2.263(5) 2.252(4) 2.299(4)		EA, EI-MS, XPR	46

[Zr(**L**^{23})$_2$(NEt$_2$)$_2$] (**80**)		197.5 (C_6D_6)	EA, ^{1}H, ^{13}C NMR	47
[Ti(**L**^{24})$_2$Cl$_2$] (**81**)	2.264(2) 2.275(2)	226.8 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR, HRMS, X-ray	56
[Zr(**L**^{24})$_2$Cl$_2$] (**82**)	2.452(4) 2.438(4)	226.8 (CD_2Cl_2)	^{13}C NMR, HRMS, X-ray	56
[Ti(**L**^{25})(THF)Cl$_2$] (**83**)	2.200(9)	164.0 ($CDCl_3$)	EA, ^{1}H, ^{13}C NMR, X-ray	48
[Ti(**L**^{25})(THF)Br$_2$] (**84**)		164.8 ($CDCl_3$)	EA, ^{1}H, ^{13}C NMR	52
[Ti^{III}(**L**^{25})(THF)$_2$Br] (**85**)	2.18(1)		EA	51
[Zr(**L**^{25})(THF)Cl$_2$] (**86**)	2.35(1)	183.5 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	49
[Zr(**L**^{25})$_2$] (**87**)	2.383(3) 2.380(3)	185.5 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	49
[Ti(**L**^{25})$_2$] (**88**)	2.205(4) 2.196(4)	182.4 ($CDCl_3$)	EA, ^{1}H, ^{13}C NMR, X-ray	52
[Ti(**L**^{25})Me$_2$] (**89**)	2.175(9)	185.7 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	51
[Ti(**L**^{25})Bz$_2$] (**90**)	2.187(2)	188.3 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	48
[Zr(**L**^{25})Bz$_2$] (**91**)	2.309(3)	187.5 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	49
[Zr(**L**^{25})(CH$_2$TMS)$_2$] (**92**)		185.8 (C_6D_6)	EA, ^{1}H, ^{13}C NMR	49
{[Ti(**L**^{25})Br]$_2$(μ-O)} (**93**)	2.208(5)	185.0 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	52
{[Ti(**L**^{25})]$_2$(μ-O)$_2$} (**94**)	2.250(5)	188.4 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	52
[Zr(**L**^{25})(OSiMe$_3$)(k^2-[N^O]]$_6$ (**95**)	2.415(7)	188.3 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	53
(k^2-[N^O] = 3,5-^{t}Bu$_2$-2-O$^-$-C$_6$H$_2$-CH$_2$-(C$_3$N$_2$H$_3$))				
[Zr(**L**^{25})(NMe$_2$)Br(THF)] (**96**)		186.4 (C_7D_8)^e	EA, ^{1}H, ^{13}C NMR	54
[Zr(**L**^{26})(NMe$_2$)Br(THF)] (**97**)		186.0 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	54
[Ti(**L**^{27})$_2$] (**98**)	2.222(2) 2.233(2)	199.9 (CD_2Cl_2)	^{1}H, ^{13}C NMR, HRMS, X-ray	57
[Zr(**L**^{27})$_2$] (**99**)	2.379(2) 2.387(3)	200.8 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR, HRMS, X-ray	61
[Hf(**L**^{27})$_2$] (**100**)	2.357(6) 2.351(6)	206.1(CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR, X-ray	61
[Zr(**L**^{27})Cl$_2$(THF)] (**101**-THF)	2.358(3)	197.0 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR, X-ray	58
[Ti(**L**^{27})Cl$_2$(THF)] (**102**-THF)	2.184(3)	197.0 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR, X-ray	57
[Ti(**L**^{27})Cl$_2$] (**102**)	2.160(3)	200.0 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR, X-ray	57
[Ti(**L**^{27})(O^{i}Pr)Cl(THF)] (**103**-THF)	2.166(3)	198.6 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR, X-ray	57
[Zr(**L**^{27})(O^{i}Pr)Cl(THF)] (**104**-THF)	2.360(3)	200.0 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR, X-ray	59
[Hf(**L**^{27})(O^{i}Pr)Cl(THF)] (**105**-THF)^f				60
[Ti(**L**^{27})(O^{i}Pr)$_2$] (**106**)	2.212(5)	197.9 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	57
[Hf(**L**^{27})Cl$_2$(THF)] (**107**-THF)	2.333(6)	200.5 (C_6D_6)	EA, ^{1}H, ^{13}C NMR, X-ray	60
[Ti(**L**^{27})(NMe$_2$)Cl(THF)] (**108**-THF)		203.6 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR	57
[Zr(**L**^{27})(NMe$_2$)Cl(THF)] (**109**-THF)		202.9 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR	60
[Zr(**L**^{27})(NMe$_2$)Cl(NHMe$_2$)] (**109**-NHMe$_2$)		203.6 (CD_2Cl_2)	EA, ^{3}C NMR	60
[Zr(**L**^{27})(CH$_2$Ph)Cl] (**110**)		203.6 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR	58
[Hf(**L**^{27})(CH$_2$Ph)Cl] (**111**)^f				60
[Zr(**L**^{27})(CH$_2$Ph)$_2$] (**112**)	2.333(1)	205.8 (CD_2Cl_2)	EA, ^{1}H, ^{13}C NMR, X-ray	60

	2.329(1)	205.9 (C_6D_6)	EA, ^1H, ^{13}C NMR, X-ray	65
[Hf($\mathbf{L}^{27}$)(CH_2Ph)$_2$] (**113**)	2.308(3)	212.6 (CD_2Cl_2)	EA, ^1H, ^{13}C NMR, X-ray	60
{Zr(η5-[O^N^C^N^O])Cl(THF)} (**114**-THF)	2.174(3)	100.8 (CD_2Cl_2)	EA, ^1H, ^{13}C NMR, X-ray	58
[Ti($\mathbf{L}^{28}$)(NMe_2)Br(THF)] (**115**)		208.4 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR	63
[Zr($\mathbf{L}^{28}$)(NMe_2)Br(THF)] (**116**)		209.0 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR	63
[Hf($\mathbf{L}^{28}$)(NMe_2)Br(THF)] (**117**)		213.6 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR	63
[Zr($\mathbf{L}^{28}$)(NEt_2)Br(THF)] (**118**)	2.416(2)	209.2 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR, X-ray	63
[Ti($\mathbf{L}^{28}$)(NMe_2)Cl(THF)] (**119**)		209.4 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR	63
[Zr($\mathbf{L}^{28}$)(NMe_2)Cl(THF)] (**120**)		210.1 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR	63
[Hf($\mathbf{L}^{28}$)(NMe_2)Cl(THF)] (**121**)		214.5 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR	63
[Zr($\mathbf{L}^{28}$)(NEt_2)Cl(THF)] (**122**)	2.419(2)	209.3 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR, X-ray	63
[Zr($\mathbf{L}^{29}$)(NMe_2)Cl(THF)] (**123**)	2.397(4)	212.9 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR, X-ray	63
[Ti($\mathbf{L}^{30}$)(NMe_2)Cl(THF)] (**124**)	2.252(2)	201.8 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR, X-ray	63
[Zr($\mathbf{L}^{30}$)(NMe_2)Cl(THF)] (**125**)	2.401(2)	206.2 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR, X-ray	63
[Hf($\mathbf{L}^{30}$)(NMe_2)Cl(THF)] (**126**)	2.370(3)	216.9 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR, X-ray	63
[Zr($\mathbf{L}^{30}$)(NEt_2)Cl(THF)] (**127**)	2.410(4)	214.5 (C_6D_6)	EA, ^1H, ^{13}C NMR, IR, X-ray	63
[Zr($\mathbf{L}^{32}$)$_2$] (**128**)		200.1 (C_6D_6)	^1H, ^{13}C NMR	64

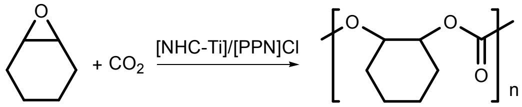
[a] Not observed. [b] Also see Ref 28. [c] Axial and equatorial geometric isomers. [d] Not determined because of low solubility in most cases. [e] At -30 °C. [f] Not isolated.

Table 2 Selected bond lengths [Å] and angles [°] for **21, 26**, **27** and **29**[a]

	21 (M =Ti)	**26** (M =Ti)	**27** (M =Ti)	**29** (M =Zr)
M-C_{NHC}	2.313(5)	2.313(3)	2.336(4)	2.435(3)
M-Cl	2.3664(16)	2.3607(15)	2.284(6)	2.465(8)
Cl·····C_{NHC}	3.112	3.061	3.264	3.234
M-N	1.876(4)	1.883(3)		2.005(2)
Cl-M-C_{NHC}	83.34(12)	81.82(9)		82.59(7)
Cl-M-Cl	163.936	163.10(4)		165.17(3)
N-M-N	109.30(18)	105.97(14)		107.07(11)
C_{NHC}-M-C_{NHC}			176.3(2)	

[a] Average values for the two crystallographically independent molecules.

Table 3 Copolymerization of CHO/CO_2 catalyzed by NHC-Ti/[PPN]Cl



complex/cocat. (equiv)	yield (%)	TOF (h^{-1})	M_n (kg/mol)	M_w/M_n
102/[PPN]Cl (1.0)	38	40	12.5	1.28
106/[PPN]Cl (1.0)	27	28	8	1.37
103-THF/[PPN]Cl (1.0)	44	46	13.8	1.38
103-THF/[PPN]NO_2 (1.0)	12	12	-	-

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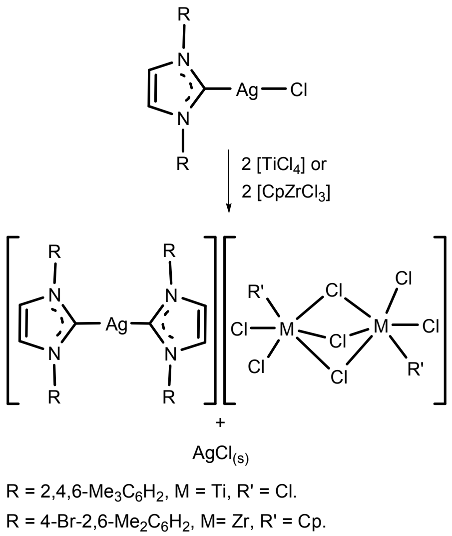
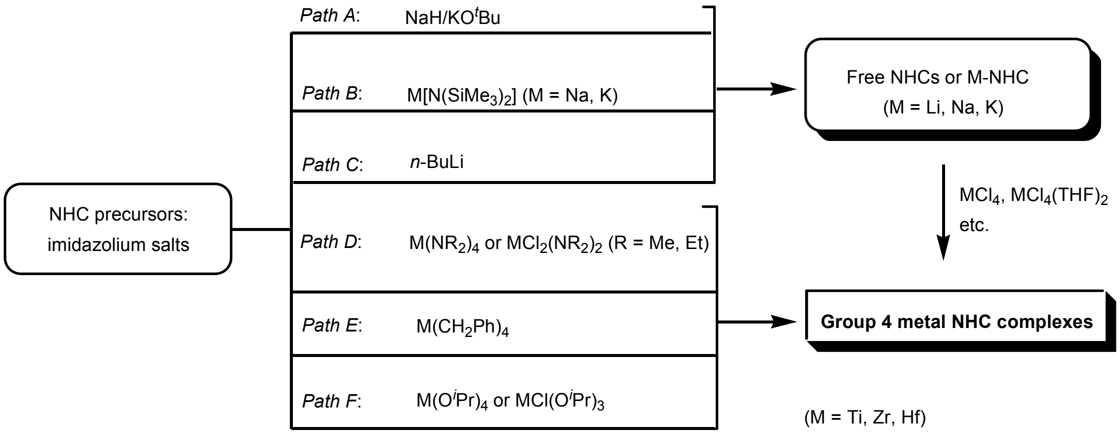
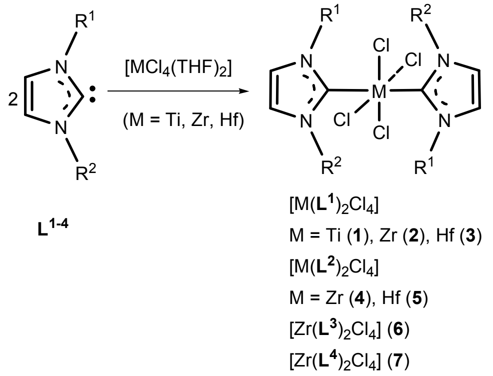


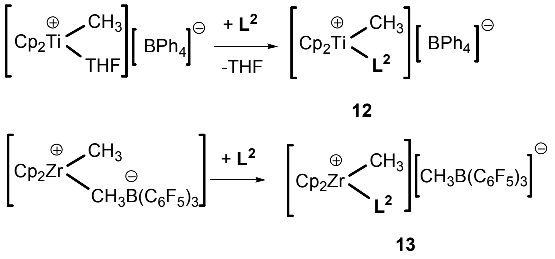
Scheme 1 Reaction of Ag-NHC complex with $TiCl_4$ or $CpZrCl_3$.



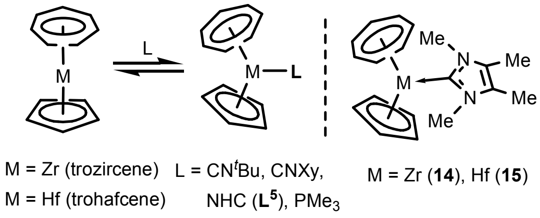
Scheme 2 Synthetic approaches to group 4 NHC complexes.



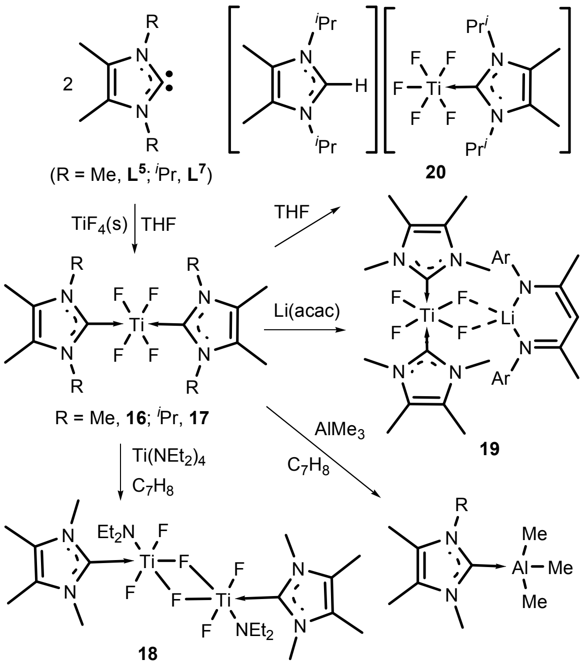
Scheme 3 Synthesis of complexes **1**-**7**.



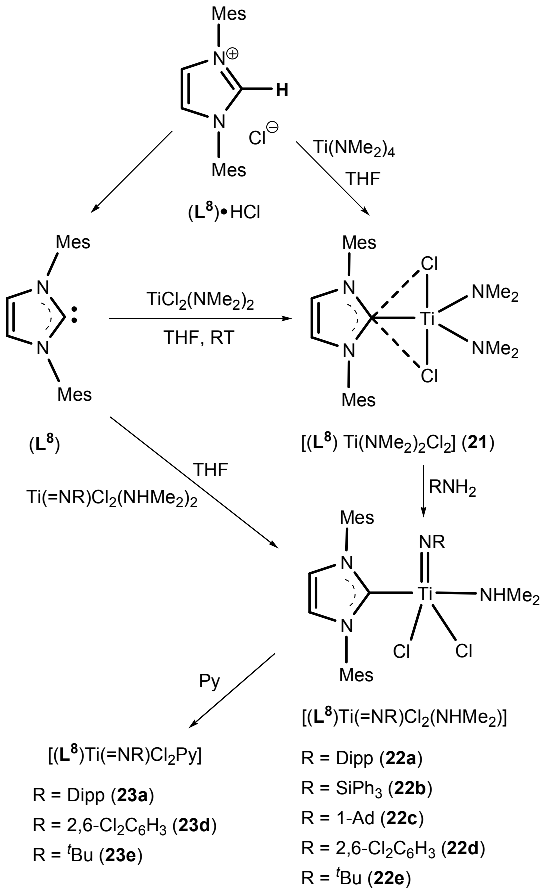
Scheme 4 Synthesis of complexes **12** and **13**.



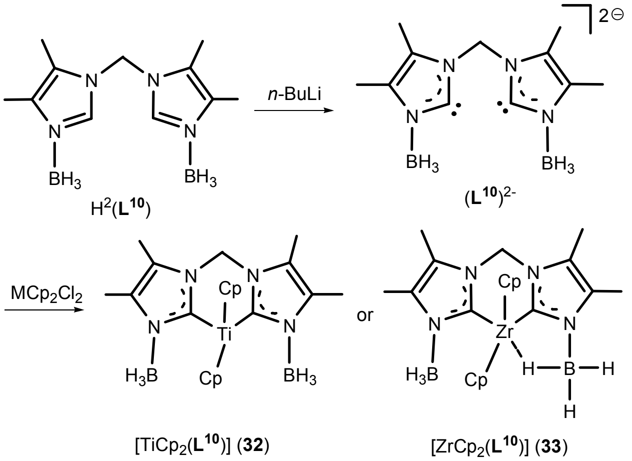
Scheme 5 Synthesis of complexes **14** and **15**.



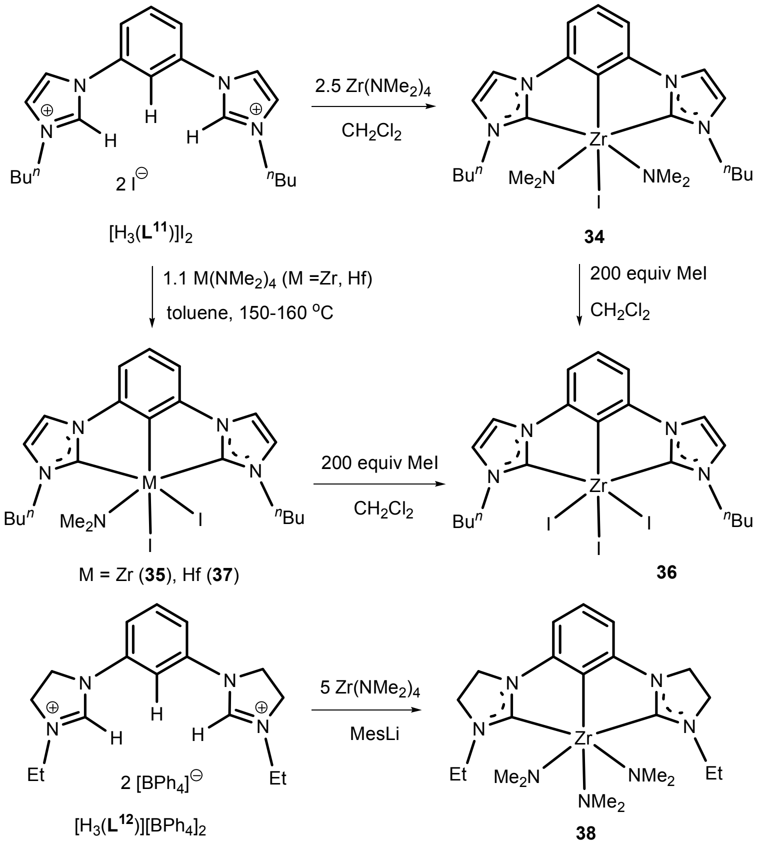
Scheme 6 Synthesis of complexes **16-20**.



Scheme 7 Synthesis of complexes **21-23**.



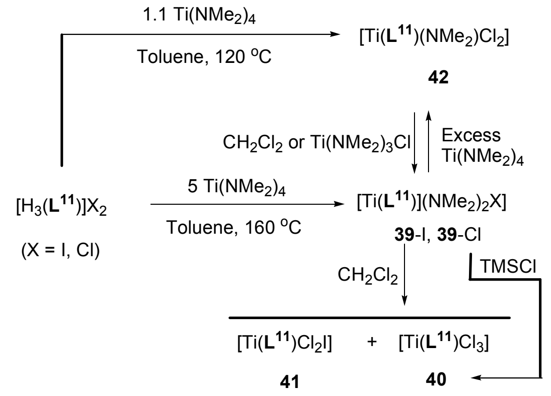
Scheme 8 Synthesis of complexes **32** and **33**.



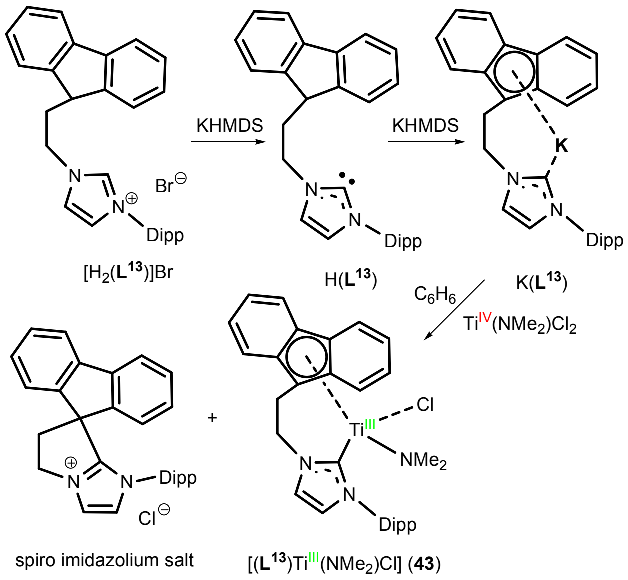
5

Scheme 9 Synthesis of complexes **34-38**.

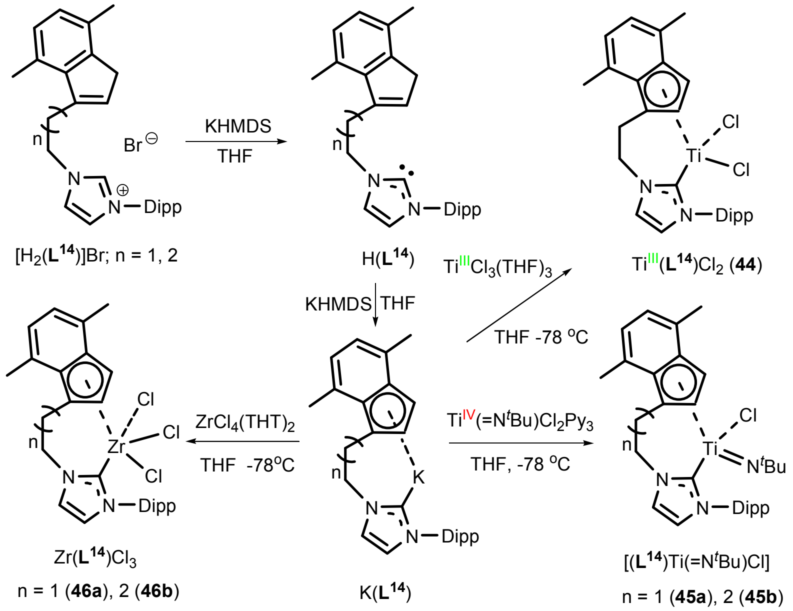
10



Scheme 10 Synthesis of complexes **39-42**.

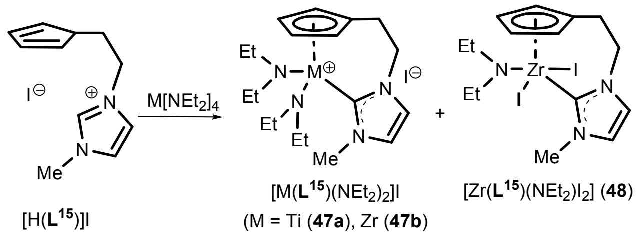


Scheme 11 Synthesis of complex **43**.

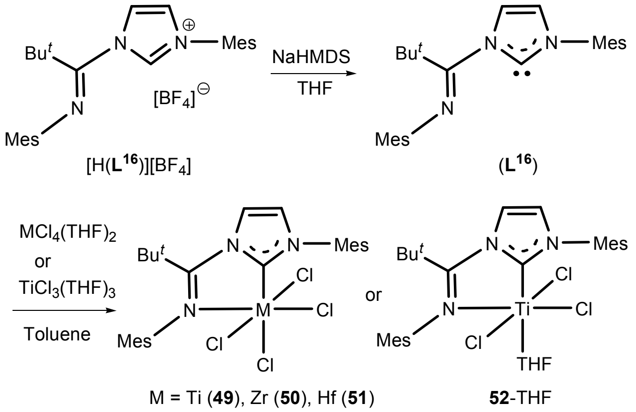


5

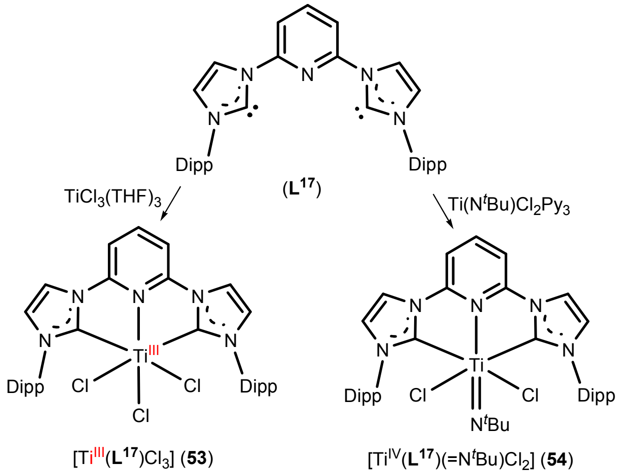
Scheme 12 Synthesis of complexes **44-46**.



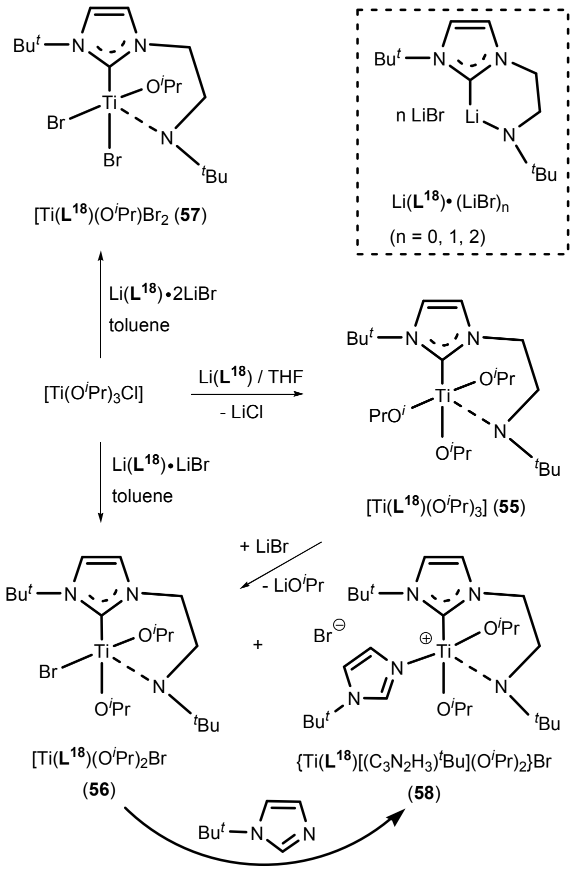
Scheme 13 Synthesis of complexes **47** and **48**.



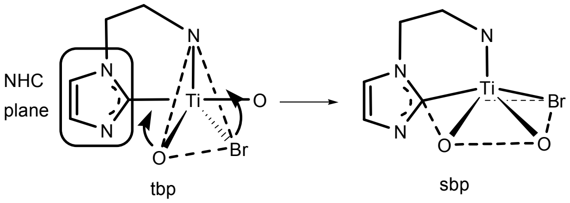
Scheme 14 Synthesis of complexes **49-52**.



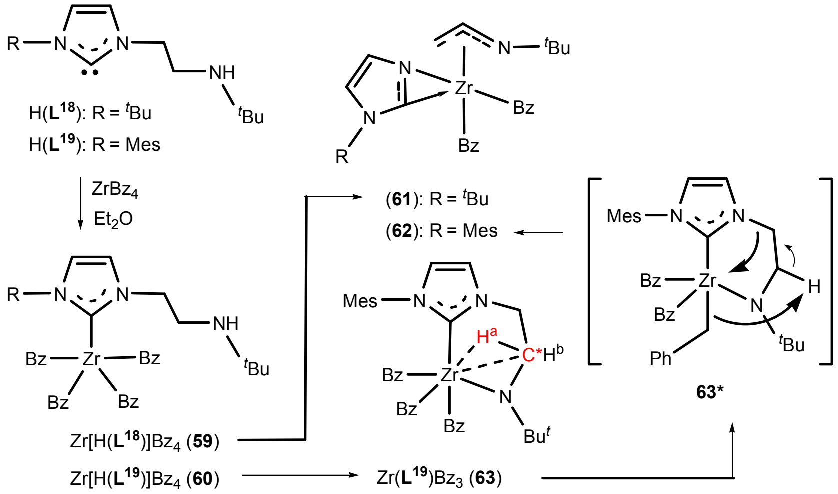
Scheme 15 Synthesis of complexes **53** and **54**.



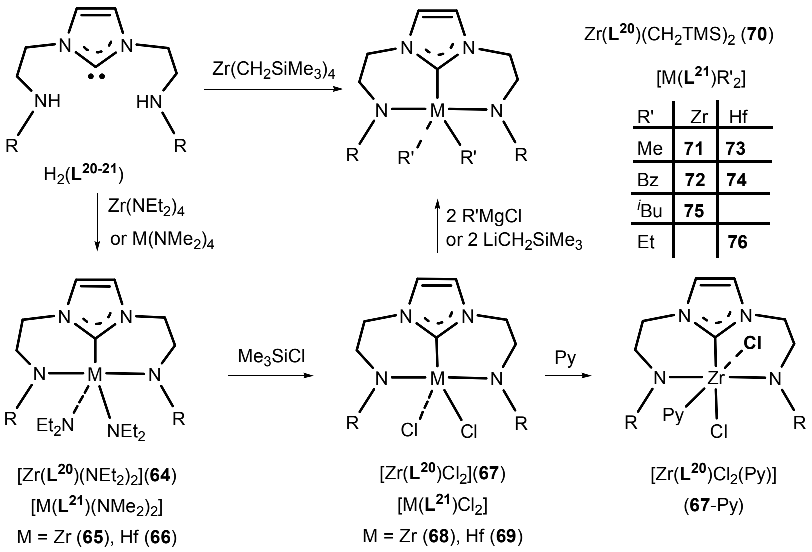
Scheme 16 Synthesis of complexes **55-58**.



Scheme 17 Structures of tbp and sbp.

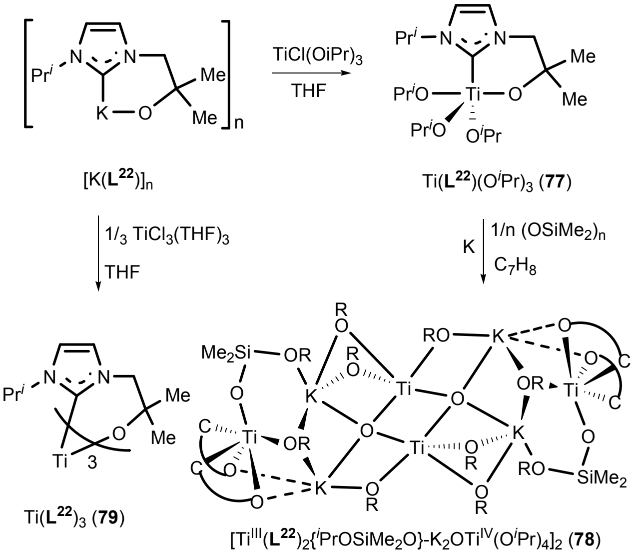


Scheme 18 Synthesis of complexes **59-63**.

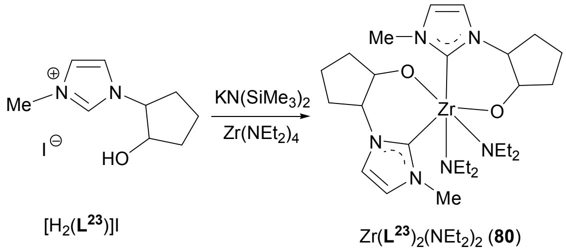


R'	Zr	Hf
Me	**71**	**73**
Bz	**72**	**74**
ⁱBu	**75**	
Et		**76**

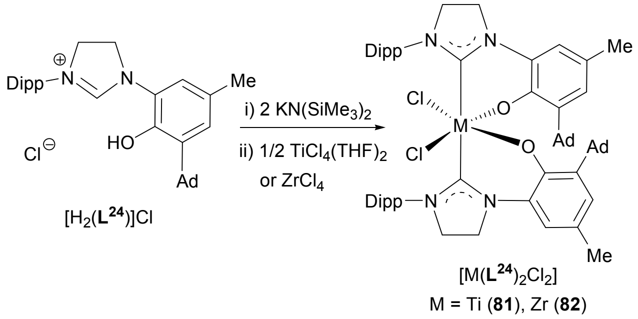
Scheme 19 Synthesis of complexes **64-76**.



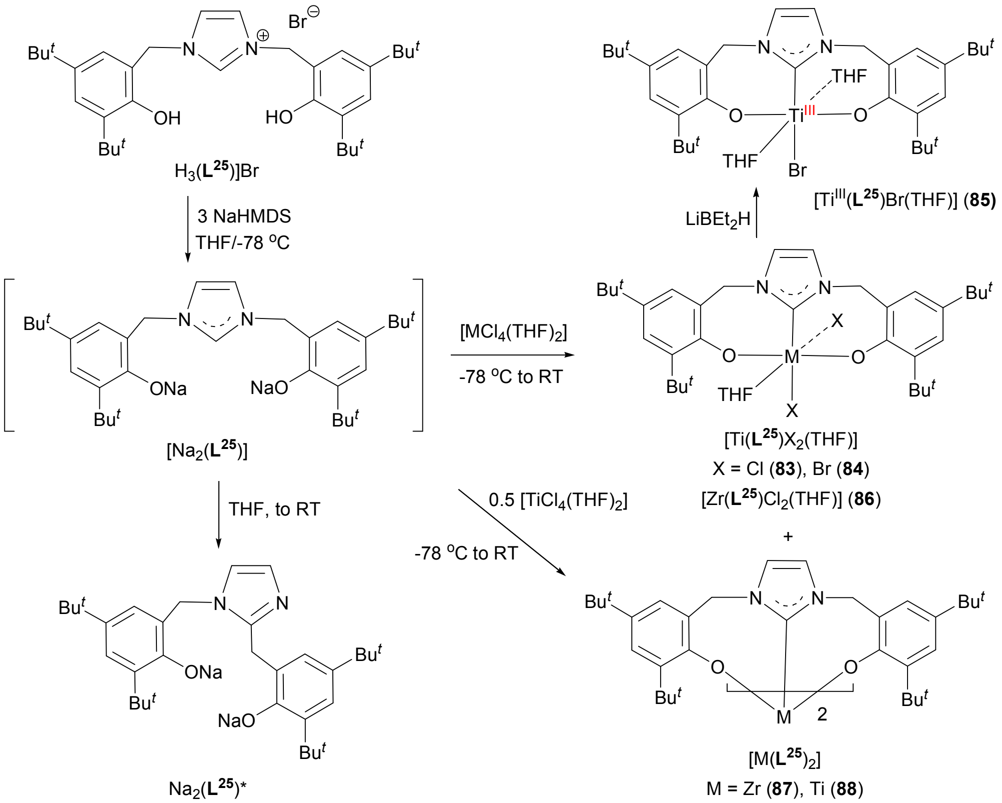
Scheme 20 Synthesis of complexes **77-79**.



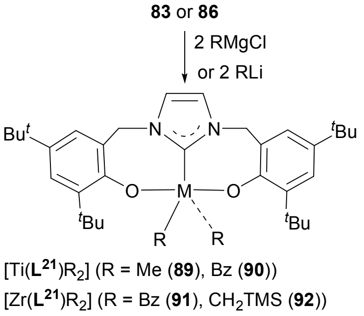
Scheme 21 Synthesis of complex **80**.



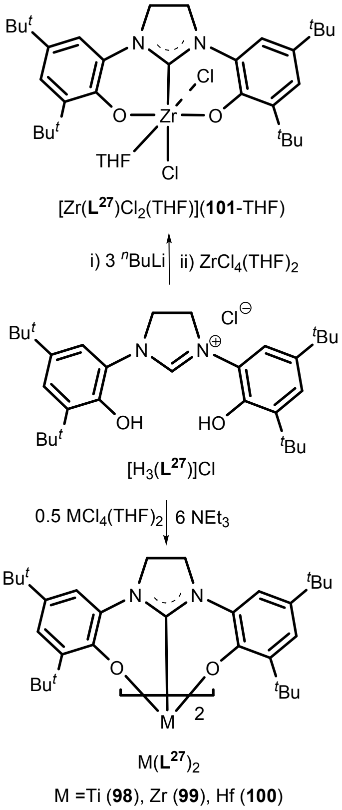
Scheme 22 Synthesis of complexes **81** and **82**.



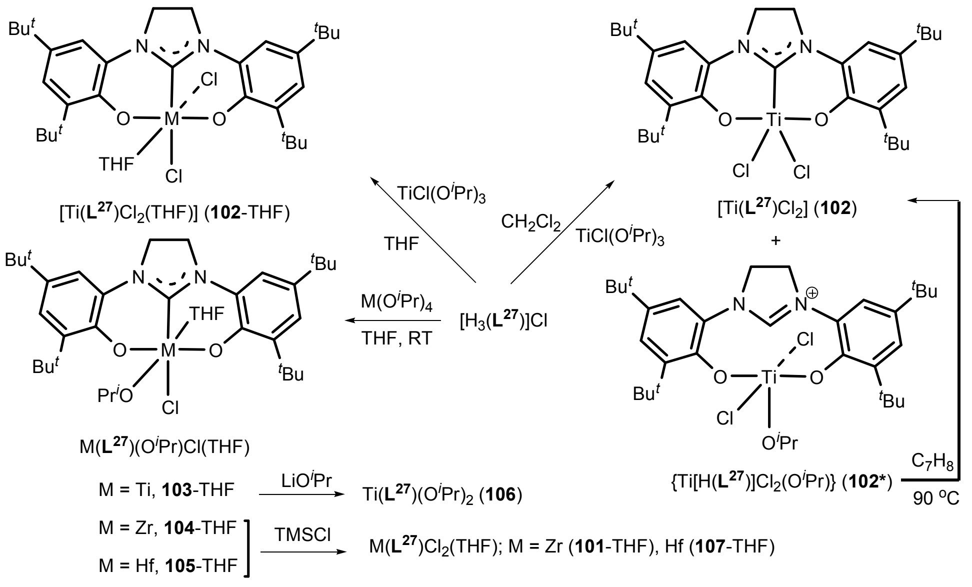
Scheme 23 Synthesis of complexes **83-88**.



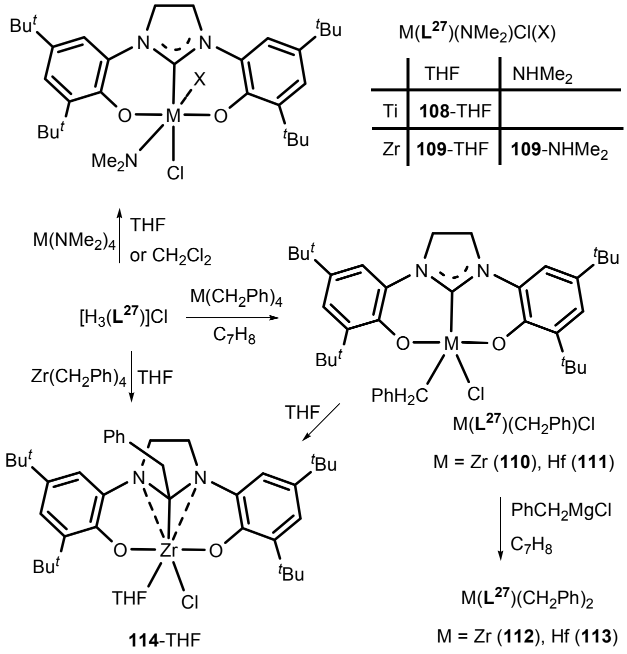
Scheme 24 Synthesis of complexes **89-92**.



Scheme 25 Synthesis of complexes **98-101**.



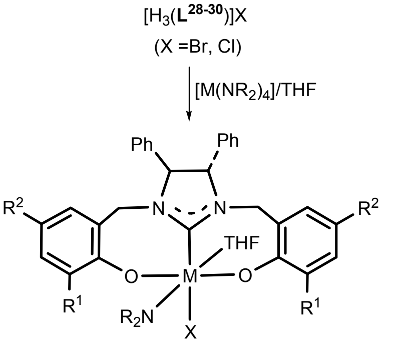
Scheme 26 Synthesis of complexes **102-107**.



M(**L^{27}**)(NMe$_2$)Cl(X)

	THF	NHMe$_2$
Ti	**108**-THF	
Zr	**109**-THF	**109**-NHMe$_2$

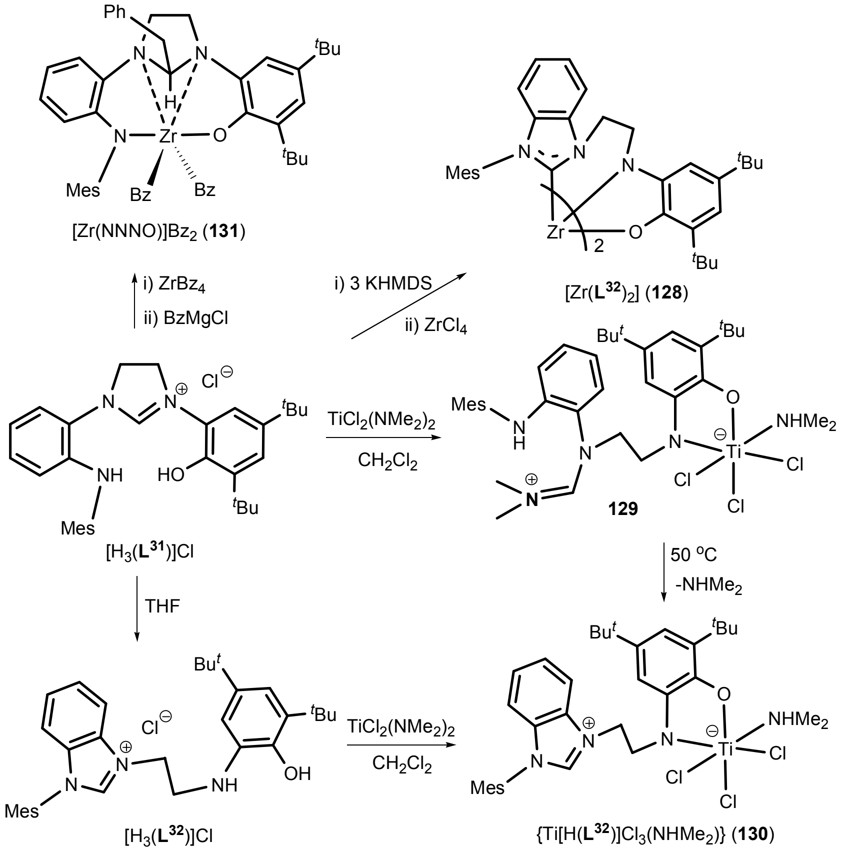
Scheme 27 Synthesis of complexes **108-114**.



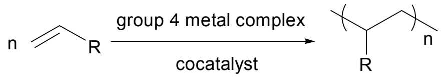
[M(**L**)(NR$_2$)X(THF)]

R^1	R^2	**L**	R	X	Ti	Zr	Hf
H	H	**L^{28}**	Me	Br	**115**	**116**	**117**
		L^{28}	Et	Br		**118**	
		L^{28}	Me	Cl	**119**	**120**	**121**
		L^{28}	Et	Cl		**122**	
^{t}Bu	H	**L^{29}**	Me	Cl		**123**	
^{t}Bu	^{t}Bu	**L^{30}**	Me	Cl	**124**	**125**	**126**
		L^{30}	Et	Cl	**127**		

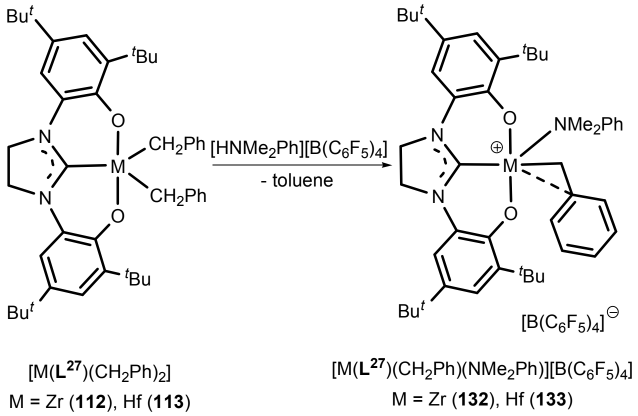
Scheme 28 Synthesis of complexes **115-127**.



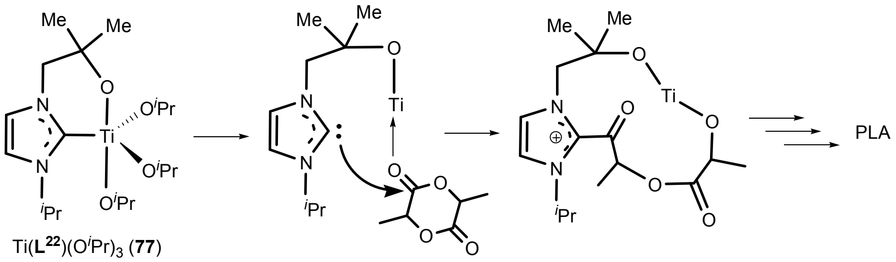
Scheme 29 Synthesis of complexes **128**-**131**.



Scheme 30 Polymerization of alkenes.

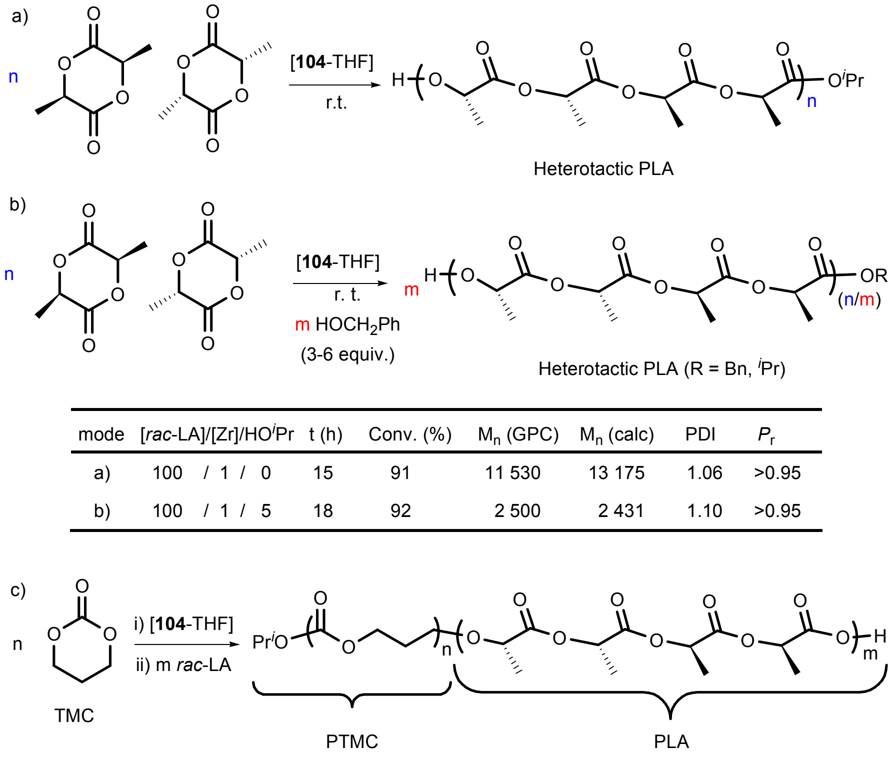


Scheme 31 Synthesis of complexes **132** and **133**.



Ti(L^{22})(O^iPr)$_3$ (**77**)

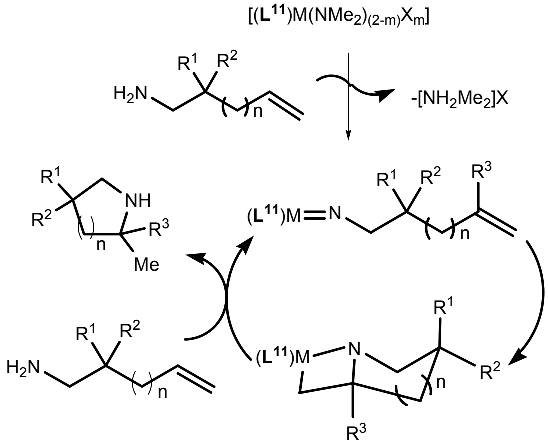
Scheme 32 Mechanism for the polymerization of lactide.



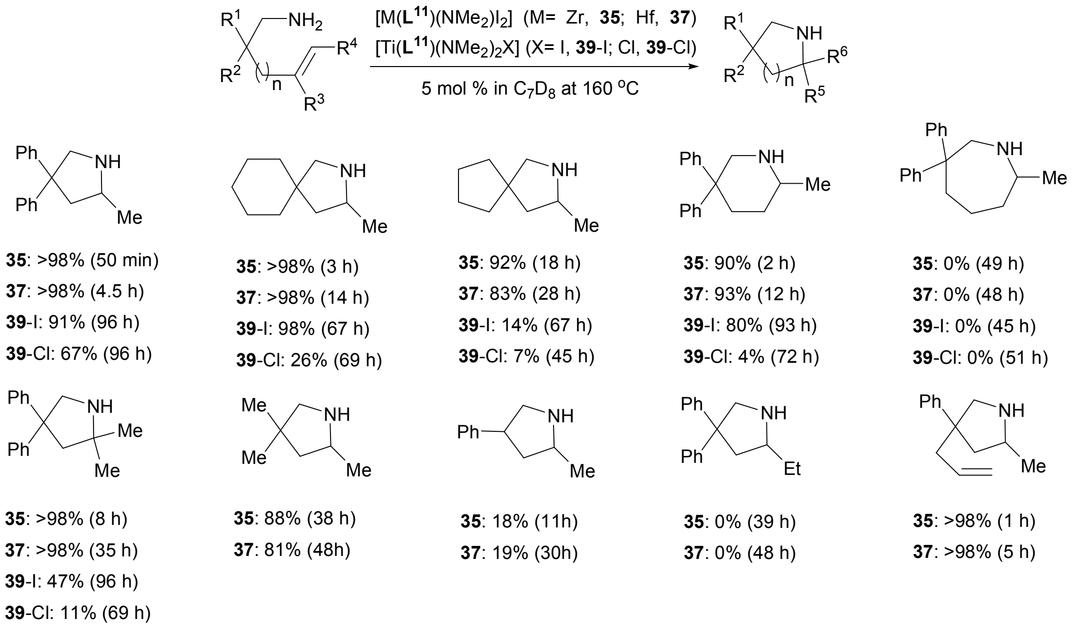
mode	[*rac*-LA]/[Zr]/HO^iPr	t (h)	Conv. (%)	M_n (GPC)	M_n (calc)	PDI	P_r
a)	100 / 1 / 0	15	91	11 530	13 175	1.06	>0.95
b)	100 / 1 / 5	18	92	2 500	2 431	1.10	>0.95

LA/TMC = 40/60, M_n = 11410 g/mol, PDI = 1.24, P_r (LA) = 0.95

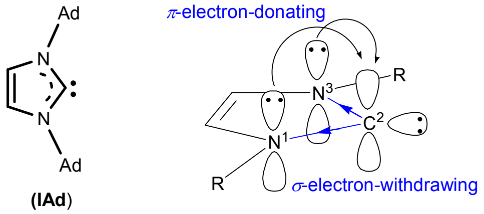
Scheme 33 Catalytic activity of complex **104**-THF.



Scheme 34 Proposed mechanism for the hydroamination /cyclization.



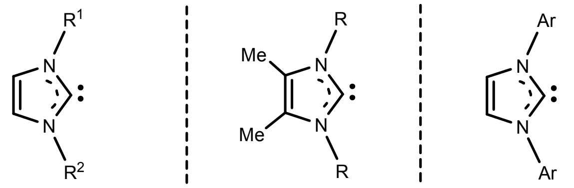
Scheme 35 Hydroamination/cyclization catalyzed by group 4 NHC complexes.



(IAd)

(a) (b)

Fig. 1 The first isolated stable NHC (a) and its ground-state electronic structure (b).



L1: $R^1 = R^2 =$ Me
L2: $R^1 = R^2 = {}^i$Pr
L3: $R^1 =$ Me, $R^2 = {}^i$Bu
L4: $R^1 =$ Me, $R^2 = CH_2$Mes

L5: R = Me
L6: R = Et
L7: R = ^{i}Pr

L8: Ar = Mes
L9: Ar = Dipp

Fig. 2 Monodentate NHCs.

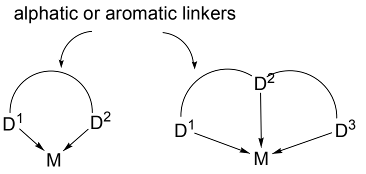
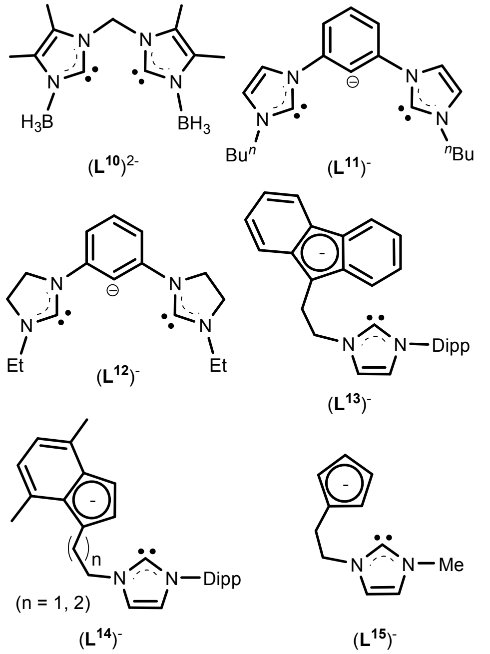
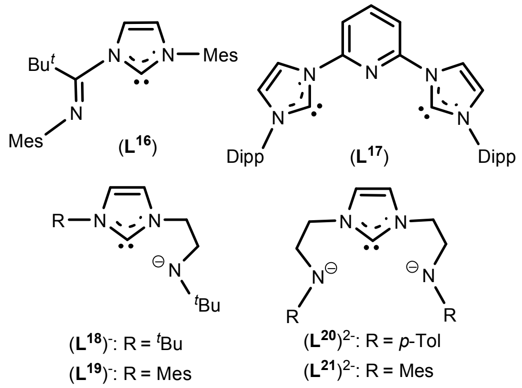


Fig. 3 Generic structures for the hybrid ligands (D^1, D^2, D^3 represents the functional dornors and at least one of donors is an NHC, M = Ti, Zr, Hf).

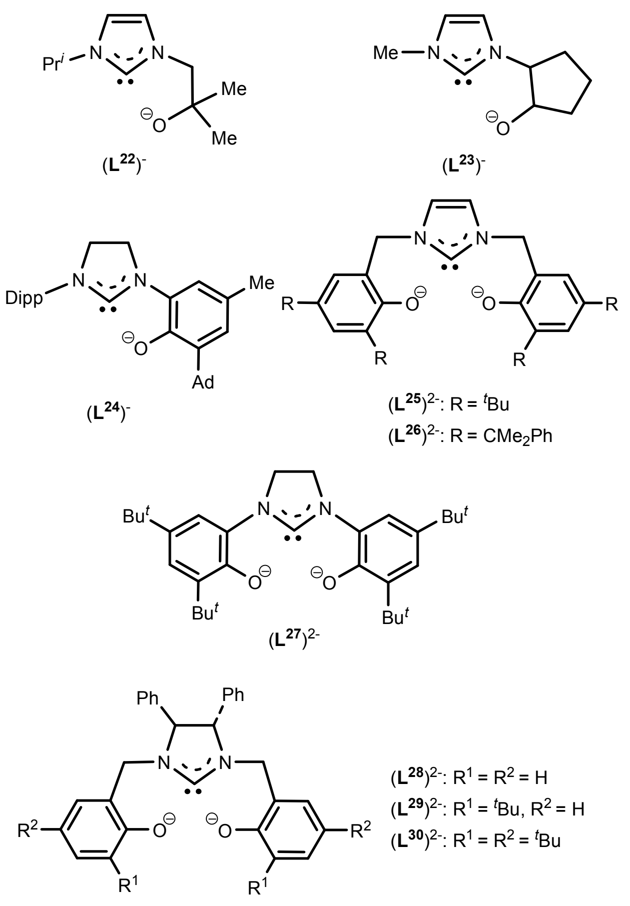
a) Carbon-functionalized NHCs



b) Nitrogen-functionalized NHCs



c) Oxygen-functionalized NHCs



d) Nitrogen/oxygen functionalized NHCs

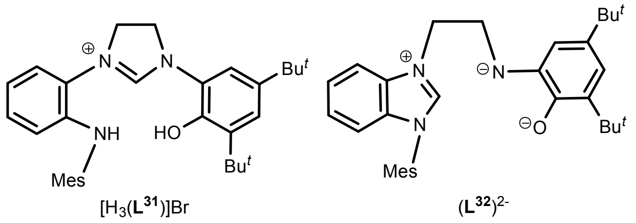


Fig. 4 Multidentate NHCs.

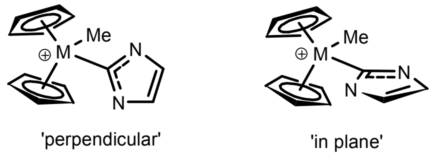


Fig. 5 Two possible arrangements of NHC ligand in complexes **12**, **14** and **15**.

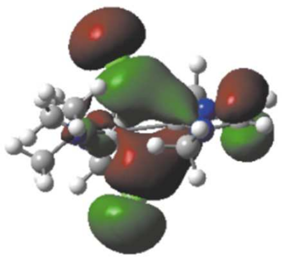


Fig. 6 The HOMO-8 orbital for compound **21**.[27]

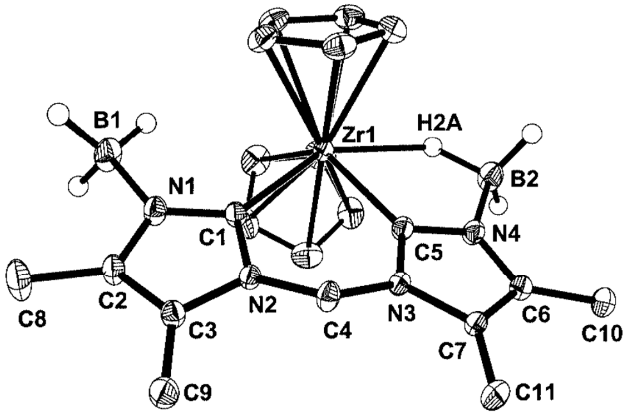


Fig.7 Molecular Structure of **33**: C1-Zr = 2.383(1), C5-Zr = 2.299(1), B2-H2A 1.23(2), H2A-Zr = 2.16(2); C1-Zr-C5 = 75.4(1), Zr-C1-N2 = 128.7(1).[31]

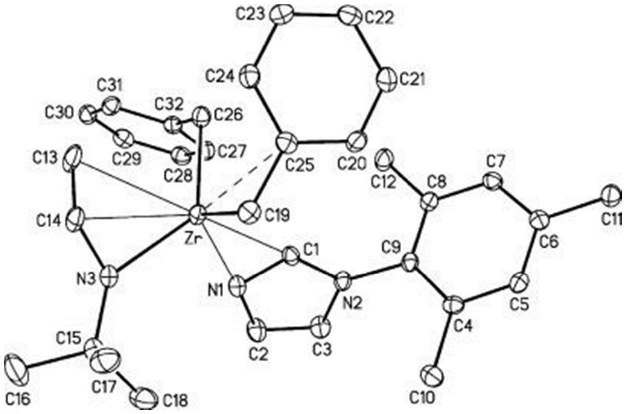


Fig. 8 Molecular structure of complex **62**.[41]

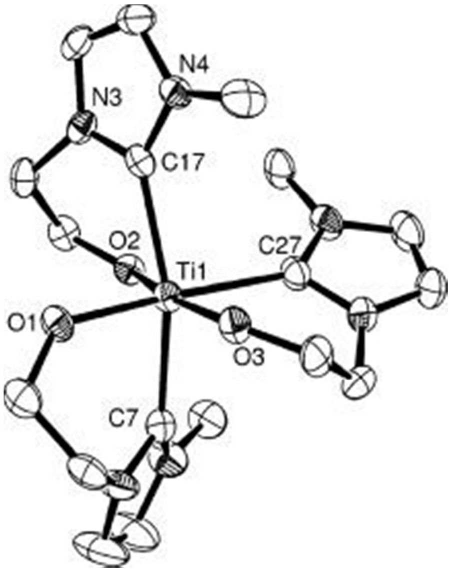
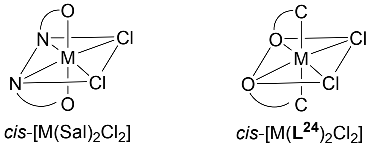
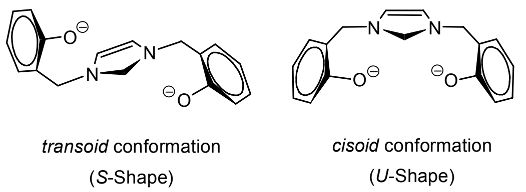


Fig. 9 Molecular structure of complex **79**.[46]



cis-$[M(Sal)_2Cl_2]$ *cis*-$[M(\mathbf{L^{24}})_2Cl_2]$

Fig. 10 *cis*-$[M(Sal)_2Cl_2]$ and *cis*-$[M(\mathbf{L^{24}})_2Cl_2]$.



transoid conformation (*S*-Shape) *cisoid* conformation (*U*-Shape)

Fig. 11 *S*- and *U*-Shapes.

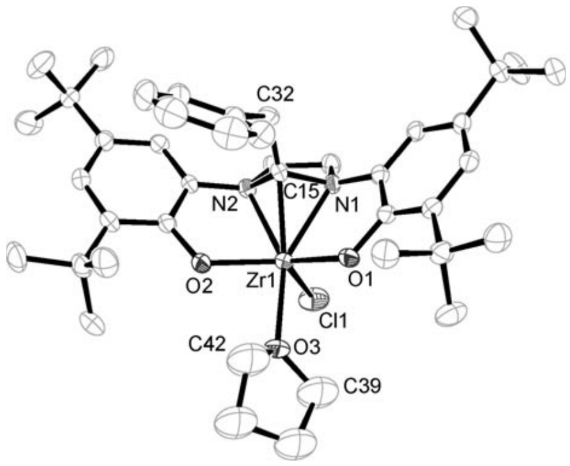


Fig. 12 Molecular Structure of complex **114**-THF. Selected bond distances [Å] and angles [°]: Zr(1)–C(15)= 2.174(3), Zr(1)–N(1) = 2.308(3), Zr(1)–N(2)= 2.310(3), Zr(1)–O(1) = 2.036(2), Zr(1)–O(2) = 2.042(2), Zr(1)–O(3) = 2.279(3), Zr(1)–Cl(1) = 2.460(1); O(1)-Zr(1)-N(1) = 74.15(9), O(2)-Zr(1)-N(2) = 73.26(9), N(1)-Zr(1)-N(2) = 56.63(9).[58]

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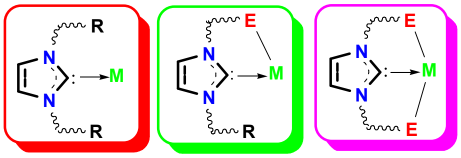

E = NHC, Phenylene, Indenyl, Fluorenyl, Cp;
Imino, Pyridylene, Amino; Alkoxy, Aryloxy
R = Alkyl, Aryl
M = Ti, Zr, Hf

This review summarizes the progress in the synthesis and catalytic activity of group 4 NHC-metal complexes.