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Review

Group 4 ketimide complexes: Synthesis, reactivity and catalytic applications

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Contents

Abstract

The synthesis and reactivity of Group 4 ketimide complexes, comprising bent-metallocene, half-sandwich and cyclopentadienyl-free compounds is described. Neutral compounds of general formulas $Cp'_2M(N{=}CR^1R^2)X$ and $Cp'_2M(N{=}CR^1R^2)_2$ have been prepared by transmetallation reactions of metal halide derivatives with appropriate lithium, tin or silicon ketimide derivatives and by acid–base reactions between ketimines and anionic ligands attached to the metals. Ti(III) and cationic M(IV) bent-metallocene complexes have been mainly prepared by nitrile insertion into metal–carbon or metal–hydride bonds of bis-Cp systems. Metallacyclic ketimide complexes are also described. These were obtained as a result of oxidative addition reactions, nitrile insertions and nitrile additions to unsaturated C–C bonds in bent-metallocene systems.

Half-sandwich and cyclopentadienyl-free complexes were prepared aiming at the synthesis of olefin polymerization catalyst precursors through transmetallation reactions. Titanium systems containing one Cp ring and one ketimide ligand in particular have proven to be highly active ethylene, propylene and 1-hexene homopolymerization catalysts when activated by MAO. The activities reported in styrene homopolymerization are slightly lower although $Cp^*Ti(N{=}C^tBu_2)Cl_2$ catalyses living styrene/ethylene copolymerization. This emerging role of ketimide ligands as ancillary ligands in the reactivity of early transition metals is quite recent and comes from their inertness towards insertion of unsaturated substrates in M–N bonds and electrophile attack.

Keywords: Titanium; Zirconium; Ketimide complexes; Olefin polymerization; Catalysis

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1. Introduction

Ketimide ligands[1] (R_2CN^-) are unsaturated, monoanionic ligands with a C–N double bond. The negative charge is centred

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[1] Ketimide ligands are also known as methyleneamido, alkylideneamido, azomethine, azaalkenylidene or azavinylidene ligands.

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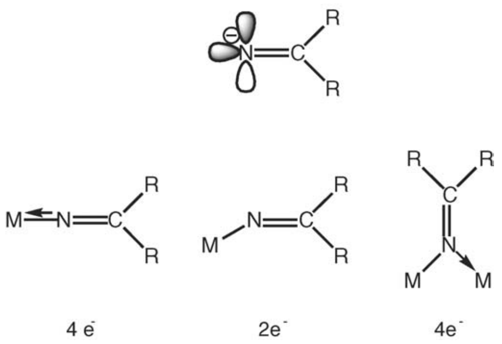


Chart 1.

on the nitrogen atom that has two orbitals available for bonding. The ketimide moiety is thus capable of donating two or four electrons to a metal centre, depending on its bonding mode, as depicted below (Chart 1).

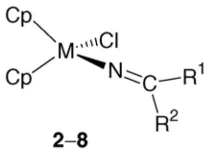
The terminal linear arrangement is the most common bonding mode in d^0 Group 4 metal complexes and it is, in general, frequently observed in transition metal derivatives. In this bonding mode, nitrogen hybridisation is *sp* and thus the M–N–C angles are close to 180°.

The first ketimide complexes were obtained while studying the reduction of nitriles with magnesium or aluminium alkyl compounds to afford ketimines [1–4], amines [5,6], aldehydes [5,7,8] and ketones [9,10]. These reactions are well known since the 1950's and although some authors inferred then that ketimide metal complexes were the intermediates in these reactions, it was not until the 1960's that metal and metalloid ketimide complexes started to be isolated and characterized [11–14]. These initial studies were extended by Lappert and co-workers to transition metals, including those of Group 4 [15,16]. Since then, many Group 4 ketimide complexes were obtained, most of them in the course of bent-metallocene systems studies. Half-sandwich and cyclopentadienyl-free ketimide-supported compounds have also been reported.

The ketimide moiety in Group 4 metal compounds is relatively robust. The terminal linear arrangement limits the reactivity of the nitrogen towards electrophiles and the ligands are also inert to insertion reactions when compared to vinylidene ligands, their carbon-based analogues. In aqueous acidic media, however, they afford the corresponding ketimine or ketone. Recently, advantage of the inertness of these ligands has been taken by using them as ancillary ligands in olefin polymerization catalysis [17]. Following the trend that has marked Group 4 metal chemistry for the last decades [18,19], in which nitrogen- and oxygen-based ligands have been replacing one or both Cp ligands of metallocenes, Group 4 ketimide complexes have proven to be active olefin homo- and co-polymerization catalysts.

2. Group 4 ketimide complexes

Group 4 ketimide complexes have been obtained as the result of several reactions as listed below (A–G). Methods A and B have been used with the purpose of synthesising ketimide complexes. The other pathways led to ketimide complexes as a result of nitrile insertion or coupling and oxidative addition reactions.



2–8

	Ref.
2 M = Ti, $R^1 = R^2 = Ph$	[15]
3 M = Ti, $R^1 = R^2 = p\text{–}MeC_6H_4$	[15]
4 M = Ti, $R^1 = R^2 = {}^tBu$	[15]
5 M = Ti, $R^1 = Ph$, $R^2 = Me$	[15]
6 M = Zr, $R^1 = R^2 = Ph$	[15]
7 M = Zr, $R^1 = R^2 = {}^tBu$	[15]
8 M = Zr, $R^1 = {}^tBu$, $R^2 = Me$	[21]

Chart 2.

(A) Transmetallation reactions involving Group 4 metal halide derivatives and the appropriate lithium, tin or silicon ketimide derivatives.
(B) Acid–base reactions involving the appropriate ketimine and anionic ligands attached to the Group 4 metal.
(C) Hydrozirconation of nitriles.
(D) Oxidative addition reactions.
(E) Insertion of nitriles in M–C bonds.
(F) Nitrile coupling reactions.
(G) Nitrile addition to unsaturated C–C bonds.

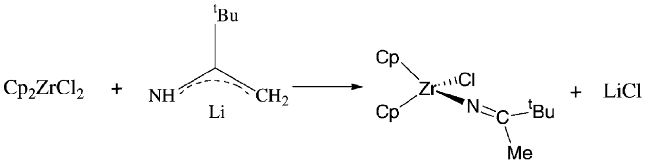
2.1. Bent-metallocene derivatives

2.1.1. $Cp'_2M(N{=}CR^1R^2)X$ compounds

Transmetallation reactions involving Group 4 metal halides and main group ketimides (Method A), especially lithium ketimides, are the most straightforward synthetic route to ketimide complexes. It is therefore not surprising that the first Group 4 ketimide compound, $Cp_2Ti[N{=}C(CF_3)_2]Cl$, **1**, was obtained by reaction between Cp_2TiCl_2 and $LiN{=}C(CF_3)_2$ [16] or $Me_3SnN{=}C(CF_3)_2$ [20]. Other complexes of the type $Cp'_2M(N{=}CR^1R^2)Cl$ prepared by metathesis reactions with lithium ketimides are described below. Compound **2** was also obtained by reaction with $Me_3SiN{=}CPh_2$ [15] (Chart 2).

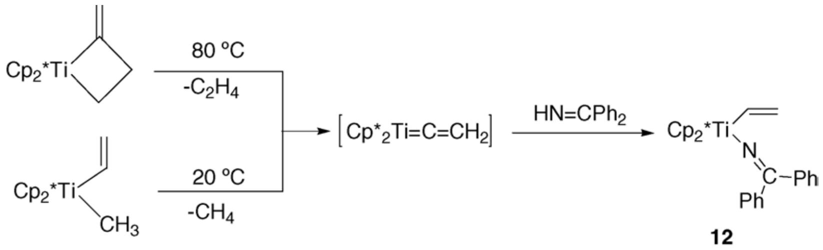
Complexes **1–8** were all obtained in good yield, with the exception of **5**, probably because the in situ generation of LiN=C(Ph)(Me) from LiMe and benzonitrile is not a suitable reaction once it is known that treatment of nitriles with LiMe does not afford the corresponding lithium ketimides in a significant extent [22].

The analogous $Cp_2Zr[N{=}C({}^tBu)(CH_3)]Cl$, **9** [23], was prepared by reaction of Cp_2ZrCl_2 with a lithium azaallyl derivative, $LiCH_2C({}^tBu)NH$, that undergoes 1,3-sigmatropic rearrangement to afford the ketimide derivative (Eq. (1)).



9 (1)

Methyl derivatives of **8** and **9**, $Cp_2Zr[N{=}C({}^tBu)(Ph)]Me$, **10** [21], and $Cp_2Zr[N{=}C({}^tBu)(CH_3)]Me$, **11** [23], were obtained by treating the parent chlorides with LiMe.

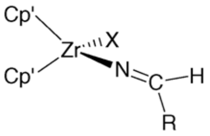


Scheme 1.

A different synthetic approach was followed in the synthesis of $Cp^*_2Ti(CH{=}CH_2)(N{=}CPh_2)$, **12** [24]. This complex was prepared by the acid–base reaction of $HN{=}CPh_2$ with the allene complex $Cp^*_2Ti({=}C{=}CH_2)$ (Method B) that was prepared in situ by thermal decomposition, as depicted in Scheme 1. The X-ray structure of **12** shows that the ketimide ligand occupies the plane that bisects the Cp(cent)–M–Cp(cent) angle and displays approximately a linear M–N–C angle, allowing, in this way, the overlap of the nitrogen π-donor orbitals with the LUMO of the bent-metallocene fragment.

Nitriles insert in Zr–H bonds to afford zirconium ketimide complexes (Method C). Compounds $Cp'_2Zr[N{=}C(H)(R)]Cl$ (**13–15**) were thus obtained by insertion of N≡CR in the Zr–H bond of Cp_2ZrHCl [25,26]. Complex **15** was characterized by single crystal X-ray diffraction and displays essentially the same structural features referred above for **12**. The hydrogen of the ketimide and the chloride attached to zirconium are *cis*, as commonly found in hydrozirconation reactions [27]. Alkylation of **15** with LiC_6H_4–*p*-Me affords $Cp_2Zr[N{=}C(H)(CH_2Ph)](p\text{-}MeC_6H_4)$, **16**. Hydrozirconation also led to $Cp^*_2ZrH\{N{=}C(H)(p\text{-}MeC_6H_4)\}$, **17**, obtained by reaction of $p\text{-}MeC_6H_4CN$ with $(Cp_2ZrH_2)_x$. Reaction of this compound with CH_3I gave $Cp^*_2ZrI\{N{=}C(H)(p\text{-}MeC_6H_4)\}$, **18** [28] (Chart 3).

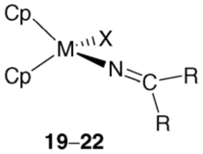
$Cp_2Ti(OSiMe_3)(N{=}CR_1R_2)$ ($R_1R_2 = Me_2$, **19**; $R_1R_2 = (CH_2)_5$, **20**), were obtained by oxidative addition (Method D) when $Cp_2Ti(Me_2SiC{\equiv}CSiMe_3)$ was treated with $R_2C{=}NOSiMe_3$. The structure of **20** was confirmed by single crystal X-ray diffraction. In this case, the Ti–N–C bond is slightly bent (165.5(2)°), possibly due to steric reasons [29]. Similarly, $Cp_2Ti(Me_2SiC{\equiv}CSiMe_3)$ and $Cp_2Zr(py)(Me_2SiC{\equiv}CSiMe_3)$ react with two equivalents of $HN{=}CPh_2$ to afford $Cp_2Ti(N{=}CPh_2)(HNCHPh_2)$, **21**, and $Cp_2Zr(N{=}CPh_2)(HNCHPh_2)$, **22**, respectively. The molecular structures of **21** and **22** show that the compounds are isostructural. The ketimide ligand is close to linear and the $-NH-CHPh_2$ fragment displays typical bonding parameters for amido ligands [30] (Chart 4).



13–18

13 Cp' = Cp, R = CH_3, X = Cl
14 Cp' = Cp, R = Ph, X = Cl
15 Cp' = Cp, R = CH_2Ph, X = Cl
16 Cp' = Cp, R = CH_2Ph, X = p-MeC_6H_4
17 Cp' = Cp*, R = p–MeC_6H_4, X = H
18 Cp' = Cp*, R = p–MeC_6H_4, X = I

Chart 3.



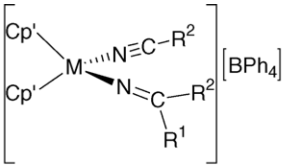
19–22

19 M = Ti, R = Me, X = $OSiMe_3$
20 M = Ti, RR = $(CH_2)_5$, X = $OSiMe_3$
21 M = Ti, R = Ph, X = $HNCHPh_2$
22 M = Zr, R = Ph, X = $HNCHPh_2$

Chart 4.

2.1.2. *$[Cp'_2M\{N{=}CR^1R^2\}(N{\equiv}CR)]^+$ compounds*

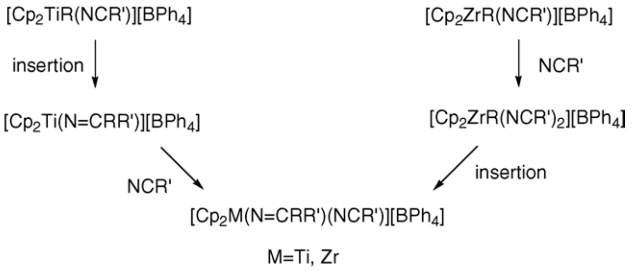
Insertion reactions of nitriles in M–C bonds of cationic titanocene and zirconocene complexes constituted a model for olefin insertion in M–C bonds. These reactions led to the synthesis of ketimide compounds of the type $[Cp'_2M\{N{=}CR^1R^2\}(N{\equiv}CR^2)][BPh_4]$ (**23–34**) (Method E) except when $Me_3SiC{\equiv}N$ is used [31–33]. In this case, the insertion reaction does not lead to a ketimide ligand but to an η^2-iminoacyl group because $Me_3SiC{\equiv}N$ exists in equilibrium with the corresponding isonitrile $Me_3SiN{\equiv}C$, which replaces the original nitrile and preferentially inserts into the metal–carbon bond, leading to $[Cp_2Ti(CNSiMe_3)\{\eta^2\text{-}C(Me){=}NSiMe_3\}][BPh_4]$ [31] (Chart 5).



23–34, 37, 38

	Ref.
23 M = Ti, Cp' = Ind, R^1 = Me, R^2 = ^tBu	[31,32]
24 M = Ti, Cp' = Ind, R^1 = Me, R^2 = Ph	[31,32]
25 M = Ti, Cp' = Cp, R^1 = Me, R^2 = Me	[31]
26 M = Ti, Cp' = Cp, R^1 = Me, R^2 = Ph	[31]
27 M = Ti, Cp' = Cp, R^1 = Me, R^2 = ^tBu	[31]
28 M = Ti, Cp' = Cp, R^1 = Me, R^2 = ^nPr	[31]
29 M = Ti, Cp' = Ind, R^1 = Me, R^2 = Me	[31]
30 M = Ti, Cp'_2 = CpCp*, R^1 = Me, R^2 = Ph	[31]
31 M = Zr, Cp' = Cp, R^1 = Ph, R^2 = Me	[33]
32 M = Zr, Cp' = MeC_5H_4, R^1 = Ph, R^2 = Me	[33]
33 M = Zr, Cp' = Cp, R^1 = Me, R^2 = Me	[33]
34 M = Zr, Cp' = MeC_5H_4, R^1 = Me, R^2 = Me	[33]
37 M = Zr, Cp' = Cp, R^1 = 2-CH_2,5-CH_3py, R^2 = Me	[34]
38 M = Zr, Cp' = Cp, R^1 = H, R^2 = CD_3	[35]

Chart 5.



Scheme 2.

It has been noted that the Cp ring influences the ease of these reactions. In the systems above, indenyl compounds afford the fastest reactions, with the insertion being complete in less than 1 h, while Cp compounds can take several days for the reaction to reach completion. Kinetic studies on the formation of **24–34** reveal that the mechanism of the insertion reactions depends on the metal center (Scheme 2). In the case of titanium, the migration of methyl to the coordinated nitrile occurs prior to the coordination of the new entering nitrile ligand, as attested by the fact that insertion rates are independent of nitrile concentration. On the other hand, the reactions mediated by zirconium require the previous coordination of nitrile and formation of 5-coordinate, 18 electron reactants where insertion takes place. The different mechanisms are primarily due to the difference in ionic radius of Ti(IV) and Zr(IV).

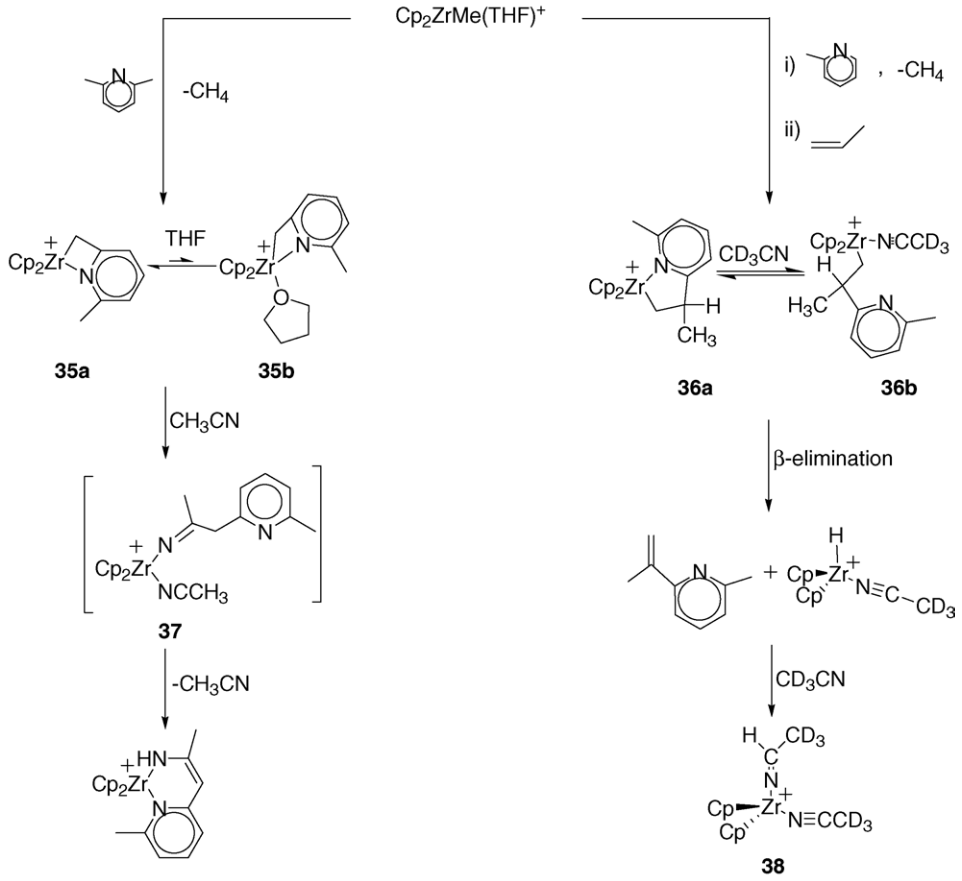
Scheme 3 depicts sequences of reactions that lead to the formation of the cationic zirconocene ketimide complexes, **37** and **38**. The ketimide ligand in **37** forms by insertion of acetonitrile in a zirconium–carbon bond of **35**, formed upon the activation of an α carbon–hydrogen bond of 2,6-lutidine, whereas **38** results from the insertion of acetonitrile in a zirconium–hydride bond, formed by H_β elimination in **36**. The driving force for these reactions is the formation of methane from the original methyl ligand of $[Cp_2Zr(Me)(THF)]^+$ and the acidic hydrogen atoms of coordinated 2,6-lutidine and α-picoline. The lack of H_β in cationic **35** is responsible for the difference in reactivity [34–36].

When treated with $B(C_6F_5)$, $Cp_2Zr[N{=}C(^tBu)(Me)]Me$, **11**, afforded the cationic complex $[Cp_2Zr\{N{=}C(^tBu)(CH_3)\}][MeB(C_6F_5)_3]$, **39**, that was characterized by NMR as an ion pair [23]. The lack of ketimide to azaallyl isomerization in **39** attests for the greater stability of the ketimide ligand, as implied by the reaction depicted in Eq. (1).

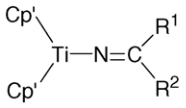
2.1.3. $Cp'_2Ti(N{=}CR^1R^2)$ compounds

Reported Ti(III) bent-metallocene complexes containing one ketimide ligand of the type $Cp'_2Ti(N{=}CR^1R^2)$ (**40–44**) are depicted below (Chart 6).

Compounds **40** and **41** were the first Ti(III) ketimide compounds to be obtained and were synthesized by insertion of acetonitrile in a titanium-allyl group bonded to a $Cp_2Ti(III)$ moiety (Method E). Although not isolated, their formation was



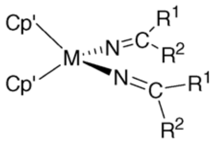
Scheme 3.



40–44

	Ref.
40 $Cp' = Cp$, $R^1 = Me$, $R^2 = CH_2CH{=}CH_2$	[37]
41 $Cp' = Cp$, $R^1 = Me$, $R^2 = CH(Me)CH{=}CH_2$	[37]
42 $Cp' = Cp^*$, $R^1 = R^2 = Ph$	[38]
43 $Cp' = Cp^*$, $R^1 = R^2 = Me$	[39]
44 $Cp' = Cp$, $R^1 = Me$, $R^2 = CH_2CH{=}CH_2$	[40]

Chart 6.

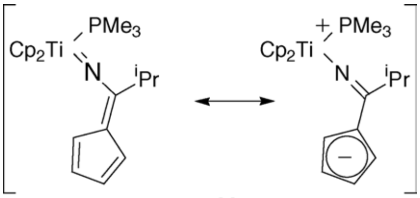


47–51

	Ref.
47 $M = Zr$, $Cp' = Cp$, $R^1 = R^2 = Ph$	[15,42]
48 $M = Zr$, $Cp' = Cp$, $R^1 = R^2 = p{-}MeC_6H_4$	[43]
49 $M = Hf$, $Cp' = Cp$, $R^1 = R^2 = Ph$	[15]
50 $M = Zr$, $Cp' = Cp^*$, $R^1 = H$, $R^2 = p{-}MeC_6H_4$	[28]
51 $M = Ti$, $Cp' = Cp$, $R^1 = R^2 = CF_3$	[15]

Chart 8.

inferred by the hydrolysis products that afforded the corresponding ketones [37]. $Cp^*_2Ti(N{=}CPh_2)$, **42**, was obtained by reaction of Cp^*_2TiCl with one equivalent of lithium ketimide (Method A). Like the two previous compounds, **42** was not isolated but detected by infrared and its structure inferred by the subsequent reaction with $AgBPh_4$ in the presence of traces of water that afforded $[Cp^*_2Ti(OH)(HN{=}CPh_2)]BPh_4$ [38]. $Cp^*_2Ti(N{=}CMe_2)$, **43**, was obtained by reaction of $Cp^*_2Ti(Me_2SiC{\equiv}CSiMe_3)$ with $Me_2C{=}N{-}N{=}CMe_2$. The X-ray structure of **43** shows the ketimide ligand close to linearity and bisecting the angle defined by both Cp^* rings [39]. It is important to note that in titanium systems the outcome of the reaction of $Me_2C{=}N{-}N{=}CMe_2$ with reduced titanium centers depends on the substituents of the Cp rings. While Cp^* affords the Ti(III) ketimide compound by a mechanism not fully understood, less substituted Cp rings led to a different outcome for the reaction, with products resulting from C–H activation of a cyclopentadienyl methyl or the formation of a methyl azine group [39]. $Cp_2Ti\{N{=}C(^iPr)(C_5H_4)\}(PMe_3)$, **44**, was obtained by thermal decomposition of the imido compound $Cp_2Ti\{{=}NCH_2C(^iPr){=}C(Me)C(Me){=}CH_2\}(PMe_3)$ that was in turn obtained by vinyl insertion of ^iPrCN in $[Cp_2Ti\{\kappa^2 C,C{-}C(Me){=}C(Me)CH_2\}]$ in the presence of an excess of PMe_3 (the insertion of nitriles in metallacycles containing both sp^2 and sp^3 metal–carbon bonds is discussed in Section 2.1.5). The molecular structure of **44** shows two molecules in the unit cell, one with a Ti–N–C angle of 172.6(9)° and other with an angle of 162.7(9)°. This latter value is rather abnormal for terminal ketimide complexes, and may be explained by the existence of two different but both significant canonical forms (see below). The zwitterionic structure depicted is consistent with near equivalence of bond lengths in the fulvene ring [40] (Chart 7).



44

Chart 7.

Closely related in structure are the titanium(IV) carborane complexes containing one ketimide ligand. $Cp^*(\eta^5{-}C_2B_9H_{11})TiMe$ reacts with acetonitrile to afford $Cp^*(\eta^5{-}C_2B_9H_{11})Ti(N{=}CMe_2)(N{\equiv}CCH_3)$, **45** (Method E). Crystallization from toluene afforded $Cp^*(\eta^5\text{-}C_2B_9H_{11})Ti(N{=}CMe_2)$, **46**. The X-ray structures of these compounds show that they both adopt a bent-metallocene type structure with the ketimide ligand close to linearity. In **45**, the ketimide and acetonitrile ligands lie in the equatorial plane between the η^5 ligands, as well as the ketimide ligand in **46** [41].

2.1.4. $Cp'_2(N{=}CR^1R^2)_2$ compounds

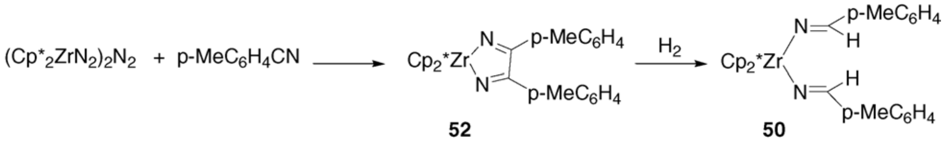
Compounds of the type $Cp_2M(N{=}CR^1R^2)_2$ (M = Zr, Hf) have been isolated and are presented below. The synthesis of similar titanium derivatives is hampered, possibly by steric reasons. However, reference to the formation of $Cp_2Ti\{N{=}C(CF_3)_2\}_2$, **51**, has been done as unpublished work [15] (Chart 8).

Compounds **47** and **48** were synthesized by metathesis of the parent chloride with the corresponding lithium ketimide (Method A) whereas **49** was obtained by reaction of $HN{=}CPh_2$ with $Cp_2Hf(NEt_2)_2$ (Method B). The same method afforded a milder synthesis of **47** [15,42,43]. The complex was characterized by single crystal X-ray diffraction that shows one ketimide ligand slightly bent (164.1(2)°) versus the other (173.7(2)°). This feature reflects the partial donation of electron density from one of the $N{=}CPh_2$ ligands to the metal centre, which may accept a maximum of 6 from the total of 8 electrons made available by the two ketimide ligands.

$[Cp^*_2Zr\{N{=}C(H)(p\text{-}MeC_6H_4)\}_2]$, **50**, was synthesized as depicted in Scheme 4 by reaction of hydrogen with the zirconacyclodiimine $[Cp^*_2\ Cp_2Zr\{\kappa^2 N,N{-}N{=}C(p\text{-}MeC_6H_4)C(p\text{-}MeC_6H_4){=}N)\}]$, **52**, obtained by reaction of $(Cp^*_2ZrN_2)_2N_2$ with $p\text{-}MeC_6H_4CN$ [28].

2.1.5. Metallacyclic compounds

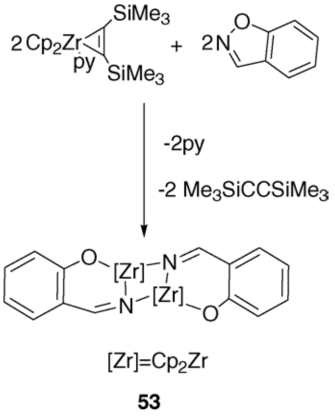
Compound **52**, obtained by reductive coupling of two nitriles (Method F), is one example of metallacyclic ketimide complexes. There are many compounds of this type that result from oxidative addition reactions (Method D), nitrile insertion in M–C bonds (Method E) or addition of nitriles to unsaturated C–C bonds (Method G). Many of these compounds were



Scheme 4.

detected by NMR but were not isolated since they readily tautomerize to enamines.

Oxidative addition of the N–O bond of benzoxazole to $Cp_2Zr(py)(Me_2SiC{\equiv}CSiMe_3)$ afforded the bimetallic complex $[Cp_2Zr\{\kappa^2 N,O{-}N{=}C(H){-}o{-}C_6H_4{-}O\}]_2$, **53** (Eq. (2)) that displays two bridging ketimide moieties [44]. The analogous reaction with $Cp_2Ti(Me_2SiC{\equiv}CSiMe_3)$ fails.

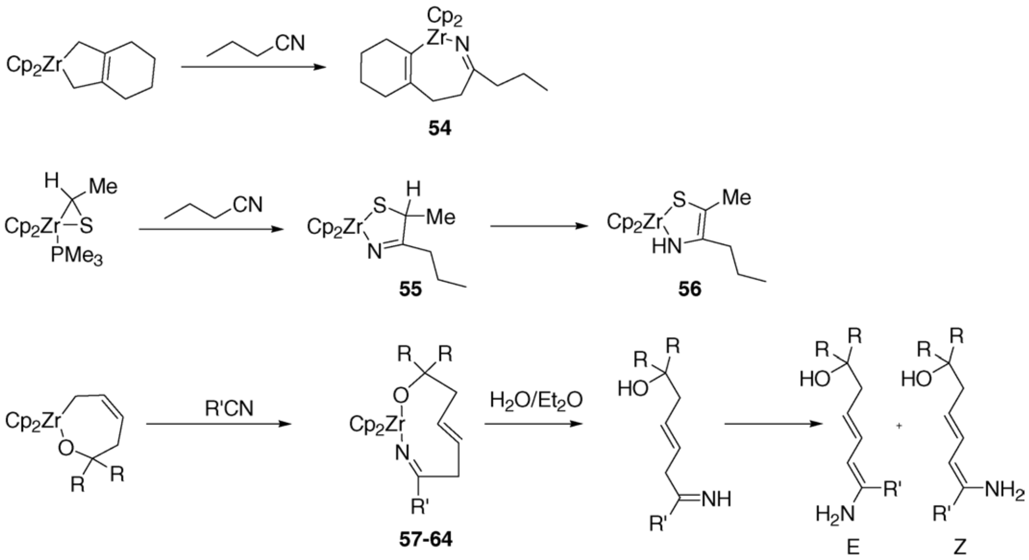


(2)

Nitrile insertion into M–C bonds of carbon- and heterometallacyclic alkyl complexes afford metallacyclic ketimide complexes with concomitant ring expansion by two members. As represented in Scheme 5, complexes $[Cp_2Zr\{\kappa^2 N,C{-}N{=}C({}^nPr)CH_2CH_2{-}o{-}C_6H_8\}]$, **54** [45], $[Cp_2Zr\{\kappa^2 N,S{-}N{=}C({}^nPr)CH(Me)S\}]$, **55** [36], and $[Cp_2Zr\{\kappa^2 N,O{-}OCR_2CH_2CH{=}CHCH_2C(R'){=}N\}]$, **57–64** [46], have been prepared.

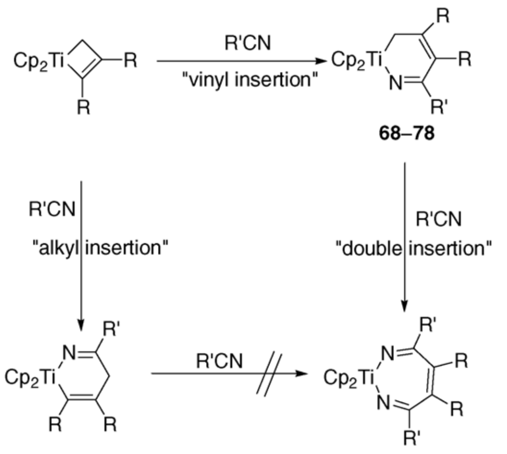
When ketimide moieties are part of a metallacycle containing γ-hydrogen atoms tautomerization to enamines is frequently observed, as exemplified by the formation of **56**. The hydrolysis of **57–64** afforded the corresponding ketimines that then rearrange to enamines obtained as mixtures of E and Z isomers [46].

Doxsee and Mouser studied the reactivity of $[Cp_2Ti\{\kappa^2 C,C{-}C(R){=}C(R)CH_2\}]$ (R = Me, Et, Ph) with nitriles and showed that when metal–vinyl and metal–alkyl bonds are present in titanocene metallacycles, the preferential site for insertion and the number of nitrile molecules inserted depends both on the vinylic substituents and on the nitrile (Scheme 6). For R = Me, Et or ${}^iPrCN$ double insertion occurs and compounds $[Cp_2Ti\{\kappa^2 N,N{-}N{=}C({}^iPr){-}C(R){=}C(R)C({}^iPr){=}N\}]$ (R = Me, **65**; R = Et, **66**) form [47], whereas (mesityl)CN reacts with $[Cp_2Ti\{\kappa^2 C,C{-}C(Me){=}C(Me)CH_2\}]$ to afford exclusively $[Cp_2Ti\{\kappa^2 N,C{-}N{=}C(mesityl){-}CH_2{-}C(Me){=}C(Me)\}]$, **67** [40]. The molecular structure of **67** shows that the Ti–N–C angle is only 143.5(3)°. This value, more consistent with sp^2 rather than sp nitrogen hybridization, is most probably due to the strain caused by the metallacyclic arrangement. For R = Ph, insertion occurs exclusively in the metal–alkyl bond regardless of the nitrile and therefore compounds of the type $[Cp_2Ti\{\kappa^2 N,C{-}N{=}C(R){-}CH_2{-}C(Ph){=}C(Ph)\}]$ **68–78** are obtained. $[Cp_2Ti\{\kappa^2 C,C{-}$



57 R = Ph, R' = p–MeC$_6$H$_4$
58 R = Ph, R' = Ph
59 R = Ph, R' = p–CNC$_6$H$_4$
60 R = Ph, R' = CH=CHCN
61 R = Ph, R' = ^{t}Bu
62 R = CH$_2$CH$_2$, R' = Ph
63 R = CH$_2$CH$_2$, R' = ^{t}Bu
64 R = Me, R' = Ph

Scheme 5.



68 R = Ph, R' = Me
69 R = Ph, R' = Et
70 R = Ph, R' = ^{i}Pr
71 R = Ph, R' = ^{t}Bu
72 R = Ph, R' = Ph
73 R = Ph, R' = p–FC$_6$H$_4$
74 R = Ph, R' = p–CH$_3$OC$_6$H$_4$
75 R = Ph, R' = p–CH$_3$C$_6$H$_4$
76 R = Ph, R' = o–CH$_3$C$_6$H$_4$
77 R = Ph, R' = p–CF$_3$C$_6$H$_4$
78 R = Ph, R' = C$_6$F$_5$

67 R = Me, R' = mesityl
79 R = Et, R' = ^{t}Bu
80 R = Me, R' = ^{t}Bu

65 R = Me, R' = ^{i}Pr
66 R = Et, R' = ^{i}Pr
81 R = Me, R' = ^{t}Bu

Scheme 6.

C(R)=C(R)CH$_2$}] reacts with ^{t}BuCN to afford [Cp$_2$Ti{κ^2*N*,*C*–N=C(^{t}Bu)–CH$_2$–C(R)=C(R)}], **79**, (R = Et) and a mixture of [Cp$_2$Ti{κ^2*N*,*C*–N=C(^{t}Bu)–CH$_2$–C(R)=C(R)}], **80**, and [Cp$_2$Ti{κ^2*N*,*N*–N=C(^{t}Bu)–C(R)=C(R)C(^{t}Bu)=N}], **81**, when R = Me. Attempts to obtain **81** by forcing the insertion in **80** have failed, which suggests that double insertion occurs only when the initial insertion takes place at the metal–vinyl bond (Scheme 6) [47].

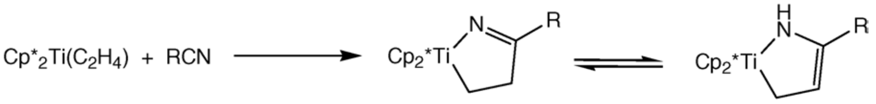
Addition of nitriles to unsaturated C–C bonds (Method G) is also an important route to metallacyclic ketimide complexes. Complexes [Cp$^*_2$Ti{κ^2*N*,*C*–N=C(R)CH$_2$CH$_2$}] (R = Me, **82**; R = Et, **83**; R = ^{t}Bu, **84**; R = *p*-MeC$_6$H$_4$, **85**) were prepared by addition of the corresponding nitrile to Cp$^*_2$Ti(C$_2$H$_4$). Tautomerization to the corresponding enamine depends on the nitrile, being fast for **82**, very slow for **83** and unobserved for **84** and **85** (Scheme 7) [48].

Similarly, addition of nitriles to zirconocene C≡C bonds led to [Cp$_2$Zr{κ^2*N*,*C*–N=C(^{n}Pr)–o–C$_6$H$_8$}], **86**, and to [Cp$_2$Zr{κ^2*N*,*C*–N=C(R)–o–C$_6$H$_4$}] (**87–94**) as depicted in Scheme 8. The X-ray structure of **94** shows it to be a dimer, with the ketimide moieties bridging the two zirconium centres, in a similar arrangement to the one found in **53**. The Zr–N–C angles are close to 120°, due to ring strain. Hydrolysis of these compounds affords the corresponding ketones, with the exception of **87** that affords a keto-alcohol, **89** that gives HN=CPh$_2$ as the major product (benzophenone is co-produced, but in a smaller extent) and **93**, which hydrolysis product is a diketone [45,49].

Cp$_2$Zr(RC≡CR′)PMe$_3$ also reacts with nitriles (R″CN) to afford compounds of the type [Cp$_2$Zr{κ^2*N*,*C*–N=C(R″)CRCR′}] (R = R′ = Et, R″ = Ph, **95**; R = H, R′ = ^{n}Bu; R″ = ^{t}Bu, **96**). The synthesis of **96** shows preferential addition to the less hindered carbon [50].

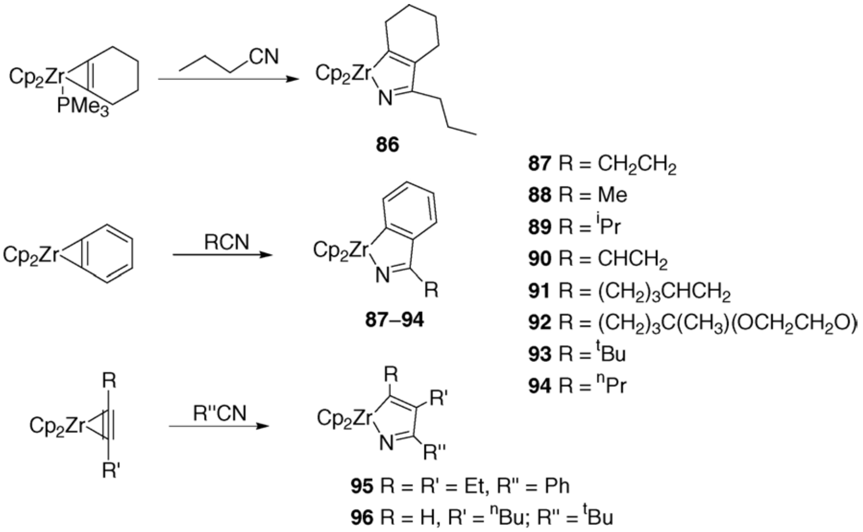
[2 + 2] addition of nitriles to [Cp$_2$Ti=CH$_2$] was shown to be a suitable pathway to the synthesis of azametallacycles (**97–109**). The titanium methylidene is assumed to be generated in situ by decomposition of titanacyclobutane [Cp$_2$Ti{κ^2*C*,*C*–CH$_2$C(^{t}Bu)CH$_2$}], dimethyl titanocene or Tebbe's reagent (Scheme 9). The number of nitriles inserted depends strongly on the nitrile: electron-withdrawing nitriles give stable 1:1 products that slowly convert to 2:1 products, whereas electronically rich nitriles favour the formation of 2:1 products. Compounds of the type [Cp$_2$Ti{κ^2*N*,*N*–N=C(R)CH$_2$C(R)=N}] (**101–108**) are unstable and tautomerize to [Cp$_2$Ti{κ^2*N*,*N*–N=C(R)CH=C(R)–NH}] [51–54]. When R = 1-adamantyl, **109**, no tautomerization takes place [53].

In the presence of PMe$_3$, metallacycles of the type of **97–100** afford imido compounds of the type [Cp$_2$Ti{=NC(=CH$_2$)R}(PMe$_3$)] (Scheme 10). These vinylimido complexes



82 R = Me
83 R = Et
84 R = ^{t}Bu
85 R = p–MeC$_6$H$_4$

Scheme 7.



Scheme 8.

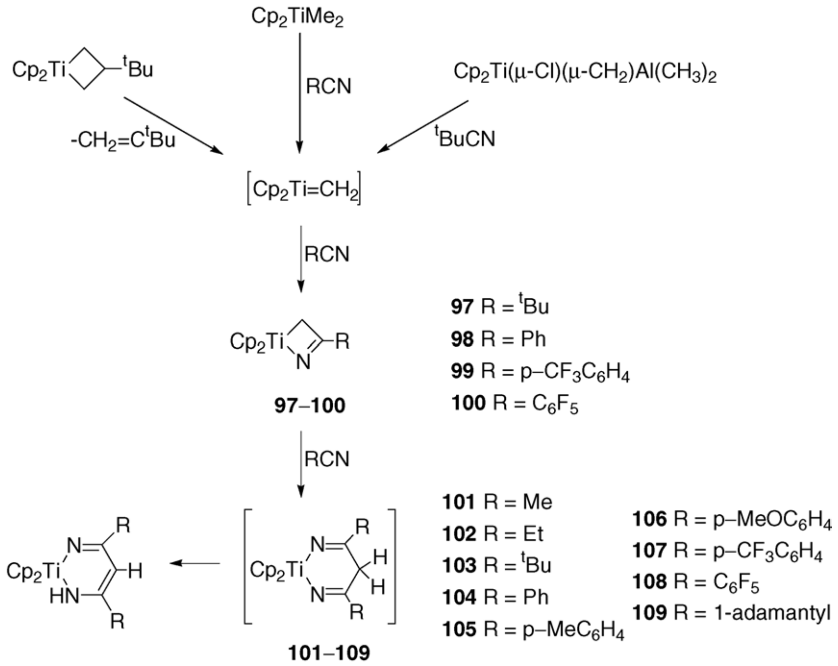
react with unsaturated organic substrates as ketones and imines to afford formal [4 + 2] adducts (**110–113**).

Zirconium compounds of the type $Cp_2Zr\{\kappa^2 N,C\text{–}N{=}C(R)\text{–}C(CH_2)C\}$ (**114–117**), have also been obtained by [2 + 2] cycloaddition of nitriles to $[Cp_2Zr(\kappa^2 C,C\text{–}CH{=}CHCH_2)]$, generated in situ (Scheme 11) [45].

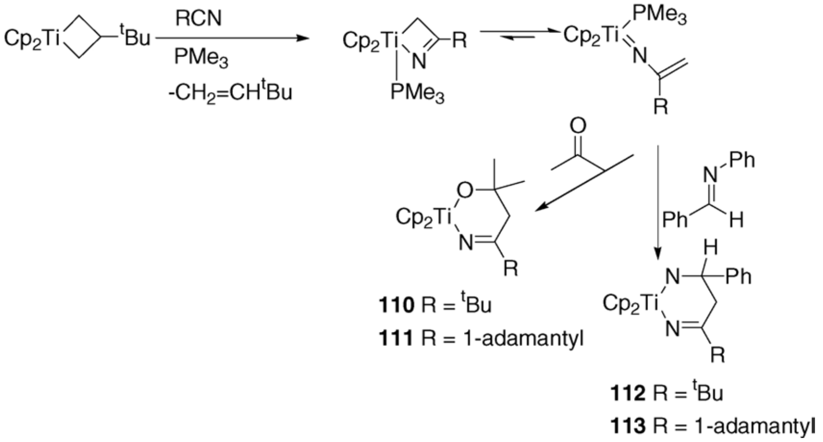
2.1.6. Bimetallic compounds containing bridging ketimide ligands

As described above, most Group 4 metal ketimide compounds have terminal ligands, the exceptions being the metallacyclic complexes **53** and **94** that have bridging ketimide moieties. In non-metallacyclic compounds, there are other examples of bridging ketimide ligands. Reactions of $Cp_2Zr[N{=}C(H)(CH_3)]Cl$, **13** and $Cp_2Zr[N{=}C(H)(Ph)]Cl$, **14** with $(Cp_2MH_2)_x$ (M = Zr, Hf) afford bimetallic compounds $Cp_2Zr[\mu\text{-}N{=}C(H)(R)](\mu\text{-}Cl)MCp_2$ (**118–120**), by dihydrogen reductive elimination from **a** (Scheme 12). The reductive elimination of aldimine via intermediate **b** is not observed since it is an unfavourable thermodynamic route [26].

The concept was extended to "early–late" heterobimetallic compounds with the synthesis of $Cp_2Ti[\mu\text{-}N{=}C(H)Ph]_2CoCp$, **121**, obtained by reaction of $[Cp_2Ti\{\kappa^2 N,N\text{–}C(H)(Ph)N\text{–}N{=}C(H)Ph\}]_2$, with $CpCo(C_2H_4)_2$. As shown in Scheme 13, the reaction proceeds via C–C and N–N cleavage. The molecular structure of **121** reveals Ti–N–C angles of about 148° possibly due to the steric hindrance between the phenyl and the Cp rings. Due to the donation of the nitrogen lone

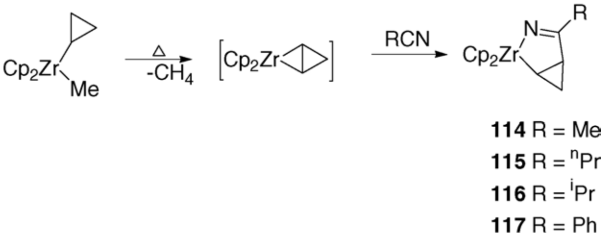


Scheme 9.



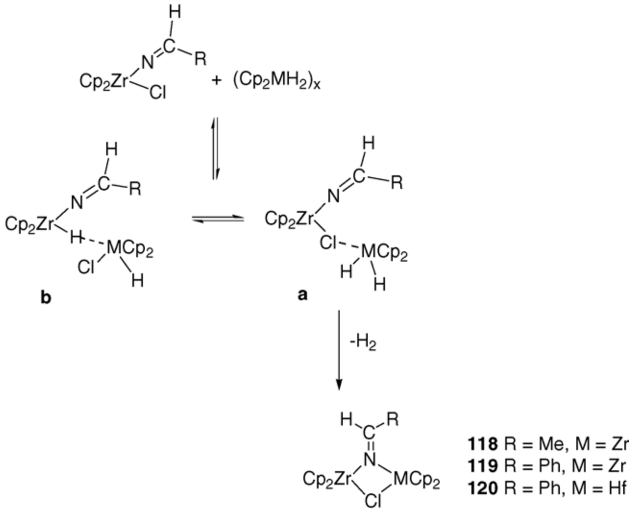
110 R = ^{t}Bu
111 R = 1-adamantyl
112 R = ^{t}Bu
113 R = 1-adamantyl

Scheme 10.



114 R = Me
115 R = ^{n}Pr
116 R = ^{i}Pr
117 R = Ph

Scheme 11.



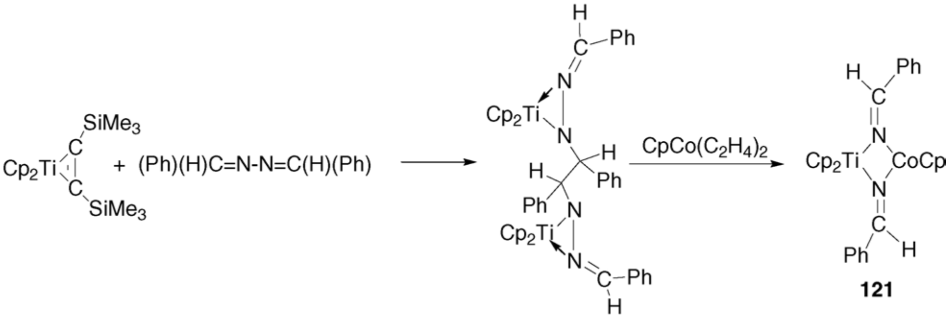
118 R = Me, M = Zr
119 R = Ph, M = Zr
120 R = Ph, M = Hf

Scheme 12.

pair to cobalt, the Ti–N bonds are unusually long for titanium ketimide complexes (about 2.0 Å) and are longer than the Co–N bonds (about 1.85 Å), which is consistent with the difference in metal radius [55]. Osakada and co-workers also reported the synthesis of $Cp_2Zr[\mu\text{-}N{=}CR_2]_2Pd(Me)Cl$ (R = Ph, **122**; R = p-MeC_6H_4, **123**), by reaction of $Cp_2Zr[N{=}CR_2]_2$ (R = Ph, **47**; R = p-MeC_6H_4, **48**) with (cod)PdCl(Me) through simple replacement of cod in the palladium coordination sphere. The molecular structures of **122** and **123** show the two bridging ketimide ligands bent at around 147°, and the Zr–N bonds slightly elongated (about 2.2 Å). As in **121**, the Zr–N distance is longer than the Pd–N distance (about 2.1 Å) [43].

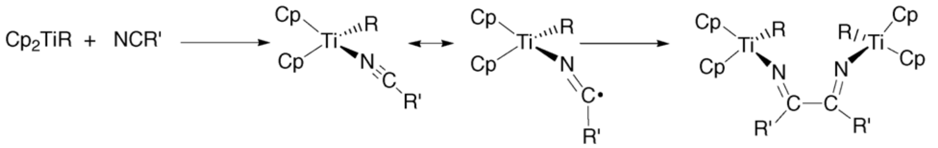
A different type of bimetallic complexes was described by Teuben et al. that report a series of bimetallic titanocene complexes of the type $Cp_2Ti(R)N{=}C(R')–C(R')NTi(R)Cp_2$ (**124–140**). The compounds were obtained from the coupling of two cyanide radicals that form upon transfer of the unpaired electron of Ti(III) to the ligand as represented in Scheme 14 (Method F). The amount of the bent canonical form depends on the extent of the metal–ligand backbonding and coupling proceeds as long as the R groups are not too bulky to prevent it by steric hindrance [56]. The overall reaction corresponds to the oxidation of titanium and reduction of the nitriles to imines.

Acidic hydrolysis of these compounds affords a synthetic route to *cis*-diketones or *cis*-diketimines. Compound **127** reacts with HCl in ether to afford PhC(=O)C(=O)Ph whereas



121

Scheme 13.



124–140

124 R = R' = Ph
125 R = Ph, R' = p–ClC_6H_4
126 R = Ph, R' = Me
127 R = o–$CH_3C_6H_4$, R' = Ph
128 R = R' = o–$CH_3C_6H_4$
129 R = o–$CH_3C_6H_4$, R' = p–ClC_6H_4
130 R = o–$CH_3C_6H_4$, R' = Me
131 R = m–$CH_3C_6H_4$, R' = Ph
132 R = m–$CH_3C_6H_4$, R' = o–$CH_3C_6H_4$
133 R = m–$CH_3C_6H_4$, R' = Me
134 R = p–$CH_3C_6H_4$, R' = Ph
135 R = p–$CH_3C_6H_4$, R' = o–$CH_3C_6H_4$
136 R = p–$CH_3C_6H_4$, R' = Me
137 R = CH_2Ph, R' = Ph
138 R = CH_2Ph, R' = o–$CH_3C_6H_4$
139 R = C_6F_5, R' = p–ClC_6H_4
140 R = Cl, R' = Ph

Scheme 14.

compound **128** affords only the diketimine o–$CH_3C_6H_4C$(=NH)C(=NH)C_6H_4–o–CH_3 that is stable towards further hydrolysis.

2.2. *Half-sandwich derivatives*

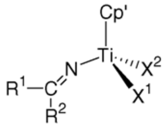
The first mono-Cp ketimide compound reported, CpTi[N=C(^{n}Bu)(^{t}Bu)]Cl_2, **141** [57], was obtained by reaction of $CpTiCl_3$ with the corresponding lithium ketimide. The X-ray structure of this compound shows that the ketimide ligand is essentially linear, with the ketimide substituents roughly parallel to the plane defined by the Cp ring. This arrangement simultaneously minimizes steric repulsion and maximizes electron donation to the metal centre, since it places the non-bonding *p* orbital of nitrogen directed towards the acceptor orbital parallel to the Cp ring plane of the $CpTiCl_2$ fragment.

No catalytic studies have been reported for **141** and it took over a decade for compounds of the type Cp′Ti[N=CR^1R^2]X^1X^2 to be recognized as extremely active catalysts in olefin polymerization catalysis. Since then, a significant number of compounds of this type were reported (see below) (Chart 9).

The dichlorides were obtained by reaction of Cp′$TiCl_3$ with one equivalent of the corresponding lithium ketimide (Method A). Alkylation of these complexes with lithium alkyls or Grignard reagents afforded the correspondent derivatives. Complex Cp*Ti[N=C^{t}Bu$_2$]MeCl, **147** was obtained by disproportion of Cp*Ti[N=C^{t}Bu$_2$]Cl_2, **145**, with Cp*Ti[N=C^{t}Bu$_2$]Me_2, **146**, catalyzed by $B(C_6F_5)_3$. Cp*Ti[N=C{CH($SiMe_3$)$_2$}(^{t}Bu)]Me_2, **160**, was obtained by methane elimination when Cp*$TiMe_3$ was treated with HN=C{CH($SiMe_3$)$_2$}$_2$ (Method B) [58]. The molecular structures of Cp*Ti[N=C^{t}Bu$_2$]Cl_2, **145**, and IndTi[N=C^{t}Bu$_2$]Cl_2, **149**, display linear ketimide ligands and, similarly to **141**, the ketimide substituents are roughly parallel to the Cp ring [59].

The applicability of Cp′Ti[N=CR^1R^2]X^1X^2 complexes in olefin polymerization catalysis led to several studies involving cationic species. Piers and co-workers studied zwitterionic compounds of the type [Cp′Ti{N=C(R)(^{t}Bu)}Me–(μ-Me)$B(C_6F_5)_3$] obtained by reaction of the dimethyl derivatives with one equivalent of $B(C_6F_5)_3$ (**161–166**) [58].

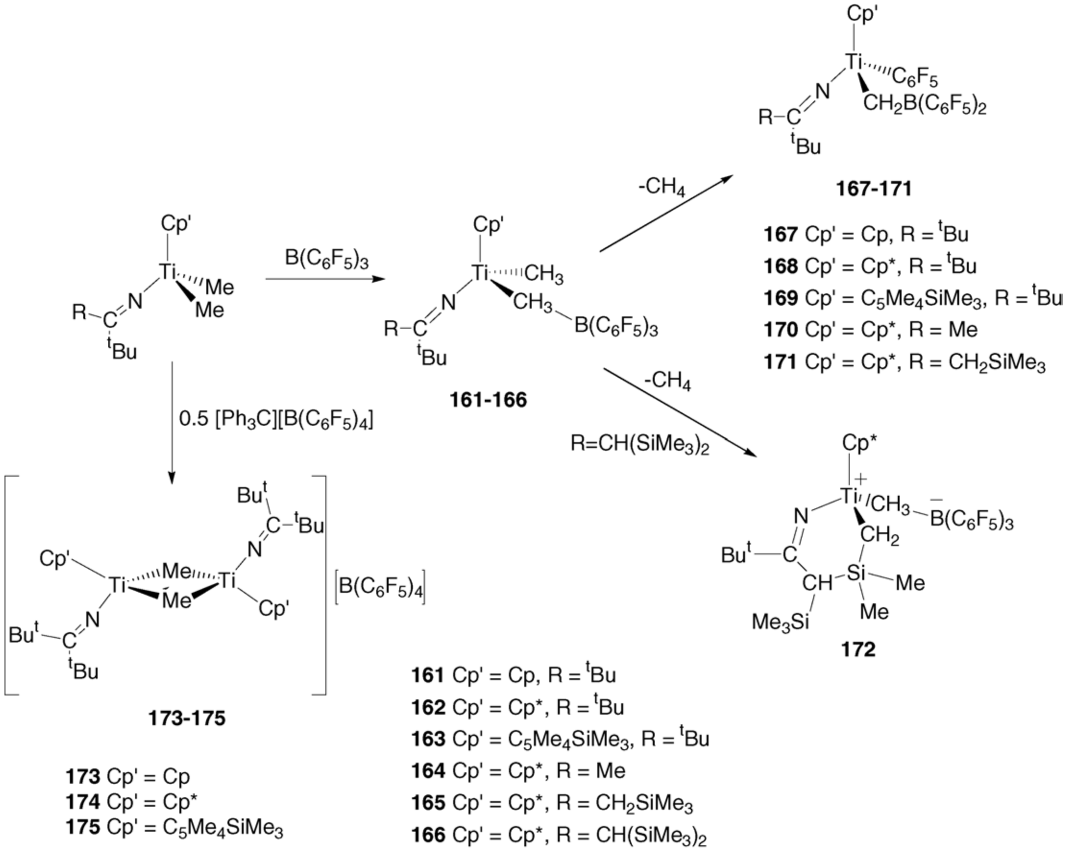
With the exception of **166**, decomposition of all complexes afford the neutral species [Cp′Ti{N=C(R)(^{t}Bu)}{$CH_2B(C_6F_5)_2$}{C_6F_5}] by methane elimination and transfer of one C_6F_5 ring to the titanium centre (**167–171**) [58]. Studies of these reactions have shown that methane elimination is intramolecular and favoured in polar solvents. **167–171** are inactive towards olefin polymerization and addition of more $B(C_6F_5)_3$ does not reactivate the catalyst, making this a fatal deactivation pathway. Compound **166** also deactivates by methane elimination but through a different decomposition pathway. In this case, one of the methyl groups of CH($SiMe_3$)$_2$ is activated and the metallacyclic zwitterionic species [CpTi{κ^2*N*, *C*−N=C(^{t}Bu)(CH)($SiMe_3$)($SiMe_2CH_2$)}(μ-CH_3)($B(C_6F_5)_3$)],



142–160

	Ref.
142 Cp' = Cp, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl	[17,58,59]
143 Cp' = Cp, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Me	[58]
144 Cp' = Cp, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = CH_2Ph	[60]
145 Cp' = Cp*, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl	[17,58,59]
146 Cp' = Cp*, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Me	[17,58]
147 Cp' = Cp*, R^1 = R^2 = ^{t}Bu, X^1 = Me, X^2 = Cl	[58]
148 Cp' = Cp*, R^1 = R^2 = ^{t}Bu, X^1 = Me, X^2 = CH_2SiMe_3	[17,58]
149 Cp' = Ind, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl	[17,59]
150 Cp' = C_4Me_4P, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl	[17]
151 Cp' = C_4Me_4P, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Me	[17]
152 Cp' = Cp, R^1 = Me, R^2 = Ph, X^1 = X^2 = Cl	[17]
153 Cp' = $C_4Me_4SiMe_3$, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl	[58]
154 Cp' = $C_4Me_4SiMe_3$, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Me	[58]
155 Cp' = Cp*, R^1 = ^{t}Bu, R^2 = Me, X^1 = X^2 = Cl	[58]
156 Cp' = Cp*, R^1 = ^{t}Bu, R^2 = Me, X^1 = X^2 = Me	[58]
157 Cp' = Cp*, R^1 = ^{t}Bu, R^2 = CH_2SiMe_3, X^1 = X^2 = Cl	[58]
158 Cp' = Cp*, R^1 = ^{t}Bu, R^2 = CH_2SiMe_3, X^1 = X^2 = Me	[58]
159 Cp' = $C_4H_4{}^t$Bu, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl	[61]
160 Cp' = Cp*, R^1 = ^{t}Bu, R^2 = CH($SiMe_3$)$_2$, X^1 = X^2 = Me	[58]

Chart 9.



Scheme 15.

172, is formed (Scheme 15). The activation of the silyl C–H bonds is frequently observed in silyl amido Group 4 metal complexes [62,63].

Methyl-bridged zwitterionic compounds $[\{Cp'Ti(N{=}C^tBu_2)Me\}_2(\mu\text{-}Me)][B(C_6F_5)_4]$ are obtained as a 1:1 mixture of rac/meso isomers ($Cp' = Cp$, **173**; $Cp' = Cp^*$, **174**; $Cp' = C_4Me_4SiMe_3$, **175**) formed by treatment of $Cp'Ti(N{=}C^tBu_2)Me_2$ ($Cp' = Cp$, **142**; $Cp' = Cp^*$, **146**; $Cp' = C_4Me_4SiMe_3$, **154**) with 0.5 equivalents of $[Ph_3C][B(C_6F_5)_4]$ [64]. NMR studies showed that decomposition proceeds by methane loss affording $[\{Cp'Ti(N{=}C^tBu_2)\}(\mu\text{-}Me)(\mu\text{-}CH_2)TiCp'(N{=}C^tBu_2)][B(C_6F_5)_4]$ ($Cp' = Cp$, **176**; $Cp' = Cp^*$, **177**; $Cp' = C_4Me_4SiMe_3$, **178**), also as a mixture of rac/meso isomers in thermodynamic equilibrium.

It is interesting to note that there are no mono-Cp mono-ketimide zirconium compounds reported. $CpZrCl_3{\cdot}dme$ reacts with one or two equivalents of $LiN{=}C^tBu_2$ to afford invariably $CpZr(N{=}C^tBu_2)_2Cl$, **179**. This is probably due to the bigger size of zirconium when compared to titanium, allied to the poor steric shielding provided by the ketimide ligand. In fact, although the *t*-butyl groups are bulky, their bulkiness is sufficiently distant to the metal centre to be an efficient shield [65]. A similar difficulty in controlling the stoichiometry of the products has currently been reported in the synthesis of Group 4 amido complexes [66].

Other mono-Cp compounds include $Cp'Ti(N{=}C^tBu_2)_3$ ($Cp' = Cp$, **180**; $Cp' = Ind$, **181**), prepared by reaction of $Ti(N{=}C^tBu_2)_3Cl$, **182** (see following section) with one equivalent of NaCp or NaInd, respectively. The X-ray structures of these compounds show two ketimide ligands close to parallel in relation to the Cp rings, whereas the third ligand stands roughly perpendicular in an arrangement that probably balances steric and electronic demands. All ketimide ligands are close to linearity. It is interesting to note that these two complexes are unexpectedly robust towards air and moisture, therefore attesting that the combination of a Cp ring and three ketimide ligands wrapped around a titanium atom provide a significant shielding of the metal centre [65].

Closely related to ketimide ligands are phosphinimide ligands, $^-N{=}PR_3$. As mentioned for $Cp'Ti(N{=}CR_2)X_2$, analogous $Cp'M(N{=}PR_3)X_2$ are olefin polymerization catalysts [67,68]. Phosphinimide moieties provide a better steric protection to the metal centres since the P(V) atom adopts a pyramidal geometry through the bonding to three substituents, as opposed to the coplanar arrangement found in ketimide ligands. This feature allows a better stoichiometric control of reactions as attested by the synthesis of mono-Cp mono-phosphinimide zirconium complexes [69] and monomeric bis-phosphinimide titanium complexes [70].

Titanium iminoimidazolide complexes represent a particular case of $N{=}CR_2$ ligands, where R_2 stands for imidazolin or NR'_2 fragments. Complexes $CpTi(L^1)Cl_2$, **183**, $CpTi(L^2)X_2$, **184**, $CpTi(L^3)X_2$, **185**, $Ti(L^1)_2Cl_2$, **186**, and $Ti(L^1)Cl_3$, **187**, have been reported [60,71] (Chart 10).

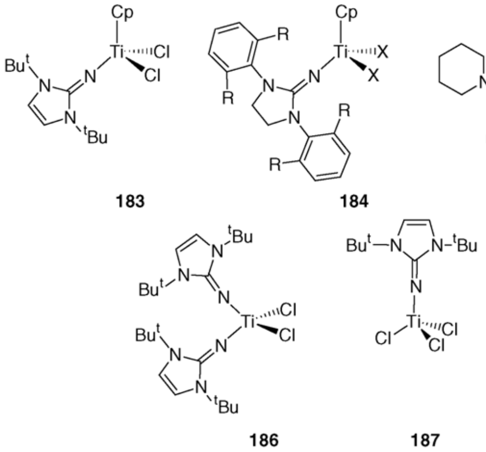


Chart 10.

Isoelectronic with the Cp ligand, consisting of an η^3-4π + 2σ electron system, is the tropidinyl anion. (trop)Ti(N=C^{t}Bu$_2$)Cl$_2$, **188**, was prepared by treatment of (trop)TiCl$_3$ with LiN=C^{t}Bu$_2$ and analogous complexes displaying phosphinimido ligands (trop)Ti(N=PR$_3$)Cl$_2$ (R = ^{t}Bu, ^{i}Pr) have been obtained using LiN=PR$_3$ [72]. Ethylene polymerisation studies have been carried on.

2.3. Cyclopentadienyl-free ketimide-supported complexes

As already mentioned, ketimide ligands failed to provide effective steric protection to the metal centre since, even when bulky substituents are present, these are relatively far away from the metal centres. While for titanium compounds the presence of one or two Cp rings is sufficient to account for this situation, zirconium is bigger and therefore only bent-metallocene systems provide stoichiometrically controlled reactions. In the absence of Cp rings even titanium reflects this feature.

Ti(N=C^{t}Bu$_2$)$_3$Cl, **182**, was prepared in moderate yield by reaction of TiCl$_4$ with two equivalents of LiN=C^{t}Bu$_2$. DFT calculations have shown that the introduction of the third ligand has a significant stabilization effect [65,73] thus hampering the synthesis of Ti(N=C^{t}Bu$_2$)$_2$Cl$_2$ by this route. The X-ray structure of **182** shows linear ketimide ligands twisted in a propeller-like way around the Ti–Cl axis. This arrangement is lost when the remaining chloride is replaced by the fourth ketimide ligand. Ti(N=C^{t}Bu$_2$)$_4$, **189**, was prepared either by reaction of **182** with one equivalent of lithium ketimide or directly by reaction of TiCl$_4$ with four equivalents of LiN=C^{t}Bu$_2$ [65]. The analogous complex Ti(N=CPh$_2$)$_4$, **190**, was obtained by reaction of Ti(NMe$_2$)$_4$ with HN=CPh$_2$ (Method B) [15].

Mixed ketimide-phosphinimide titanium compounds as Ti(N=C^{t}Bu$_2$)(N=P^{t}Bu$_3$)X$_2$, (X = Cl, **191**; X = Me, **192**) have been obtained from Ti(N=P^{t}Bu$_3$)Cl$_3$ [74].

3. Olefin polymerization catalysis

Results previously presented demonstrate that the M–N bond in Group 4 ketimide complexes is relatively robust. With the exception of proton attack on the nitrogen either by intramolecular tautomerization or by acidic hydrolysis, the ketimide moiety resists insertion, nucleophilic and electrophilic attack. This springs from the fact that in Group 4 metal complexes electron donation to the metal is efficient and therefore the nitrogen lone pair is not available for reactions. It is therefore not surprising that ketimide ligands are suitable to be used as ancillary ligands in catalytic reactions.

In 1999, Nova Chemicals patented complexes of the type Cp′Ti[N=CR^{1}R^2]X^{1}X^2 as catalysts in olefin polymerization [17]. These compounds are good catalysts able not only to polymerize α-olefins but also to give copolymers. Complexes **142** (Cp′ = Cp, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl), **145** (Cp′ = Cp*, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl), **149** (Cp′ = Ind, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl) and **159** (Cp′ = C$_4$H$_4$^{t}Bu, R^1 = R^2 = ^{t}Bu, X^1 = X^2 = Cl) are very active catalysts in ethylene homopolymerization when activated by MAO (see Table 1). When the polymerization is carried at 2 atm of ethylene, the order of activities is **149** > **145** > **142**, the maximum activity occurring at 60 °C. At higher temperatures, deactivation probably occurs, since a decrease in activity is observed [59]. At higher ethylene pressures (6 atm), **142** and **145** display higher activities, whereas **149** shows a considerable decrease [61,75]. At all pressures, the activity increases with the increase of the Al/Ti ratio. MAO plays an important role in the stabilization of the active species since the activity of CpTi[N=C^{t}Bu$_2$](CH$_2$Ph)$_2$, **144**, when activated by B(C$_6$F$_5$)$_3$ or a mixture of B(C$_6$F$_5$)$_3$ and Al^{i}Bu$_3$ is considerably smaller [60]. Once more, this may be due to the fact that ketimide ligands fail to afford a good steric protection to the metals but the nature of the bonding between the hard nitrogen donor and the metal cannot be underestimated. All these complexes afforded linear polyethylene, with relatively small M_w/M_n values, except for Cp*Ti[N=C^{t}Bu$_2$]Cl$_2$, **145**, that leads to a large M_w/M_n value of 74.4, when the polymerization is carried at 6 atm.

Complexes Cp$_2$Zr[N=C(^{t}Bu)(Ph)]Cl, **8**, Cp$_2$Zr[N=C(^{t}Bu)-(CH$_3$)]Cl, **9**, Cp$_2$Zr[N=C(^{t}Bu)(Ph)]Me, **10**, Cp$_2$Zr[N=C(^{t}Bu)-(CH$_3$)]Me, **11**, CpZr(N=C^{t}Bu$_2$)$_2$Cl, **179**, CpTi(N=C^{t}Bu$_2$)$_3$, **180**, IndTi(N=C^{t}Bu$_2$)$_3$, **181** and Ti(N=C^{t}Bu$_2$)$_3$Cl, **182**, are also reported to polymerize ethylene, although they are less active (with the exception of **179**) then the half-sandwich complexes described above (see Table 1). In common, these complexes posses a surplus of ancillary ligands and require the removal of at least one ketimide ligand to generate a cationic species with one vacant coordination site. Compounds **8** and **10** are reported to polymerize ethylene in the presence of MAO. When compared to Cp$_2$ZrCl$_2$, these are less active, probably because Zr–N bonds are more difficult to cleave then Zr–Cl bonds. They are also less active then Cp$_2$ZrCl(amido) systems, which accounts for a stronger Zr–N bond in ketimide complexes [21]. A similar situation is encountered for complexes **9** and **11** that also show slightly lower activities when compared to Cp$_2$ZrCl$_2$. When activated by B(C$_6$F$_5$)$_3$ these complexes are inactive in ethylene polymerization, however, for **11**, the combination of B(C$_6$F$_5$)$_3$ with Al^{i}Bu$_3$ or MAO affords polyethylene [23]. These results suggest that aluminium alkyls are capable of removing one ketimide ligand and replace it with an alkyl. Compound **179** is a very active catalyst in ethylene polymerization, with activ-

Table 1
Ethylene polymerization data using titanium and zirconium ketimide compounds as catalyst precursors

Compound	Co-Cat; Co-Cat:M	T (°C)	Activity (kg-polym/mol M h)	Ref.
Cp$_2$Zr[N=C(^{t}Bu)(Ph)]Cl, **8**	MAO; 1000	20	32	[21]
Cp$_2$Zr[N=C(^{t}Bu)(CH$_3$)]Cl, **9**	MAO; 1000	20	109	[23]
Cp$_2$Zr[N=C(^{t}Bu)(Ph)]Me, **10**	MAO; 1000	20	240	[21]
Cp$_2$Zr[N=C(^{t}Bu)(CH$_3$)]Me, **11**	MAO; 1000	20	233	[23]
	B(C$_5$F$_5$)$_3$/Al^{i}Bu$_3$; 1/1	20	327	[23]
CpTi[N=C^{t}Bu$_2$]Cl$_2$, **142**	MAO; 2000	60	7092	[59]
	MAO; 15000	40	22100	[61,75]
CpTi[N=C^{t}Bu$_2$](CH$_2$Ph)$_2$, **144**	B(C$_5$F$_5$)$_3$; 1.1	80	353	[60]
	B(C$_5$F$_5$)$_3$/Al^{i}Bu$_3$; 1.1/20	80	464	[60]
Cp*Ti[N=C^{t}Bu$_2$]Cl$_2$, **145**	MAO; 15000	40	16600	[76]
	MAO; 60000	25	30600	[76]
	MAO; 2000	60	19710	[59]
	MAO; 15000	40	16600	[61,75]
IndTi(N=C^{t}Bu$_2$)Cl$_2$, **149**	MAO; 15000	40	7700	[61]
	MAO; 2000	60	28820	[59]
(C$_4$H$_4$^{t}Bu)Ti[N=C^{t}Bu$_2$]Cl$_2$, **159**	MAO; 15000	40	14300	[61,75]
CpZr(N=C^{t}Bu$_2$)$_2$Cl, **179**	MAO; 2000	80	5730	[65]
CpTi(N=C^{t}Bu$_2$)$_3$, **180**	MAO; 2000	100	8.8	[65]
IndTi(N=C^{t}Bu$_2$)$_3$, **181**	MAO; 2000	80	190	[65]
Ti(N=C^{t}Bu$_2$)$_3$Cl, **182**	MAO; 2000	80	131	[65]

ities comparable to those obtained by Cp′Ti[N=CR^{1}R^2]X^{1}X^2 systems. Compounds **180–182** also polymerize ethylene in the presence of MAO. In the case of **182**, one ketimide ligand has to be replaced by an alkyl group whereas for **180** and **181**, it is likely that two ketimide ligands are removed, despite the removal of Cp or indenyl, although less probable, may not be excluded [65].

Compounds **142**, **145** and **149** are also active in propylene polymerization (see Table 2). Here, the order of activities is **149** > **142** > **145**. When compared to the order of activities in ethylene polymerization at the same pressure, **142** and **145** are in reversed positions. Steric factors involving the methyl groups of the Cp* ring are believed to be at the origin of this. The polypropylene produced is atactic [59].

Other α-olefin homopolymerization studies involving compounds **142**, **145**, **149** and **159** include styrene and 1-hexene polymerization. Complexes **142**, **145** and **159** afford syndiospecific polystyrene in moderate activities when activated by MAO. Activity increases with temperature, with the maximum obtained at 80 °C. The Cp* compound **145** affords the highest activity as well as the lowest value of M_w/M_n (see Table 3). All catalysts give syndiospecific polystyrene with unimodal molecular distributions [75]. 1-Hexene polymerization studies with **142**, **145**, **149** and **159** reveal that the Cp complex **142** is the most active, whereas the Cp* compound shows the lowest activity. The order of activities, **142** > **149** > **159** > **145**, (see Table 4) suggests that like in propylene polymerization, steric effects of the Cp ring influence the systems activity [61,75].

142, **145** and **149** have been reported to give ethylene copolymers with 10-undecen-1-ol (see Table 5). Compound **142** affords the polymer with the highest incorporation of 10-undecen-1-ol, probably because it is more resistant to decomposition by the comonomer than the other two. Overall, the activity is much lower than for ethylene polymerization under the same conditions [59]. Ethylene and 1-hexene copolymerization has also been reported [61]. Complexes **142** and **149** show remarkable activities, even higher than for ethylene polymerization. The activity depends on the concentration of 1-hexene, the Al/Ti ratio and on ethylene pressure. The M_w values are higher than those obtained for ethylene homopolymerization when complexes **142** and **149** are used as catalyst precursors. For **149**, the M_w/M_n value is large (varying between 2.4 and 3.6). The most remarkable copolymerization results are those involving the living copolymerization of ethylene and styrene, catalyzed by **142**/MAO [76]. Consistently, M_n increases linearly with time. No loss of activity is detected with time and the activity increases with ethylene pressure and with the temperature. The M_w/M_n value lies between 1.14 and 1.36 and styrene is uniformly distributed in the polymer.

Table 2
Propylene polymerization data using titanium ketimide compounds as catalyst precursors

Compound	Co-Cat; Co-Cat:M	T (°C)	Activity (kg-polym/mol M h)	Ref.
CpTi[N=C^{t}Bu$_2$]Cl$_2$, **142**	MAO; 1500	20	12420	[59]
Cp*Ti[N=C^{t}Bu$_2$]Cl$_2$, **145**	MAO; 1000	0	1076	[59]
IndTi(N=C^{t}Bu$_2$)Cl$_2$, **149**	MAO; 2000	0	49600	[59]

Table 3
Styrene polymerization data using titanium ketimide compounds as catalyst precursors

Compound	Co-Cat; Co-Cat:M	*T* (°C)	Activity (kg-polym/mol M h)	Ref.
$\mathrm{CpTi[N{=}C^{t}Bu_{2}]Cl_{2}}$, **142**	MAO; 7500	80	580	[75]
$\mathrm{Cp^{*}Ti[N{=}C^{t}Bu_{2}]Cl_{2}}$, **145**	MAO; 7500	25	1790	[75]
$\mathrm{(C_{4}H_{4}{}^{t}Bu)Ti[N{=}C^{t}Bu_{2}]Cl_{2}}$, **159**	MAO; 7500	80	930	[75]

Table 4
1-Hexene polymerization data using titanium ketimide compounds as catalyst precursors

Compound	Co-Cat; Co-Cat:M	*T* (°C)	Activity (kg-polym/mol M h)	Ref.
$\mathrm{CpTi[N{=}C^{t}Bu_{2}]Cl_{2}}$, **142**	MAO; 8000	25	37500	[75]
	MAO; 8000	25	16800	[61]
$\mathrm{Cp^{*}Ti[N{=}C^{t}Bu_{2}]Cl_{2}}$, **145**	MAO; 800	25	569	[61,75]
$\mathrm{IndTi[N{=}C^{t}Bu_{2}]Cl_{2}}$, **149**	MAO; 12000	25	12700	[61]
$\mathrm{(C_{4}H_{4}{}^{t}Bu)Ti[N{=}C^{t}Bu_{2}]Cl_{2}}$, **159**	MAO; 800	25	1310	[61,75]

Table 5
Ethylene co-polymerization data using titanium ketimide compounds as catalyst precursors

Compound	Co-monomer	Co-Cat; Co-Cat:M	*T* (°C)	Co-monomer content (%mol)	Activity (kg-polym/mol M h)	Ref.
$\mathrm{CpTi[N{=}C^{t}Bu_{2}]Cl_{2}}$, **142**	10-Undecen-1-ol	MAO; 2000	25	9.5	124	[59]
$\mathrm{Cp^{*}Ti[N{=}C^{t}Bu_{2}]Cl_{2}}$, **145**	10-Undecen-1-ol	MAO; 2000	25	6.2	7	[59]
$\mathrm{IndTi(N{=}C^{t}Bu_{2})Cl_{2}}$, **149**	10-Undecen-1-ol	MAO; 2000	25	4.8	376	[59]
$\mathrm{CpTi[N{=}C^{t}Bu_{2}]Cl_{2}}$, **142**	1-Hexene	MAO; 200000	40	38.7	283000	[61]
$\mathrm{Cp^{*}Ti[N{=}C^{t}Bu_{2}]Cl_{2}}$, **145**	1-Hexene	MAO; 10000	40	40.1	17000	[61]
$\mathrm{IndTi(N{=}C^{t}Bu_{2})Cl_{2}}$, **149**	1-hexene	MAO; 200000	40	30.8	860000	[61]
$\mathrm{(C_{4}H_{4}{}^{t}Bu)Ti[N{=}C^{t}Bu_{2}]Cl_{2}}$, **159**	1-Hexene	MAO; 10000	40	39.5	18000	[61]
$\mathrm{Cp^{*}Ti[N{=}C^{t}Bu_{2}]Cl_{2}}$, **145**	Styrene	MAO; 1500	70	12.2	1290	[76]

Since no repeated styrene groups are detected in the NMR, it is believed that styrene insertion inhibits chain transfer, allowing the polymerization to occur in a living fashion.

4. Concluding remarks

Group 4 ketimide complexes have been obtained by a variety of methods that include transmetallation reactions involving Group 4 metal halide derivatives and the appropriate lithium, tin or silicon ketimide derivatives, acid–base reactions involving the ketimine and an anionic ligand attached to the Group 4 metal complex, hydrozirconation of nitriles, oxidative addition reactions, insertion of nitriles in M–C bonds, nitrile coupling reactions and nitrile additions to unsaturated C–C bonds. While bent-metallocene compounds have mainly been obtained from reactivity studies of elementary reactions promoted by bis-Cp systems, mono-Cp and cyclopentadienyl-free ketimide-supported complexes were essentially obtained to provide olefin polymerization catalyst precursors. The use of ketimides as ancillary ligands in olefin polymerizations is possible due to the robustness of the M–N bond. Apart from reactions involving acidic protons, such as intramolecular tautomerization or hydrolysis reactions to afford ketimines and ketones, these ligands are essentially inert. The lack of adequate steric protection provided by ketimide ligands to the metal centers hampers the synthesis of some compounds that have no other bulky ligands and of mono-Cp mono-ketimide complexes of the heavier elements of this Group. However, Group 4 ketimide catalysts, especially titanium complexes that combine a Cp ring with one ketimide ligand, have proven to be exceptional catalysts in ethylene, propylene and 1-hexene homopolymerizations. With styrene, the activities are modest. The ketimide moiety may be removed by MAO and replaced by an alkyl group when required, to afford cationic active species. For mono-Cp mono-ketimide titanium systems, copolymerizations with polar and apolar co-monomers have also been described. In particular, the $\mathrm{Cp^{*}Ti(N{=}C^{t}Bu_{2})Cl_{2}}$ system was reported to afford living ethylene and styrene copolymerization.

The tunning of electronic and stereochemical properties provided by different ketimide R groups and the modulation of reactivity achieved by combining ketimide moieties with other ligands is still poorly explored. Nevertheless, the results described suggest that the employ of those ligands as ancillaries of early transition metal reactivity may give rise to new and interesting achievements.

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