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The Chemistry of *β*-Diketiminatometal Complexes

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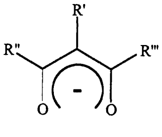
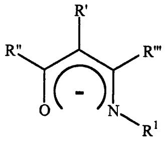
1. Introduction

1.1. Definition of the *β*-Diketiminato Ligand and Scope of This Review

Although the *β*-diketonato[1] **I** and *β*-enaminoketonato[2,3] **II** ligands are among the most ubiquitous chelating systems in coordination chemistry, the isoelectronic *β*-diketiminato ligands **III** have received only recent, but significantly increasing, attention.



I



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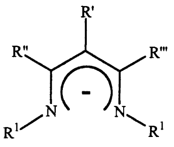

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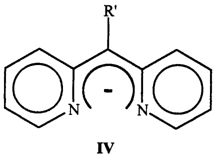

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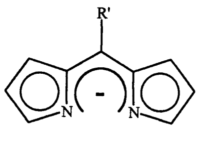
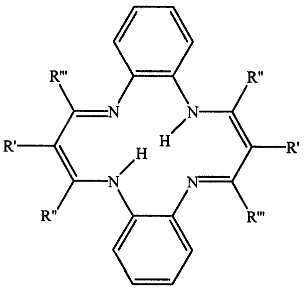


V

This system is obviously of great interest considering the scope for variation of the R^1 groups on nitrogen, which may be hydrogen or alkyl, aryl, or silyl groups. The R^1 groups can also be linked with the R''/R''' groups to form either neighboring fused six-membered (**IV**) or five-membered (**V**) heterocyclic rings.

The *β*-diketimine is also related to a number of macrocyclic compounds, such as **VI** and **VII**. Macrocycles **VI** may, for example, be prepared either by (i) a template reaction involving the co-condensation of a bis(*β*-diketonato)nickel complex with an *o*-phenylenediamine or (ii) a co-condensation reaction of pentane-2,4-dione with an *o*-phenylenediamine.[4] Metal complexes derived from **VI** usually form out-of-plane metal complexes, as do the natural macrocycles such as porphyrin (**VII**), porphodimethane, chlorin, bacterchlorin, and isobacterchlorin.[5]



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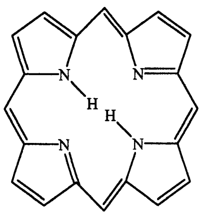

VII

For the purpose of this review, focus will be solely on complexes of the monoanionic ligands, such as **III**−**V**. Our aim is to have covered the literature comprehensively to the end of 2001 (but see section 8).

The *β*-dialdiminato ligand **III** has $R'' = H$, and a few derived metal complexes have been made. The term *β*-diiminatometal complexes, used by some authors, is therefore more comprehensive. [Curiously, a paper concerned with *β*-diketiminatoM(II) com-

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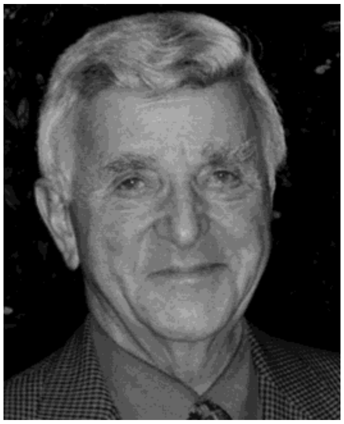
Laurence Bourget-Merle was born in 1970 in Nantes, France. Graduate of the University of Aix-Marseille III (France) in 1992, her Master's degree was followed by a Ph.D. in chemistry (1996) at the University of Montpellier II (with R. Corriu and A. Vioux) on the preparation of polysiloxanes by nonhydrolytic condensation reactions catalyzed by Lewis acids. She was a Research Fellow (1997–2000, Marie Curie Grant) in the group of Michael F. Lappert at the University of Sussex (England), where she worked on the synthesis of tin and aluminum complexes based on *N*,*N*′-centered ligands. She is currently working in the G. van Koten group, at the University of Utrecht, Netherlands, on the preparation and characterization (MALDI-TOF) of dendrimers.



Michael Lappert is Research Professor of Chemistry at the University of Sussex. A graduate of Northern Polytechnic, his B.Sc. was followed by a Ph.D. (with W. Gerrard) to which in 1960 he added a D.Sc. (University of London). He has been at Sussex since 1964, having previously been at UMIST (1959–1964). He was the recipient of the first Chemical Society Award for Main Group Metal Chemistry (1970) and then of the Organometallic Award (1978). He won the ACS–F. S. Kipping Award for Organosilicon Chemistry (1976); with the RSC (he was its Dalton Division President, 1989–1991), he has been a Tilden (1972), Nyholm (1994), and Sir Edward Frankland (1998) Medallist and Lecturer. He was elected FRS in 1979 and was awarded an honorary doctorate from Ludwig-Maximilians-Universität (München, 1989). With co-workers he has published almost 700 papers, 2 books, numerous reviews (including 5 previously in *Chem. Rev.*; the first in 1956), and a few patents on various aspects of inorganic and organometallic chemistry.

John Severn was born in Doncaster, U.K., in 1971. He attended the University of Sussex, where he received his B.Sc. (Hons, 1994) in chemistry with management studies. He carried out his doctoral work in coordination chemistry under the supervision of Prof. M. F. Lappert. After finishing his D.Phil. degree, he spent 14 months working on reactive extrusion of polyolefins, for a cable-manufacturing company. Since then he has been a postdoctoral researcher at the Technische Universiteit Eindhoven, working with Dr. R. Duchateau and Prof. R. A. van Santen on silsesquioxanes as molecular models for immobilized single-site α-olefin polymerization catalyst systems, funded by DSM Polyolefins. At present he is working with Dr. J. C. Chadwick and Prof. C. E. Koning for the Dutch Polymer Institute on a similar subject.

plexes (M = Mn, Zn, Cd) referred to these as “vinamidinemetal” derivatives;[6a] another labeled some Zr complexes as “β-iminatoaminates”.[7]] The acronym “$[\mathrm{R}^1{}_2\mathrm{nacnac}]^-$” has recently been used for **III** with R′ = H and R″ = Me = R‴, by analogy with acac$^-$; e.g., **III** with $\mathrm{R}^1 = \mathrm{C_6H_3{}^iPr_2}$-2,6, R′ = H, and R″ = Me = R‴ has been referred to as the ligand $[\mathrm{Dipp_2nacnac}]^-$.

Throughout this review the symbol R = $\mathrm{SiMe_3}$.

1.2. Some Significant Developments

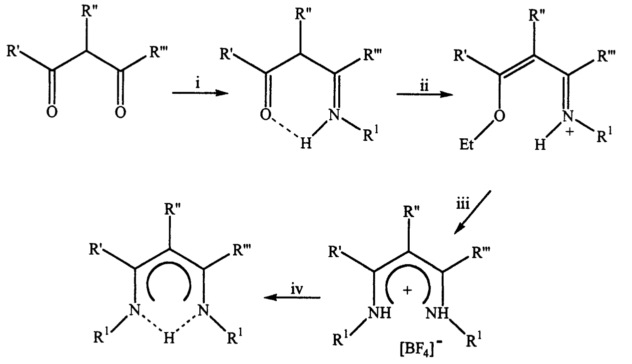
The field owes its genesis in the mid to late 1960s to classical coordination chemistry studies of homoleptic M(II) β-diketiminates (M = Co, Ni, Cu); the emphasis was on their synthesis, spectra, magnetism, and structures.[2,8a−17]

A major development in the mid 1990s was the recognition that β-diketiminates **III** could play a useful role as *spectator ligands*, like cyclopentadienyls, by virtue of their strong metal−ligand bonds and their exceptional and tunable (by variation of the substituent R^1) steric demands. Thus, in 1994 we reported on the ligands $[\{\mathrm{N(R)C(Ph)}\}_2\mathrm{CH}]^-$ (≡ L^-), $[\{\mathrm{N(H)C(Ph)}\}_2\mathrm{CH}]^-$ (≡ L'^-), and $[\mathrm{N(R)C(Ph)C(H)C(^tBu)N(R)}]^-$ (≡ L''^-) in the context inter alia of the synthesis and X-ray structures of the crystalline metal complexes $[\mathrm{LiL}]_2$,[18] $[\mathrm{SnL(Cl)Me_2}]$,[18] $[\mathrm{SnL'(Cl)Me_2}]$,[18] and $[\mathrm{ZrL''Cl_3}]$[19] and showed that the last of these was an effective catalyst (with methylaluminoxane, MAO) for the polymerization of $\mathrm{C_2H_4}$ or $\mathrm{C_3H_6}$.[20,21]

These and other aspects were reviewed in 1995, in connection with the transformation of the bis(trimethylsilyl)methyl $[\mathrm{CHR_2}]^-$ into the 1-azaallyl, such as $[\mathrm{N(R)C(^tBu)C(H)R}]^-$, or β-diketiminato ($\mathrm{L}^-$, L'^-, L''^-) ligand;[22] for a review of metal 1-azaallyls, see ref 23. The significance of steric effects was further demonstrated by noting that (i) whereas $[\mathrm{CoL_2}]$ is a tetrahedral d^7 complex, $[\mathrm{CoL'_2}]$ is square planar;[24] (ii) $\mathrm{SnL_2}$ is too sterically hindered to be accessible, but crystalline $[\mathrm{Sn(L)Br}]$ is a monomer;[24] as is (iii) $[\mathrm{NdL_2Cl}]$.[54] As for (iii), it is noteworthy that even the most bulky substituted bis(cyclopentadienyl)neodymium chloride is a dimer. It also was already evident at that time that there was a *diversity of bonding modes* possible for such β-diketiminato ligands in their metal complexes; for example, in $[\mathrm{ZrL''Cl_3}]$ the ligand may be regarded as being η^5-bonded to the metal, whereas in $[\mathrm{CoL_2}]$ or $[\mathrm{CoL'_2}]$ it is an *N*,*N*′-bonded chelate.[22,24]

In 1997, the synthesis of a new β-diketimine, the conjugate acid of the β-diketiminate $[\{\mathrm{N(C_6H_3{}^iPr_2}$-

Scheme 1. Reagents and Conditions[a]



[a] (i) NH_2R^1, C_6H_6, azeotropic distillation; (ii) $[Et_3O][BF_4]$, Et_2O, −78 °C; (iii) NH_2R^1, Et_2O; (iv) NaOMe, MeOH.

2,6)C(Me)}$_2$CH]$^-$ (≡ L‴$^-$), was published.[25] This ligand, in which each *N*-aryl substituent is almost orthogonal to the NCCCN plane (as also is the case for other *N*,*N*′-diaryl analogues), is playing an increasingly important role, as the following selected examples i−viii, drawn from the post 2000 literature, demonstrate. (i) The crystalline complexes [ML‴] have Al[26] and Ga[27] in the rare M(I) oxidation state. (ii) $[GeL'''][HO\{B(C_6F_5)_3\}_2]$ is at present the only germanium(II) cationic complex.[28] (iii) [Fe(L‴)Cl] is a three-coordinate Fe(II) complex[29a] and is a source of $[\{Fe(L''')\}_2(\mu\text{-}N_2)]$ and $M_2[\{Fe(L''')\}_2(\mu\text{-}N_2)]$ (M = Na, K).[29b] (iv) $[Cr(L''')(Me)(\mu\text{-}Cl)]_2$ with $AlClEt_2$ is an active catalyst for C_2H_4 polymerization.[30] (v) $[Pt(L''')Me_3]$ is a moderately stable, coordinatively unsaturated, five-coordinate d^6 16-electron complex.[31] (vi) The Cu(II) complex $[\overline{Cu(L''')\{S(Me)CH_2CPh_2S}\}]$ is a structural model for a type 1 copper protein active site.[32] (vii) $[Zn(L''')(O^iPr)]_2$[33] and $[Sn(L''')(O^iPr)]$[34] are active catalysts for the living polymerization of *rac*- and *meso*-lactide to yield poly(lactic acid).[33] (viii) $[Zn(L''')\{N(SiMe_3)_2\}]$ is highly active catalyst for the living copolymerization of cyclohexene oxide and CO_2.[35]

β-Diketiminates are now known for a large number of s-, p-, d- and f-block metals and a wide variety of substituents R^1, R′, and R″ for the ligands **III**, as summarized in Table 1.

2. Preparation of β-Diketimines and Their Metal Complexes

There are various synthetic routes to the β-diketiminato ligand, either as its conjugate acid or as a metal complex. Most involve the condensation reaction of a primary amine with either a β-diketone or 1,1,3,3-tetraethoxypropane, thereby producing a range of β-diketimines. The other main method involves the reaction of a metal alkyl with 2 equiv of a nitrile, or the reaction of a metal 1-azaallyl with 1 equiv of a nitrile.

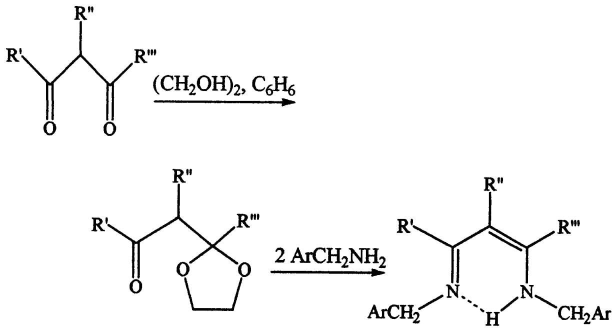
2.1 Synthesis of a β-Diketimine from a β-Diketone or 1,1,3,3-Tetraalkoxypropane

Until a few years ago the above procedures were the most common synthetic routes for the production of β-diketimines. Advantages include acceptable yields, the use of relatively inexpensive or easily synthesized reagents, and their availability for production in large quantities.

There are at present only two synthetic procedures for the conversion of a β-diketone into a β-diketimine. Both take advantage of the fundamental co-condensation reaction of a ketone and a primary amine. It should be noted that some modification has to be made (see steps ii−iv of Scheme 1) to avoid the reaction stopping after the first condensation, giving the enaminoketone (step i in Scheme 1).

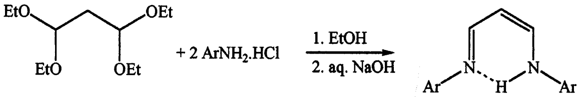
The first of the reactions of Scheme 1 was reported over three decades ago.[8a]

An alternative procedure involved converting a 1,3-diketone into successively a ketoketal and then the β-diketimine (eq 1).[8b]



(1)

A 1,1,3,3-tetraalkoxypropane (a β-diacetal) is also a convenient precursor. A standard preparation involved treating 1,1,3,3-tetraethoxypropane with an aromatic amine hydrochloride in aqueous ethanol at 50 °C for 1 h, followed by storage at ambient temperature to crystallize the β-diketimine hydrochloride and finally release of the β-diketimine with aqueous sodium hydroxide (eq 2).[8c]



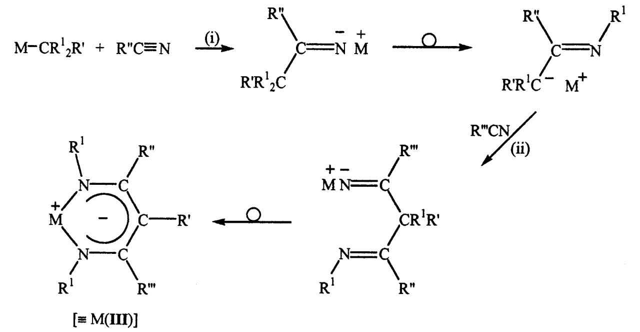
(2)

The reaction conditions of Scheme 1 and eqs 1 and 2 should be regarded as illustrative rather than prescriptive. For example, $H\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH$ was made from 2,4-pentadienone, or 1,1,3,3-tetramethoxypropane, and successively ethanolic HCl and aqueous Na_2CO_3[25] (see also ref 37). This procedure was used for a series of related β-diketimines and -dialdimines.[35]

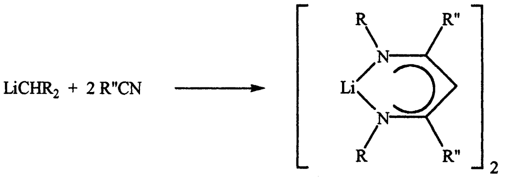
2.2. Synthesis of a Metal β-Diketiminate by Nitrile or Isonitrile Insertion into a Metal–Alkyl Bond

This involves insertion of an α-hydrogen-free nitrile R″CN or R‴CN into the $M-C_{sp^3}$ bond of $M-CR^1{}_2R'$, where R^1 = a silyl group, such as $SiMe_3$ (≡ R), or (rarely) hydrogen. The probable reaction pathway is shown in Scheme 2. An alternative, starting with step ii of Scheme 2, is the insertion of the α-hydrogen-free nitrile R‴CN into the M−C bond of a 1-azaallylmetal fragment.

Scheme 2

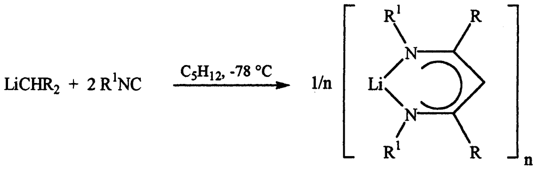


The proposal of Scheme 2 was first suggested in the context of the reaction of eq 3 ($R^1 = SiMe_3 = R$, $R'' = Ph$ or C_6H_4Me-4).[18] Both steps i and ii of Scheme 2 involve an initial C−C coupling followed by a 1,3-migration of the group R^1 from carbon to nitrogen. Such shifts are much more facile for $R^1 = SiMe_3$ than for $R^1 = H$. For example, the reactions of eq 3 proceeded rapidly in high yield in diethyl ether at 0 °C.[18] Related anionic $SiMe_3$ shifts are well documented, but 1,2-rearrangements from carbon to nitrogen are more common[38] than the 1,3 here noted.



(3)

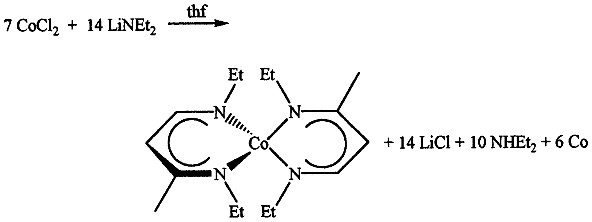
It was further shown that isonitriles R^1NC undergo similar insertions, as illustrated in eq 4 ($R^1 = C_6H_3Me_2$-2,6).[39,40] This reaction was believed to proceed via two successive C−C couplings and 1,2-trimethylsilyl migrations.



(4)

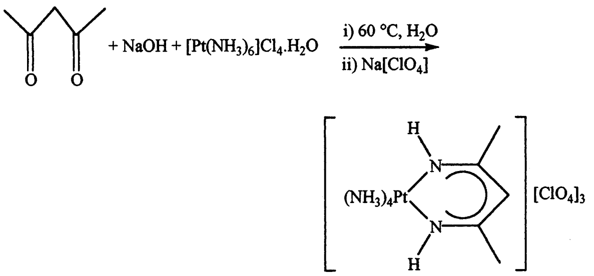
2.3. Various Other Synthetic Routes to Metal β-Diketiminates

These have generally been restricted to transition metals. Treatment of a Ni(II) or Co(II) halide with $LiNEt_2$ has led to a number of β-diketiminatometal complexes, although in relatively poor yield, as in eq 5 (13% yield).[9,10]



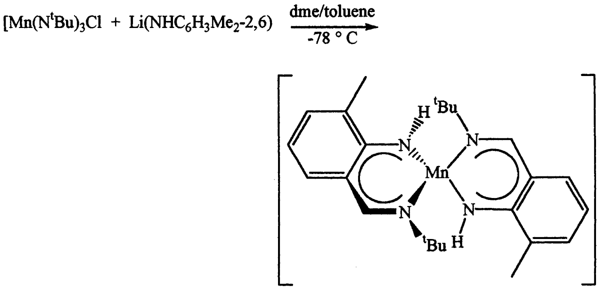
(5)

A platinum(IV) β-diketiminate was obtained by the co-condensation of eq 6.[41]



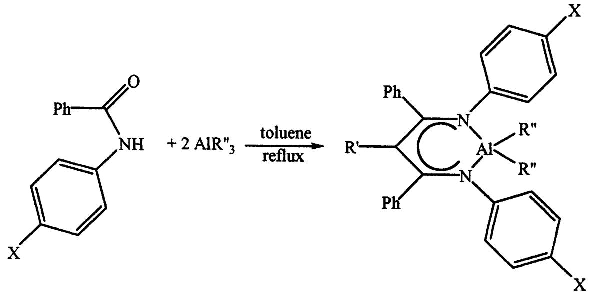
(6)

Interaction of a lithium amide and a tris(imido)manganese(VII) chloride under mild reaction conditions afforded the bis(β-diketiminato)manganese(II) complex of eq 7.[42]



(7)

A useful route to *N*,*N*′-diaryl-β-diketiminatoaluminum dialkyls involved condensation between a benzanilide and AlR''_3, eq 8 [$R'' = Me$, $R' = H$, $X = H$; $R'' = Et$, $R' = Me$, $X = H$; $R'' = Et$, $R' = Me$, $X = Cl$; $R'' = Me$, $R' = H$, $X = Cl$; $R'' = Me$, $R' = H$, $X = Me$; $R'' = Et$, $R' = Me$, $X = Me$].[43] The reaction pathway leading to the β-diketiminatoaluminum dimethyl [Al{(N(Ph)C(Ph))$_2$CH}(Me)$_2$] ($R'' = Me$, $R' = H$, $X = H$ in eq 8) is shown in Scheme 3. In the absence of an excess of $AlMe_3$, the macrocycle **VIII** was isolable.[43]



(8)

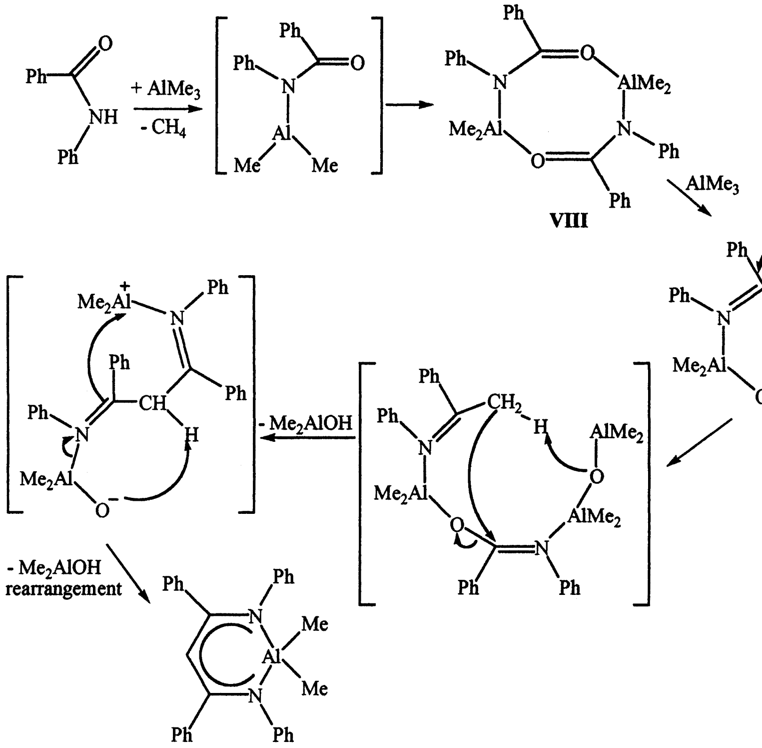
A β-diketiminatocobalt(III) complex was obtained recently via a new exotic route, consisting of condensation of propargylamine with a polymeric Co(II) basic pivaloate and oxygen gas (Scheme 4).[44]

In some instances, notably for ligands such as [{N(R)C(Ph)}$_2$CH]$^-$ ($R = SiMe_3$), it is useful to gain access to the derived β-diketimine. This has been achieved by treating the alkali metal (M) β-diketiminate (M = Li, Na, K) with water (a controlled quantity),[18] 1,2-dibromoethane,[18] or cyclopentadiene,[45] with concomitant elimination of MOH, $MBr + CH_2{=}CHBr$, or MCp, respectively. Use of dibromomethane generated the CH_2-bridged bis(diketimine).[18,46]

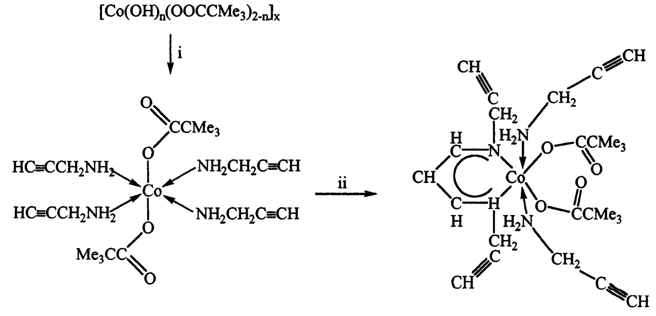
2.4. Other Synthetic Routes to β-Diketimines

An unusual route to a β-diketimine involved the reaction of a 4-aryl-1,2-dithiolium perchlorate or

Scheme 3

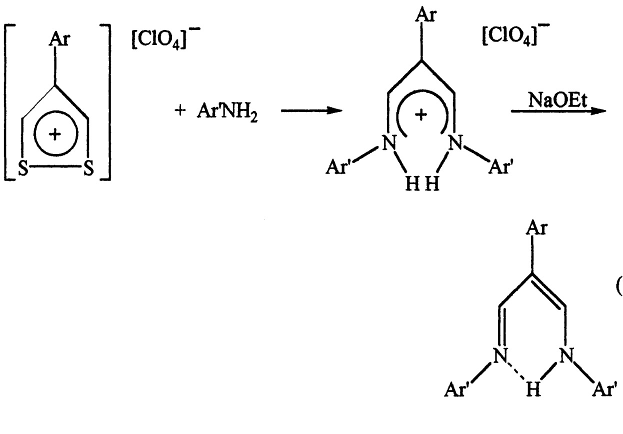


Scheme 4. Reagents and Conditions[a]



[a] (i) $4\mathrm{NH_2CH_2C{\equiv}CH}$, $\mathrm{CH_2Cl_2}$, Ar atmosphere; (ii) 1−2 equiv of $\mathrm{NH_2CH_2C{\equiv}CH}$, $\mathrm{CH_2Cl_2}$, or toluene, in air.

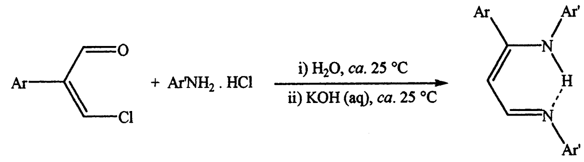
sulfate with a primary aromatic amine, to produce a β-diketimine as its perchlorate or sulfate, which with sodium ethoxide afforded the free β-diketimine (eq 9).[47]



(9)

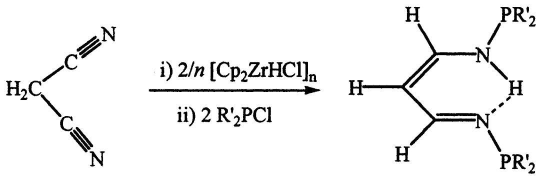
A low-yield route to $[\mathrm{H}\{(\mathrm{N}(^t\mathrm{Bu})\mathrm{C}(\mathrm{Me}))_2\mathrm{CH}\}]$ employed ROC(Me)C(H)C(Me)CO and $2(^t\mathrm{BuNH_2})$ as starting materials.[48a]

Another procedure was based on treatment of β-chlorocinnamaldehyde with a concentrated aqueous solution of the hydrochloride of a primary arylamine and subsequent neutralization (eq 10) (e.g., Ar = Ph = Ar′).[48b]



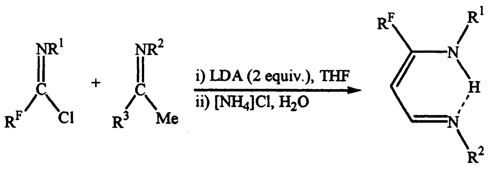
(10)

Unprecedented N,N'-bis(phosphino)-β-diketimines $\mathrm{H}\{(\mathrm{N}(\mathrm{PR'_2})\mathrm{C}(\mathrm{H}))_2\mathrm{CH}\}$ (R′ = Ph, $\mathrm{N^iPr_2}$) have been prepared in a one-pot synthesis using malonodinitrile, the Schwartz reagent, and a chlorophosphine $\mathrm{R'_2PCl}$ (R′ = Ph, $\mathrm{N^iPr_2}$) (eq 11).[49]



(11)

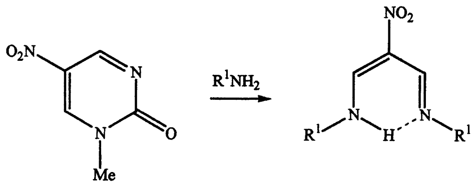
Reaction of a fluorinated imidoyl chloride with a ketimine yielded a β-diketimine (eq 12) (e.g., $\mathrm{R^1} = \mathrm{C_6H_4OMe}$-4, $\mathrm{R^F} = \mathrm{CF_3}$, $\mathrm{R^2} = \mathrm{Ph} = \mathrm{R^3}$).[50a]



(12)

5-Silyl-3-pyrazolines were isomerized upon heating to yield a diimine tautomer of a β-diketimine, for example, N(Ph)C(Me)C($SiMe_2Ph$)(H)C(Me)NMe from N(Ph)C(Me)C(H)C($SiMe_2Ph$)(Me)NMe.[50b]

A remarkable low-yield conversion of a 5-nitropyrimidin-2(1*H*)-one into a nitro-substituted β-diketimine is illustrated in eq 13 ($R^1 = C_6H_2Me_3$-2,4,6).[51]

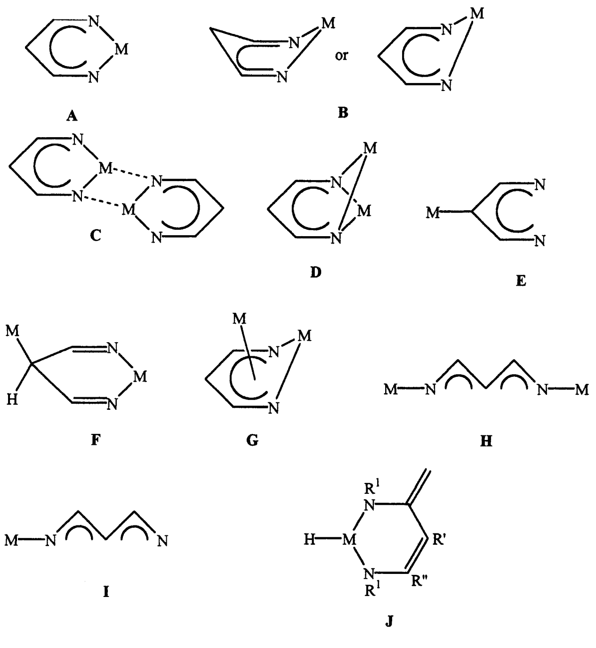


(13)

The β-diketimines are often precursors of their metal derivatives, either directly by metalation with an electrophilic metal (e.g., Li, Al, Zn) alkyl or amide or indirectly by a ligand transfer reaction between an alkali metal (often Li) β-diketiminate and the required metal halide (often Cl). In other instances, as in section 2.2, the metal acts as a template in the synthesis of the metal β-diketiminate.

3. Bonding Modes and Structural Features of β-Diketiminatometal Complexes

There is a considerable diversity of bonding modes for β-diketiminatometal complexes, as outlined schematically in **A**−**J**, in which, for the sake of clarity, (i) the single pendant groups R^1, R', R'', and R''' (cf. **III**) are omitted (except for **J**) and (ii) the rings in **A**−**E** and **G**−**I** are shown as being delocalized.



Bonding mode **A** corresponds to the situation in which the MNCCCN ring is planar and the β-diketiminato ligand **III** behaves in a terminal *N*,*N*′-chelating fashion. The conformational variant **B** shows the six-membered metallacyclic ring in boat form and, in the limit, the M...CR′ contact is close enough for **III** to be regarded as being η^5-π-bound, particularly if the metal has unfilled d orbitals of appropriate symmetry (see, especially, section 4.3); in some cases, however, only the metal atom M is out of the almost planar NCCCN moiety. The essential feature of type **C** is that the ligand **III** in a binuclear complex is both chelating and bridging, so that one of the nitrogen atoms of **III** is three-coordinate and the other four-coordinate; the conformation of the metallacyclic rings may vary. Mode **D** is that in which a binuclear complex **III** is both chelating and bridging, but in this instance implicating both of the four-coordinate nitrogen atoms. Type **E** has been realized in one example [Ge{C(C(Me)N($C_6H_3{}^iPr_2$-2,6))$_2$}Cl_3];[52] an analogue of the derived conjugate acid [H{N(R)C(Ph))$_2$C}$_2CH_2$] is known.[18] Thus, in principle, the monoanionic ligand **III**, at present almost invariably *N*,*N*′- or *N*-centered (see **I**), has recently been found in a *C*-centered environment in the above germanium(IV) chloride.[52] Strictly **F** is not directly relevant; it represents an M−(**III**-H) fragment, and bis(imine)metal complexes are increasingly of interest as olefin polymerization catalysts; an example is shown in **2** ($R^1 = C_6H_3{}^iPr_2$-2,6).[25] Mode **G** is a variant of **D**, both being rare. Type **H** differs from **C** in that the bridging ligand **III** has both of the three-coordinate nitrogen atoms functioning as terminal ligands to the two metal atoms. Finally, **J** represents a tautomer of **A** or **B**. In the following section, selected examples are chosen to illustrate each mode **A**−**J**.

Mononuclear β-diketiminatometal complexes having a tetrahedral or distorted tetrahedral metal environment generally adopt the bonding mode **A**. Examples based on the ligand [{N(R)C(Ph)}$_2$CH]$^-$ (≡ L) include [LiL(thf)$_2$],[45] [CoL_2],[22,24] and [MgL_2].[53] Mode **A** is also found in (i) most β-diketiminatometal(II) square planar complexes, as in [CoL'_2], L′ = [{N(H)C(Ph)}$_2$CH];[22,24] (ii) heteroleptic tetravalent metal complexes, if the substituents R^1 on the nitrogen atoms are hydrogen, as in [SnL′(Cl)Me_2];[18] and (iii) the β-diketiminatotin(II) chlorides [SnL″Cl][22,24] and [Sn{N(H)C(Ph)C(H)C(^{t}Bu)N(H)}Cl][24] [L″ = N(R)C(Ph)C(H)C(^{t}Bu)NR]. For complexes of metals having low-lying formally vacant d orbitals of appropriate symmetry, there is the possibility of the β-diketiminato ligand participating not only in σ- but also in π-bonding, the anionic ligand thus being variously a 4- or 6-electron donor; the latter may be significant particularly for late transition metal complexes.

To discuss the bonding in the complex [Cu{(N(C_6H_3-^{i}Pr_2-2,6)C(Me))$_2$CH}($SCPh_3$)] (see section 4.4), the electronic structure of the planar, conjugated β-diketiminato ligand core **A**, modeled as planar $C_3N_2H_5$, was probed using Amsterdam Density Functional Theory Calculations.[103] (As the aromatic rings are orthogonal to the C_3N_2Cu plane they are not part of the conjugated π-system.) These yielded the calculated highest energy levels which, with schematic representations, are shown in Figure 1. The HOMO, 2b1, is characterized by out-of-plane p-type orbitals on the two nitrogen atoms and the central carbon (C3) atom. The 5b2, of only slightly lower energy, has

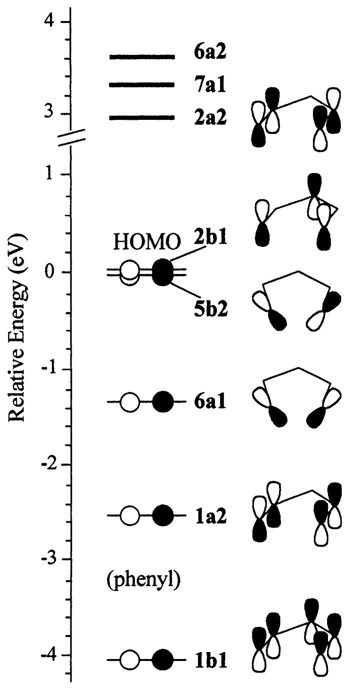


Figure 1.

in-plane, out-of-phase nitrogen-centered orbitals with lobes directed toward the metal; the wave function character is distributed among the out-of-plane orbitals on C3 (37% C_{calcd}) and the terminal N5 (28% N_{calcd} per N). To deeper energy lies the 6a1 orbital that is also able to participate in ligand−metal bonding, although it would be weaker because the energy denominator would be larger. The still deeper binding energy out-of-plane 1a2 and 1b1 orbitals are unlikely to interact significantly with the metal. Thus, the majority of the bonding occurs through the in-plane orbitals 5b2 and 6a1, which form σ-bonds to the metal, implying that the ligand functions as a 4-electron donor (see also ref 81). Only if the metal−ligand metallacycle is strongly boat-shaped (**B**), as in some of the Ti(IV) and Zr(IV) β-diketiminates (see section 4.3.2), is a 6-electron $2\sigma+\pi$-bonding description, involving additionally the 2b1 out-of-plane orbital, appropriate, but it is unlikely to be significant for the less puckered Sc complexes (see section 4.3.1).[76]

The change from **A** to **B** is caused by steric crowding around the metal center; examples include $[PdL_2]$,[45] $[NdL_2Cl]$,[54] and $[ZrL''Cl_3]$.[19] Likewise, the change from a square planar to a tetrahedral late 3d homoleptic M(II) β-diketiminate has a steric origin, as first demonstrated for $[CoL_2]$ and $[CoL'_2]$.[22] For the d^8 $[ML_2]$ complexes, whereas the smaller, paramagnetic, tetrahedral Ni complex adopts mode **A**, mode **B** was observed for the larger, diamagnetic, centrosymmetric, square planar Pd analogue **1**.[45] Further illustrations of selected geometric parameters for some of these complexes and an example of mode **C**, $[LiL]_2$,[18] are shown in Figure 2. Another case of **C** is in $[Li\{N(R)C(^tBu)C(H)(C_5H_4N\text{-}2)\}]_2$.[36] There are only a few examples of mode **D**, as in $[LiL\{Li(CHR_2)\}(thf)]$; selected bond lengths are in Figure 2g.[55] The crystalline dinuclear barium complex $[Ba_2\{(N(C_6H_{11}\text{-}c)C(Me))_3CH\}_3(NR_2)]$ is unusual in that bonding illustrates three different types, **B**, **G**, and **H**, as shown in **2** ($R^1 = C_6H_{11}$-c).[56] Other examples of type **H** include $[KL'(thf)_2]_2$,[45] and $[Li\{\mu\text{-}(N(R)C(Ph))_2C\}]_2CH_2$ (Figure 2i).[46] Type **I** is represented by two examples, the Sc(III) complex **3**, in which the two scandium atoms are not only in an eight-membered ring but also part of both a penta- and a hexa-atomic metallacycle,[57] and in a germanium compound **4** (see **49** in section 4.7).[58]

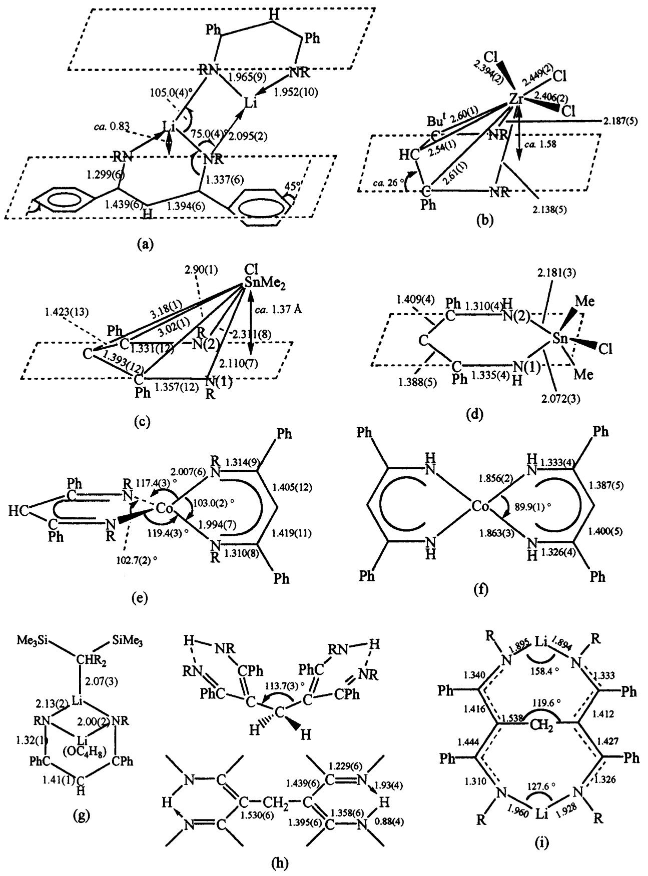
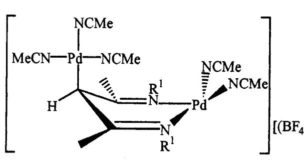
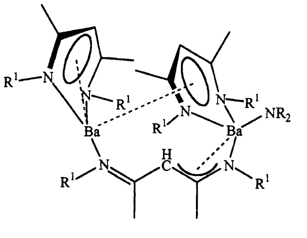


Figure 2. Selected geometric parameters for crystalline (a) $[LiL]_2$, (b) $[ZrL''Cl_3]$, (c) $[SnL(Cl)Me_2]$, (d) $[SnL'(Cl)Me_2]$, (e) $[CoL_2]$, (f) $[CoL'_2]$, (g) $[LiL\{Li(CHR_2)\}(thf)]$, (h) $[H\{N(R)C(Ph)\}_2C]_2{-}CH_2$, and (i) $[Li\{\mu\text{-}(N(R)C(Ph))_2C\}]_2CH_2$.



1



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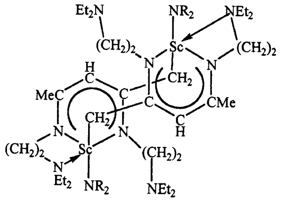

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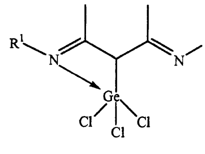

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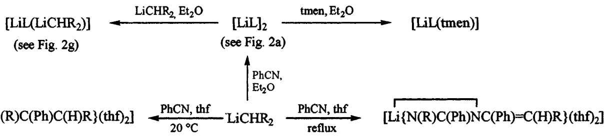
Scheme 5



4. Discussion of Specific *β*-Diketiminatometal Complexes

The following sections concern *β*-diketiminatometal complexes reported in the literature and include also some unpublished work from the Sussex group. A summary is provided in Table 1.

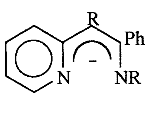
4.1. Group 1 Metal *β*-Diketiminates

The first fully characterized crystalline alkali metal *β*-diketiminate, $[Li\{(N(R)C(Ph))_2CH\}]_2$ ($\equiv [LiL]_2$, Figure 2a), was reported in 1994 ($R = SiMe_3$); it was obtained from $LiCHR_2$ and PhCN in diethyl ether (eq 3).[18] Reactions of $LiCHR_2$ and related lithium trimethylsilylmethyls were later described in a wider context and shown to provide a variety of products, depending on the reaction conditions and the absence or presence of a neutral coligand.[55] This is exemplified by the reactions between $LiCHR_2$ and PhCN shown in Scheme 5.[55] The reaction pathway to the lithium 1-azaallyl and *β*-diketiminate is shown in Scheme 2; the formation of the lithium 1,3-diazaallyl (an isomer of the *β*-diketiminate) was attributed to the reaction of the 1-azaallyl $Li\{N(R)C(Ph)C(H)R\}$, functioning as an *N*-centered nucleophile, with PhCN.

Related *β*-diketiminates $[Li\{(N(R^1)C(R))_2CH\}]$, $[Li\{N(R^1)C(R)C(H)C(Ph)NR\}(tmen)]$, and $[Li\{(N(^tBu)C(R))_2CH\}(CN^tBu)(LiCHR_2)]$ ($R^1 = C_6H_3Me_2\text{-}2,6$) were obtained from $LiCHR_2$ and the appropriate isonitrile R^1NC.[39,40]

Ligands of the type **IV**, $[(2\text{-}NC_5H_4)_2CH]$ ($\equiv L^1$), **5** ($\equiv L^2$), and **6** ($\equiv L^3$) have featured in the X-ray-characterized complexes $[LiL^1(thf)_2]$,[59] $[Li(12\text{-}crown\text{-}4)_2][LiL^1_2]$,[59] $[LiL^2]_2$,[36,60] and $[LiL^3]_2$.[36,60] Those based on L^1 were made from HL^1 and Li^nBu [59] and the others from the appropriate lithium 1-azaallyl and benzonitrile.[36,60]

The vast majority of other lithium *β*-diketiminates are also conveniently prepared from the appropriate diketimine and Li^nBu. Such lithiation of $H[\{N(Ph)C(H)\}_2CH]$ in the presence of hmpa yielded the unusual crystalline complex **7**.[61] A remarkable lithiation is that of eq 14; the formation of the crystalline product was interpreted to involve the sequence of Scheme 6.[46]



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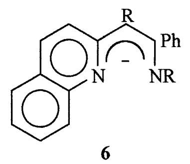
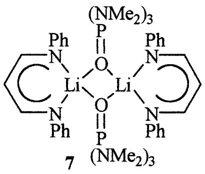


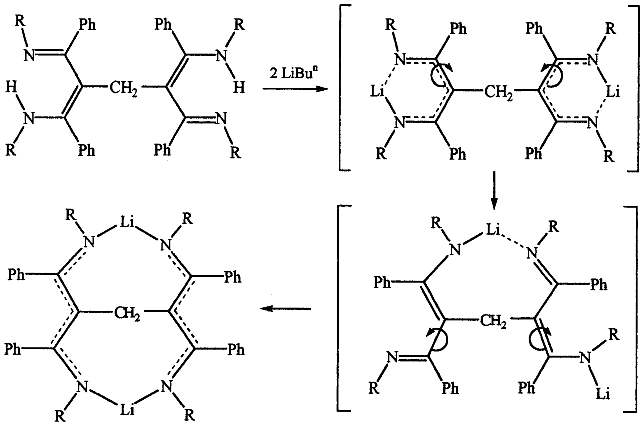
6



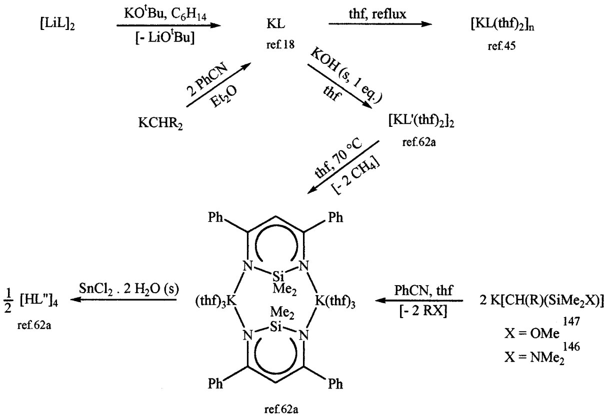
7

$$[\{H(N(R)C(Ph))_2C\}_2CH_2] \xrightarrow{Li^nBu,\ Et_2O} [Li\{\mu\text{-}(N(R)C(Ph))_2C\}]_2CH_2 \quad (14)$$

Scheme 6



Scheme 7



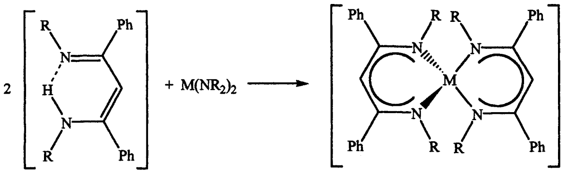
The compound $Li\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}$ ($\equiv$ LiL) has been obtained in two crystalline forms.[37] One, a dimer, has a double η^3-allylic bridge from one aryl ligand acting as π-donor to the adjacent Li^+ ion. The other, a dodecamer, has been described as having a slipped ladder structure, the asymmetric unit of which consists of a chain of six LiL units associated by interactions of each Li^+ ion with one or two carbon atoms of the aryl ring of the adjacent LiL moiety.

Lithium *β*-diketiminates are widely used as ligand transfer reagents by reacting them with various metal chlorides. However, we have found that it is often more practicable (although rarely used) to employ the corresponding sodium or potassium derivative, because the heavier alkali metal chloride coproducts are more readily separated in such reactions than LiCl. The only X-ray-characterized sodium complex is $[NaL(thf)_2]$.[45] Potassium *β*-diketiminates have been studied more intensively, as summarized in Scheme 7 ($L = [\{N(R)C(Ph)\}_2CH]$, $L' = [N(R)C(Ph)C(H)C(Ph)NH]$, $L'' = [Me_2Si\{NC(Ph)\}_2CH]$). Each of the crystalline compounds shown in square brackets has been structurally defined. In $[KL(thf)_2]_n$, the *β*-diketiminate L behaves as a bridging open-chain ligand (type **H**),[45] as also is the case for L′ in $[KL'(thf)_2]_2$ with the NH nitrogen center as the donor site.[62a] The tricyclic dinuclear complex has L″ functioning as a cyclic bridging ligand.[62a] Its derived diketimine is a cyclotetramer, each unit joined to the next by a hydrogen bond with the four nitrogen atoms coplanar.[62a]

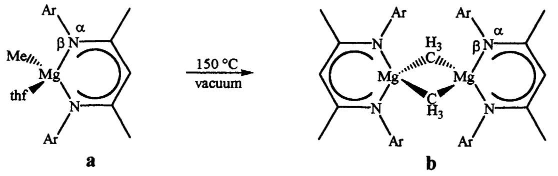
The crystalline compound $[K\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}]\cdot PhMe$ was obtained from $K(NR_2)$ and $H[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]$ in toluene;[62b] it is essentially a monomer, except for a single η^5-contact (excluding the *ipso*-C) of one of the $C_6H_3{}^iPr_2$-2,6 substituents to a neighboring K atom.

4.2. Group 2 Metal β-Diketiminates

The compound $[Mg\{(N(Me)C(Me))_2CH\}_2]$ was obtained from $MgMe_2$ and the β-diketimine.[63] Reaction of $[Li\{(N(R)C(Ph))_2CH\}_2]$ with $MgBr_2$ produced crystalline $[Mg\{(N(R)C(Ph))_2CH\}_2]$.[53] Heavier group 2 metal analogues were more readily obtained by the transamination reaction of eq 15.[64]

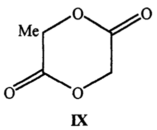


(15)

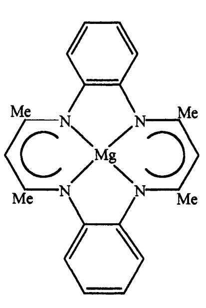


(16)

Treatment of $[Li\{(N(Ar)C(Me))_2CH\}]$ (Ar = $C_6H_3{}^iPr_2$-2,6) with MeMgCl in thf yielded $[Mg\{(N(Ar)C(Me))_2CH\}(Me)(thf)]$ (**a**), which when heated under vacuum at 150 °C afforded the methyl-bridged dimeric complex $[Mg\{(N(Ar)C(Me))_2CH\}(\mu\text{-}Me)]_2$ (**b**) (eq 16).[65] Alternatively, the latter was also obtained from the corresponding β-diketimine and dimethylmagnesium.[65,66] Likewise, using $\{H(N(Ar)C({}^tBu))_2CH\}$ (Ar = $C_6H_3{}^iPr_2$-2,6) and $MgMe_2$ in thf gave $[Mg\{(N(Ar)C({}^tBu))_2CH\}(Me)(thf)]$ (**c**), which under vacuum at 150 °C afforded the mononuclear three-coordinate metal complex $[Mg\{(N(Ar)C({}^tBu))_2CH\}(Me)]$ (**d**).[67] This is clearly due to a steric blocking of methyl bridging in (**d**), as evident by noting the values for (**a**–**d**) of the C_{ipso}–N–C (α) [117.7(4)° **a**, 115.4(3)° **b**, 124.4° av **c**, 125.7(2)° **d**] and C_{ipso}–N–Mg (β) [121.1(3)° **a**, 123.2(2)° **b**, 117.3° av **c**, 110.4(2)° **d**] angles.[65–67] (A similar effect has been observed in related Sc compounds, see section 4.3.1.) Similar methods were used to prepare the crystalline allyl analogue which, however, is a hexamer, the allyl group acting as a 1,3-bridge; the thf adduct is a monomer.[68] Crystalline magnesium β-diketiminates derived from the ligand $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]$ ($\equiv$ L) include (i) $[MgL(\mu\text{-}O^iPr)]_2$, which was shown to be an active catalyst for the living polymerization of lactide **IX**[33,72] (for a review of various catalysts used for this process, see ref 70); (ii) $[MgL(X)(OEt_2)]$ (X = O^iPr, O^tBu, I);[69] and (iii) $[MgL(\mu_3\text{-}BH_4)(OEt_2)]$ (octahedral Mg).[69] The compound MgL(Cl)(thf) behaved as a ligand transfer agent when treated with $FeCl_2(thf)_{1.5}$ (see Scheme 16).[29a] Treatment of dibenzylmagnesium with the appropriate tetracyclic diamine yielded the crystalline complex **8**.[71]



IX



8

To date the sole, crystallographically characterized β-diketiminate of the two heaviest natural group 2 metals is the dinuclear complex **2** (see section 3) obtained from $[Ba(NR_2)_2(thf)_2]$ (R = $SiMe_3$) and $H\{N(R^1)C(Me)\}_2CH$ (3 equiv).[56]

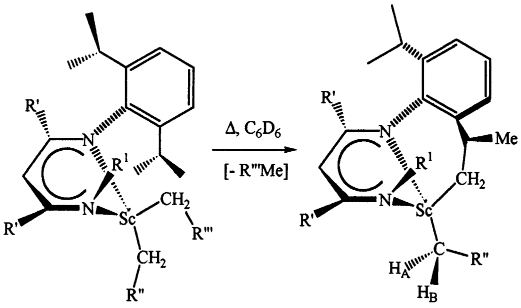
The crystalline compound $[MgL(O^tBu)(thf)]$, obtained from LiL and MeMgCl(thf), was an active catalyst for the ring-opening polymerization of *L*- or *rac*-lactide in CH_2Cl_2;[72] for a further discussion, using zinc catalysts, see section 4.5.

4.3. Early Transition Metal β-Diketiminates

4.3.1. Scandium β-Diketiminates

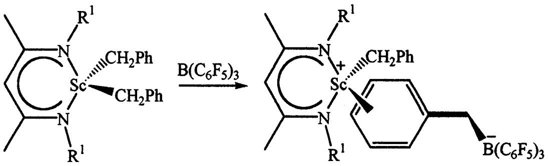
Two different approaches have been reported for the synthesis of scandium β-diketiminates: (i) the insertion of a nitrile into a scandium–1-azaallyl or a scandium–alkyl bond and (ii) the simple ligand transfer between the appropriate lithium β-diketiminate and scandium chloride. Procedure i was established for $[ScCp^*{}_2\{(N(H)C(C_6H_4OMe\text{-}4))_2CH\}]$; the proposed pathway is shown in Scheme 8 (R′ = C_6H_4-OMe-4).[73]

Examples of both neutral and zwitterionic β-diketiminatoscandium complexes have been prepared, as summarized in Schemes 9 and 10 and eqs 17 and 18.[74–76] Several of these compounds have been iso-



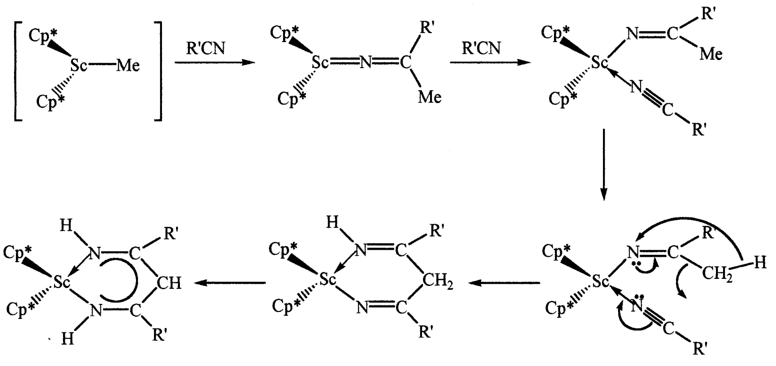
(17)

R'	R'' = R'''
^{t}Bu	H
^{t}Bu	Me
Me	Ph
^{t}Bu	Ph
Me	^{t}Bu
^{t}Bu	^{t}Bu
Me	R
^{t}Bu	R

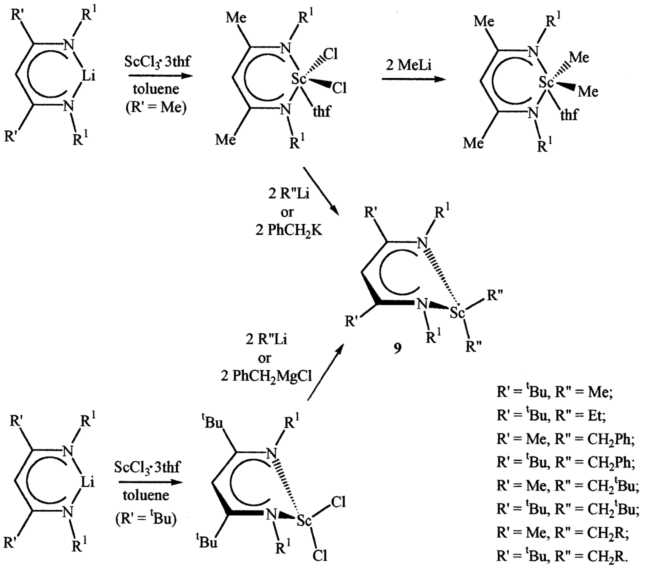


(18)

Scheme 8

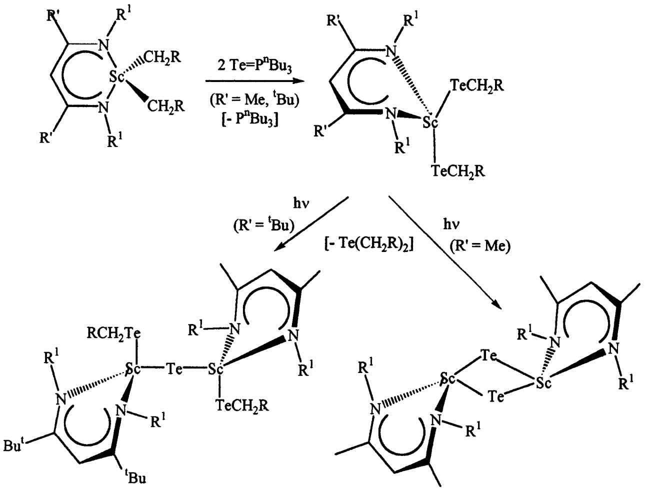


Scheme 9



$R' = {}^tBu$, $R'' = Me$;
$R' = {}^tBu$, $R'' = Et$;
$R' = Me$, $R'' = CH_2Ph$;
$R' = {}^tBu$, $R'' = CH_2Ph$;
$R' = Me$, $R'' = CH_2{}^tBu$;
$R' = {}^tBu$, $R'' = CH_2{}^tBu$;
$R' = Me$, $R'' = CH_2R$;
$R' = {}^tBu$, $R'' = CH_2R$.

Scheme 10

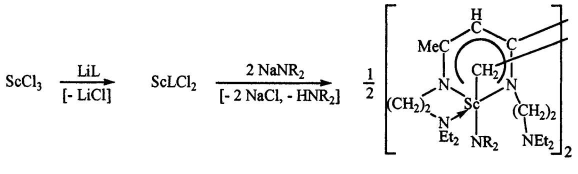


lated as base-free four-coordinate metal complexes. Steric interactions between $C_6H_3{}^iPr_2$-2,6 (= R^1) and the Sc-alkyl groups force the scandium in **9** (Scheme 9) to adopt the bonding mode **B**, with the β-diketiminato ligand functioning as a 4-electron donor (see section 3).[76] Variable-temperature NMR spectroscopy revealed coalescence behavior for these, consistent with equilibration of two such equivalent out-of-plane structures via a C_{2v} symmetric transition state of mode **A** (for **A** and **B**, see section 3); kinetic parameters for these fluxions were obtained.[76] The four-coordinate Sc dialkyls were somewhat thermally unstable in benzene solution, due to the cyclometalation of eq 17; these products (not included in Table 1) were identified spectroscopically.[76]

Treatment of $[Sc\{(N(R^1)C(Me))_2CH\}(CH_2Ph)_2]$ ($R^1 = C_6H_3{}^iPr_2$-2,6) with tris(pentafluorophenyl)borane gave the zwitterionic product of eq 18.[74]

A number of crystalline tellurium-containing β-diketiminatoscandium complexes were obtained as summarized in Scheme 10.[75]

Two crystalline scandium β-diketiminates based on the ligand $[\{N(CH_2CH_2NEt_2)C(Me)\}_2CH]^-$ ($\equiv L^-$) were prepared as shown in eq 19.[57] The distorted octahedral scandium dichloride (Cl−Sc−Cl′, 167°) upon treatment with $NaN(SiMe_3)_2$ underwent an unusual activation of one of the methyl groups of the ligand L^- to give the pentacyclic $(\mu$-$CH_2)_2$ dinuclear complex **4** (see section 3).



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(19)

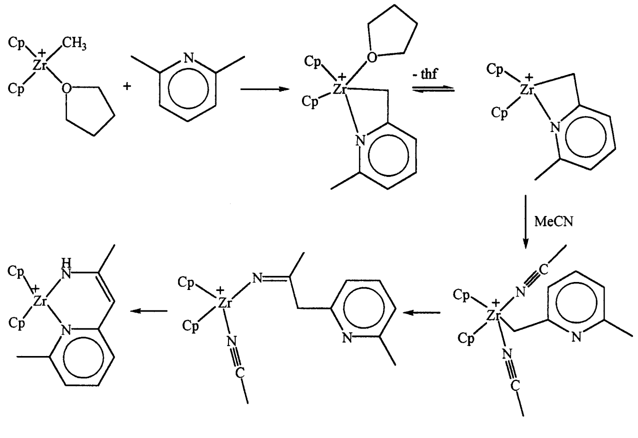
4.3.2. Group 4 Metal β-Diketiminates

The first β-diketiminatotitanium complexes were reported in 1998, partly in the context of their role as procatalysts for the polymerization of olefins.[77−80] The complex $[Ti\{(N(Ph)C(Me))_2CH\}Cl_2(thf)_2]$ was prepared from the corresponding lithium β-diketiminate and $[TiCl_3(thf)_3]$.[77,80] Similarly, using the ligand $[\{N(C_6H_2Me_3$-2,4,6$)C(R')\}_2CH]^-$ ($R' = Me$ or ${}^tBu$) or $[\{N(C_6H_3{}^iPr_2$-2,6$)C(Me)\}_2CH]^-$ afforded the crystalline Ti(III) dichlorides, which with LiMe gave the appropriate Ti(III) dimethyls which, except for the one derived from the 2,6-diisopropyl-substituted ligand, were thermally labile.[78] The crystalline $[Ti\{(N(C_6H_3{}^iPr_2$-2,6$)C(Me))_2CH\}Me_2]$ with $B(C_6F_5)_3$, unlike the isoleptic V(III) complex, was a low-activity catalyst for the polymerization of C_3H_6 or CH_2=CH-${}^nBu$, a process inhibited by toluene.[78] A DFT computational study on mono(β-diketiminato)M(III) alkyls (M = Ti, V, Cr) has shown that their propensity for undergoing insertion and chain termination by β-H transfer, when used as catalysts for olefin polymerization, was similar to catalysts such as corresponding M(III) complexes including $M(NMe_2)_2R$ or $[CrCp^*(X)R']$.[81]

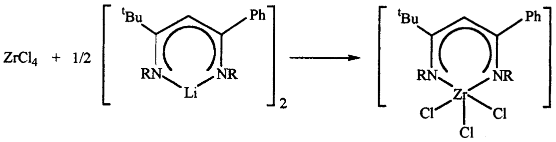
Using the ligand $[\{N(C_6H_4Me\text{-}4)C(Me)\}_2CH]^-$ (≡ L^-), the crystalline Ti(IV) complexes $[Ti(L)X_3]$ were obtained from $Ti(NMe_2)_4$ with HL (for X = NMe_2) or $TiCl_4$ with LiL (for X = Cl).[79]

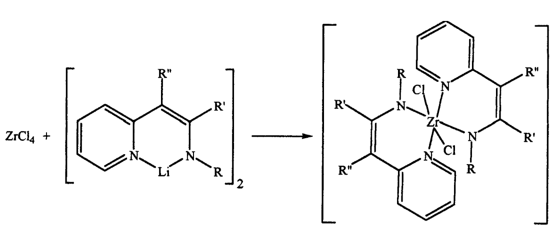
The first zirconium β-diketiminate complex of type **IV** was prepared in 1991 by the insertion of acetonitrile into a 1-azaallyl−Zr bond of a cationic Zr(IV) complex (Scheme 11); the anion was $[BF_4]^-$.[82]

Scheme 11



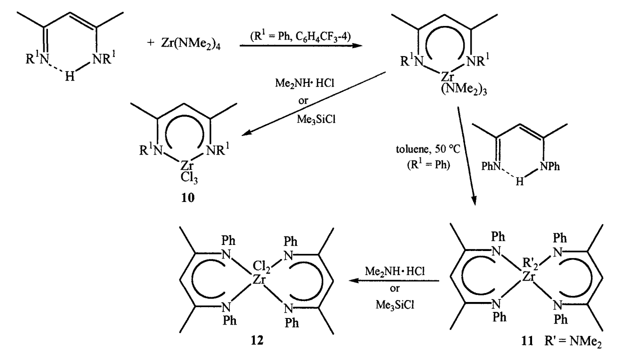
Several X-ray-characterized mono-[19,45] and bis-[60] β-diketiminatozirconium chlorides, produced by the reactions of eqs 20[54] [for structure, see Figure 2b, suggested to be an η^5-ligand−metal complex[19]] (or an analogue[45]) and 21 (or its quinolyl analogue, see **6**) (R′ = Ph or ${}^tBu$, R″ = H or R),[36,60,83,84] were shown to be active catalysts with MAO for the polymerization of ethylene and, to a lesser extent, propylene.


(20)

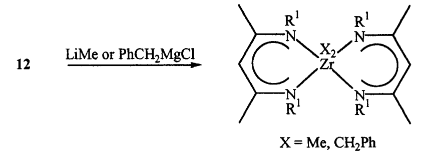

(21)

An alternative approach to the synthesis of β-diketiminatozirconium chlorides and dimethylamides was by amine eliminations, as shown for **10**−**12** in Scheme 12; the complexes **11** and **12**, like **13**, featured η^5-(2σ+π)-6-electron-bound (bonding mode **B**) ligands (for further discussion, see section 3).[85]

Scheme 12



From the Zr(IV) chlorides **10** and **12**, further complexes were obtained (eqs 22 and 23) (R^1 = Me or CH_2Ph).[85]



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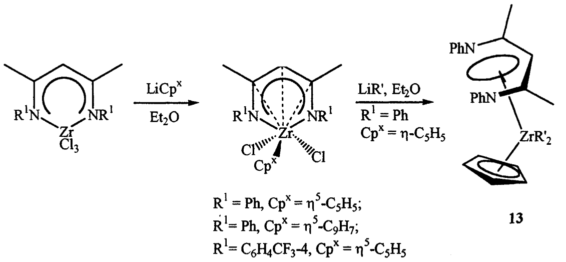
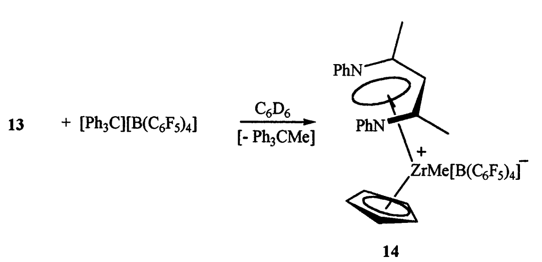


(23)

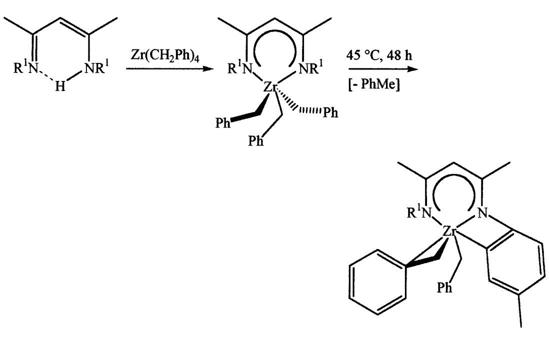
Ethylene polymerizations were conducted using the β-diketiminatozirconium complexes of Scheme 12 and eqs 22 and 23 in the presence of MAO.[86] The mono-β-diketiminates possessed low activity and provided polyethylenes (PEs) with a trimodal, very broad molecular weight distribution. Both the disubstituted complexes **11** and **12** and the cyclopentadienyl-type derivatives of eq 23 behaved as single-site catalysts under the same conditions, with the activity of the latter considerably higher. The dialkylated zirconium complexes afforded PEs with a significantly narrower molecular weight distribution than the corresponding dichlorides. The use of $[Ph_3C][B(C_6F_5)_4]$ and **13** yielded the salt **14** of eq 24 which, with small amounts of MAO, showed increase in catalytic activity. The $[B(Ar_F)_4]$ analogue of **14** with **13** gave the catalytically inactive $[(ZrCp\{(N(Ph)C(Me))_2CH\}Me)_2(\mu\text{-}Me)][B(Ar_F)_4]$, which with $AlMe_3$ yielded a compound formulated as $[ZrCp\{(N(Ph)C(Me))_2CH\}$-



(24)

(μ-Me)$_2$AlMe$_2$]$^+$; the latter with MAO was an active catalyst.

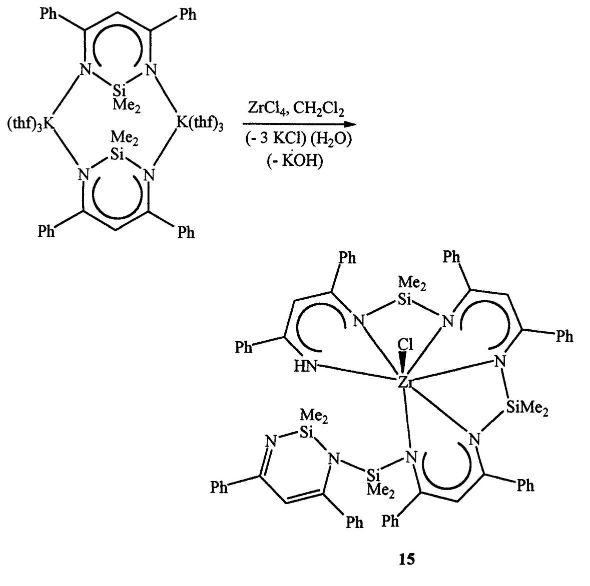
Interesting results on the synthesis and structures of various other five- and six-coordinate Zr(IV) β-diketiminates have been reported using the ligand [{N(C$_6$H$_4$Me-4)C(Me)}$_2$CH]$^-$ (≡ L$^-$).[79,87] The crystalline complex [ZrL(CH$_2$Ph)$_3$], obtained from [Zr(CH$_2$Ph)$_4$] and HL, eliminated toluene when heated, giving the crystalline cyclometalated product of eq 25 (R^1 = C$_6$H$_4$Me-4); the κ^2-formulation for one of the benzyl ligands in the final product is supported by the short Zr−C$_{ipso}$ bond length of 2.584(2) Å [cf. the Zr−CH$_2$ bond length of 2.302(2) Å].[87] The bulkier β-diketiminato ligand [{N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me)}$_2$CH]$^-$ (≡ L′$^-$) in the thermally more stable trialkyl [ZrL′Me$_3$], was obtained from ZrCl$_4$ and successively LiL′ and LiMe.[87] The crystalline compounds [ZrL′Cl$_3$(thf)], [ZrL′Cl$_3$], and [ZrL′$_2$Cl$_2$] were fully characterized.[79]



(25)

The amine elimination route was also (see Scheme 12) used for the synthesis of [ZrL(NMe$_2$)$_3$] and [ZrL$_2$(NMe$_2$)$_2$] from Zr(NMe$_2$)$_4$ and HL. With Ti(NMe$_2$)$_4$ only the tris(amido)TiL was accessible.[79] The amides with the appropriate R′OH gave [ZrL$_2$(OR′)$_2$] and [ZrL(OMe)$_3$] (R′ = Me, OC$_6$H$_4$Me-4, OCH$_2$C$_6$H$_4$Me-4).[79]

The fused pentacyclic crystalline tris(β-diketiminato)zirconium chloride **15** was obtained from the dinuclear potassium precursor (see Scheme 7) as shown in eq 26.[62a]



(26)

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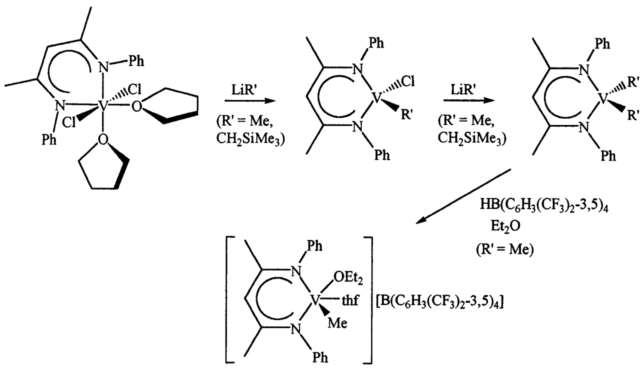
4.3.3. Group 5–7 Metal β-Diketiminates

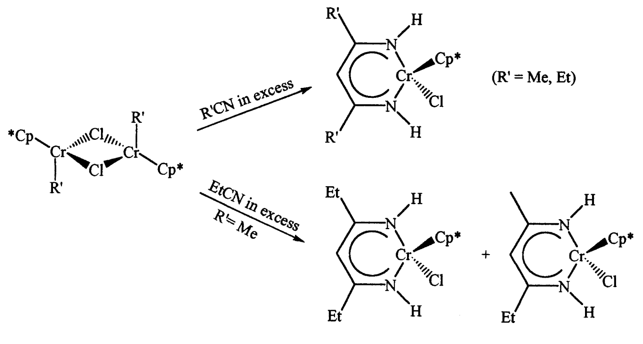
β-Diketiminatovanadium complexes date from 1998.[77,78] The complexes [VLCl$_2$] and [VLCl$_2$(thf)$_2$] [L = {N(Ph)C(Me)}$_2$CH] were prepared from LiL and VCl$_3$ or [VCl$_3$(thf)$_3$], respectively.[78] Some reactions of the latter are shown in Scheme 13. The [B(Ar$_F$)$_4$]$^-$ salt, like the adduct from the neutral dialkyl and B(C$_6$F$_5$)$_3$, was a catalyst for ethylene polymerization.[79,87] Further dichlorides and dialkyls were obtained similarly: [V{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}X$_2$] (X = Cl, Me, ^{n}Bu) and [V{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(^{t}Bu))$_2$CH}Cl$_2$].[78]

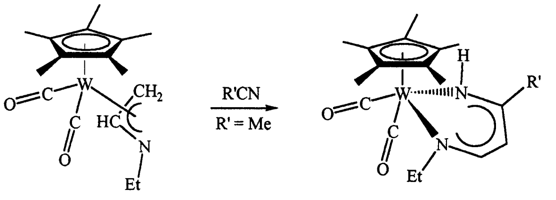
Scheme 13



The first chromium(III)[88] (1989) and tungsten(III)[89] (1993) β-diketiminates were prepared by the insertion methods of Scheme 14 and eq 27.

Scheme 14



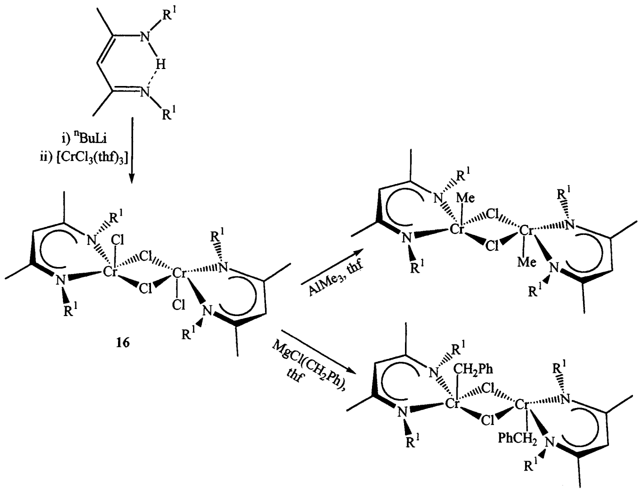


(27)

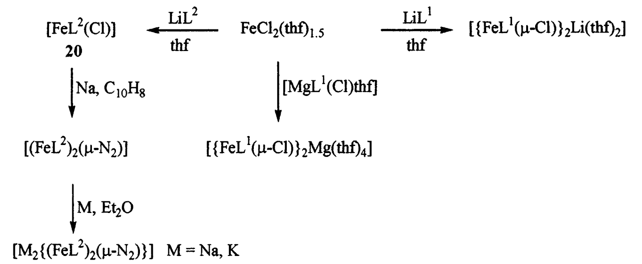
The crystalline chromium β-diketiminates, prepared according to Scheme 15 (R^1 = C$_6$H$_3$^{i}Pr$_2$-2,6), were shown to be active catalysts (with MAO, AlClEt$_2$ or AlClMe$_2$) for ethylene polymerization, yielding high molecular weight PEs.[30,90]

In contrast to the alkylation reactions of complex **16**, in which the (μ-Cl)$_2$ bridges were retained (Scheme 15), treatment of **16** with NaOC(O)R′ or Li-

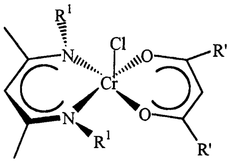
Scheme 15



Scheme 16



{(O(R′)C)$_2$CH} gave the mononuclear crystalline complexes **17** and **18**.[90]



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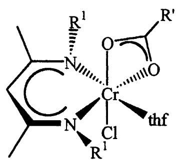
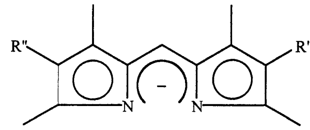


18

The first β-iminatomanganese compound was obtained in poor yield by the unusual redox reaction of eq 7.[42] Orange crystals of [Mn{(N(R)C(Ph))$_2$CH}$_2$] were obtained in almost quantitative yield from MnCl$_2$ and the lithium β-diketiminate.[91] Using MnI$_2$ and [LiL(OEt$_2$)] in diethyl ether gave the X-ray-characterized complex [MnL(μ-I)$_2$Li(OEt$_2$)], (L = [{N-(C$_6$H$_3{}^i$Pr$_2$-2,6)C(Me)}$_2$CH]).[6]

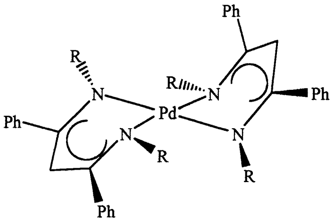
4.4. Late Transition Metal β-Diketiminates

Complexes considered in this section are those of the group 8−11 metals. In a 1966 review of the stereochemistry of bis(chelate)metal(II) complexes, a short section was devoted to the then available data on bis(β-iminate)s; these were then restricted to the homoleptic M(II) complexes of Co, Ni, and Cu.[2] The first of these was [Cu{(N(Ph)C(H))$_2$CH}$_2$].[12,13] Others, studied during 1964−1968, were of formula [M-{(N(R^1)C(R′))$_2$CH}$_2$] (R^1 = H, Me, Et, CH$_2$Ph, Ph, C$_6$H$_4$Me-3, C$_6$H$_4$Me-4; R′ = H, Me).[8a,11−13,16,17,92−94] The interest then was to establish their structures, in most cases by measurements of magnetic moments, ligand field spectra, and isotropic ^{1}H NMR spectral shifts. Of such complexes, only those with R^1 = H were judged to have a planar four-coordinate metal environment, the others being tetrahedral (Co) or distorted tetrahedral. The first X-ray structural data were reported for homoleptic complexes derived from a ligand **XI**: the distorted tetrahedral Cu(II) complex (R″ = CO$_2$Et, 1969)[15] and the D_2-symmetric Ni(II) analogue (R″ = H, 1970).[14]



XI

The effect on the metal environment of changing the N,N'-substituents on the nitrogen atoms from hydrogen (square planar) to trimethylsilyl (= R, distorted tetrahedral) was first demonstrated crystallographically in 1995 for the Co(II) complexes [M-{(N(R^1)C(Ph))$_2$CH}$_2$] [see Figure 2e,f][22,24] and has subsequently been reinforced by similar data for the Cu(II)[91,95] and Ni(II) (R^1 = R,[45] H[91,95]) analogues. In the spiro tetrahedral metal complexes [M{(N(R)C-(Ph))$_2$CH}$_2$], each of the six-membered metallacycles is coplanar (bonding mode **A**) for M = Fe, Co, Ni, or Cu but changes to planar and bonding mode **B** for M = Pd, as shown in **19**.[45] The dihedral angles between



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the two ligand planes in the tetrahedral complexes are 85.8° (Fe),[91,95] 90° (Co),[22,24] 78.4° (Ni),[45] and 71.7° (Cu);[91,95] this compares with 82.1° in [Ni{(N(Ph)C-(Me))$_2$CH}$_2$][96] and 84.2° in [Ni{(N(C$_6$H$_4$Cl-4)C-(H))$_2$Ph}$_2$].[97] The electronic perturbation due to the transmission of unpaired spin density from a Ni atom into the ligand for a series of homoleptic Ni(II) β-diketiminates has provided a tool for their conformational analysis,[98] by measuring the paramagnetically induced ^{1}H NMR chemical shifts.[99] Furthermore, if the substituents at C-2 and C-4 of the NCCCN backbone differed, such asymmetric complexes could be chiral and configurationally stable on the NMR time scale.[100]

The syntheses of the above homoleptic M(II) complexes were unexceptional (but see eq 5[9,10] and Scheme 4[44]) and involved the reaction of the β-diketimine or its hydrochloride with [NEt$_4$][MX$_4$] (X = Cl or Br[8a]) or M(OAc)$_2$ in the presence of a base such as NaOMe or aqueous ammonia.[8a,11−13,92−94] Alternatively, the reaction between [LiL]$_2$ and anhydrous MCl$_2$ (L = [{N(R)C(Ph)}$_2$CH]$^-$) or [PdCl$_2$(cod)] in diethyl ether yielded [M{(N(R)C(Ph))$_2$CH}$_2$] (M = Co,[22,24] Ni,[45] Cu,[91,95] Pd[45]). Treatment of [LiL]$_2$ with hydrated CoSO$_4$ gave [CoL′$_2$],[22,24] and the corresponding Ni and Cu complexes were obtained from the appropriate MCl$_2$ in the presence of a trace of water

($L' = [\{N(H)C(Ph)\}_2CH]$).[91,95] Other homoleptic M(II) β-diiminates reported were $[Co\{N(R^1)C(R'')C(R')C(R''')NR^1\}_2]$ [R^1 = Ph = R'', R' = H = R'''; R^1 = C_6H_4X-4 (X = Me, OMe, Br), R'' = Ph, R' = H = R'''; R^1 = C_6H_4Br-4 = R'', R' = H = R'''] and close Ni(II) and Cu(II) analogues.[48b]

The influence of varying the substituent R′ at C-2 and C-4 of the ligand $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(R')\}_2CH]^-$ ($\equiv [L^1]^-$ for R′ = Me, or $[L^2]^-$ for R′ = ^{t}Bu) has been demonstrated by the reactions of Scheme 16; the more bulky $[L^2]^-$ ligand gave rise to the crystalline, high-spin, three-coordinate Fe(II) complex **20**, whereas the other two, derived from $[L^1]^-$, were shown to have a high-spin, tetrahedral Fe(II) environment.[29a]

Complex **20** with sodium naphthalenide yielded the crystalline dinitrogen-bridged complex having a long N−N bond of 1.182(5) Å, which on further reaction with sodium or potassium gave the salts containing the corresponding dianion in which each of the N atoms of the bridging N_2 had short contacts to M (Na or K).[29b]

The crystalline, trigonal, planar Cu(I) complexes $[CuL^3]_n$ (bridging through the nitro group) and $[CuL^3(PPh_3)]$ were obtained as shown in eq 28,[51] whereas

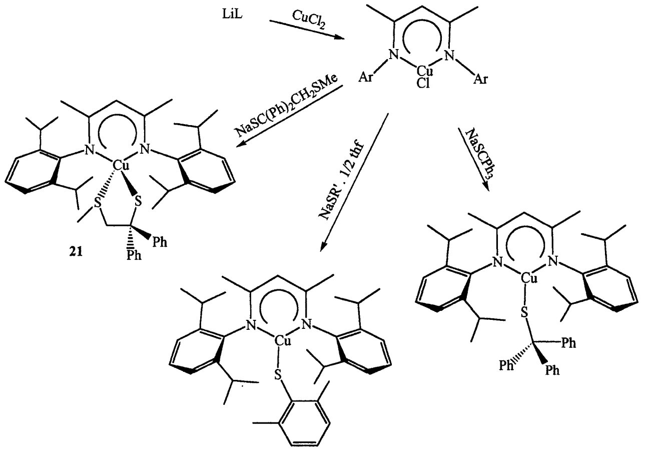
$$HL^3 + [Cu(NCMe)_4][PF_6] \xrightarrow{Et_3N,\ MeOH} \frac{1}{n}(CuL^3)_n \xrightarrow{PPh_3,\ MeOH} [CuL^3(PPh_3)] \quad (28)$$

$$TlL^4 + CuBr(SMe_2) \xrightarrow{CH_2=CHR} [Cu(L^4)(\eta\text{-}CH_2=CHR)] \quad (29)$$

the Cu(I)(L^4)-η-$CH_2{=}CHR'$ (R′ = H or Ph) complexes arose from the reactions of eq 29, which with O_2 yielded $[\{CuL^4(\mu\text{-}OH)\}_2]$ via a suggested $[\{CuL^4(\mu\text{-}O)\}_2]$ intermediate[101] [$L^3 = [\{N(C_6H_2Me_3\text{-}2,4,6)C(H)\}_2CNO_2]$, $L^4 = [\{N(C_6H_3Me_2\text{-}2,6)C(Me)\}_2CH]$].

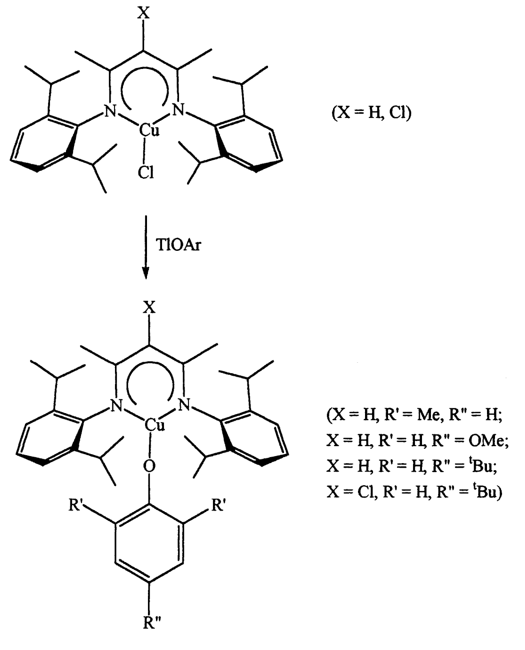
A number of crystalline β-diketiminatocopper(II) thiolates have been reported (Scheme 17, R′ = $C_6H_3Me_2$-2,6) and were regarded as structural models [especially the four-coordinate copper complex **21**; the $SC(Ph)_2CH_2OMe$ analogue was also obtained[32]] for a type 1 copper protein active site.[32,102,103]

Scheme 17



A further series of three-coordinate copper(II) complexes was obtained as shown in Scheme 18.[104] The phenolates were thermally stable but dioxygen-sensitive. These results were taken as shedding further light on the possible nature of intermediates involved in the processing of phenolic species by Cu(II) sites in biology and catalysis.

Scheme 18



The first rhodium β-diketiminate $[Rh\{(N(Ph)C(Me))_2CH\}(CO)_2][BF_4]$, obtained from $[Rh\{(COD)(\mu\text{-}Cl)\}_2]$ and the β-diketiminium tetrafluoroborate in EtOH, was reported in 1979; it comprised weak dimers, stacked in a columnar fashion, with Rh···Rh contacts of 3.271(3) Å.[105] The complex $[Rh\{(N(CH(Me)Ph\text{-}R)C(H))_2CH\}(COD)]$ was a catalyst for enantioselective hydrosilylation of prochiral ketones.[106]

The bulky $[\{N(C_6H_3X_2\text{-}2,6)C(Me)\}_2CH]^-$ (L^5, X = Me; L^6, X = Cl) ligands were effective in stabilizing the robust, crystalline, three-coordinate 14 e^{-1} Rh(I) complexes $[RhL^5(COE)]$,[150] $[RhL^6(COE)]$ (which has an additional Rh···Cl close contact)[151] and $[RhL^5(NBE)]$, prepared from LiL^5 or LiL^6 and the appropriate Rh(I) precursor; the four-coordinate Rh(I) complexes $[RhL^5(COD)\text{-}1,5]$, $[RhL^5(C_2H_4)_2]$, $[RhL^6(C_2H_4)_2]$, and $[RhL^5(COE)(NCMe)]$ were also obtained.[151] Solution NMR and IR spectroscopic data provided evidence for the existence of $[RhL^5(COE)(N_2)]$, $[RhL^5(COD\text{-}1,4)]$, $[RhL^5(Me_2C{=}CMe_2)]$, $[RhL^5(COE)(H_2)]$, and $[\{RhL^5(COE)(\mu\text{-}H)\}_2]$ (COE = cyclooctene, COD = cyclooctadiene, NBE = norbornene).[151] In solution, $[RhL^5(COE)]$ was fluxional (attributed to an allyl/hydride mechanism), implicating the $[RhL^5(cyclooctyl)H]$ isomer, which in the case of the iridium analogue $[IrL^5(cyclooctyl)H]$ was the preferred product, although with H_2 it yielded the crystalline $[IrL^5(COE)(H)_2]$.[151] Some ADF calculations were carried out to probe the observed hydrogenation and isomerization.[150,151]

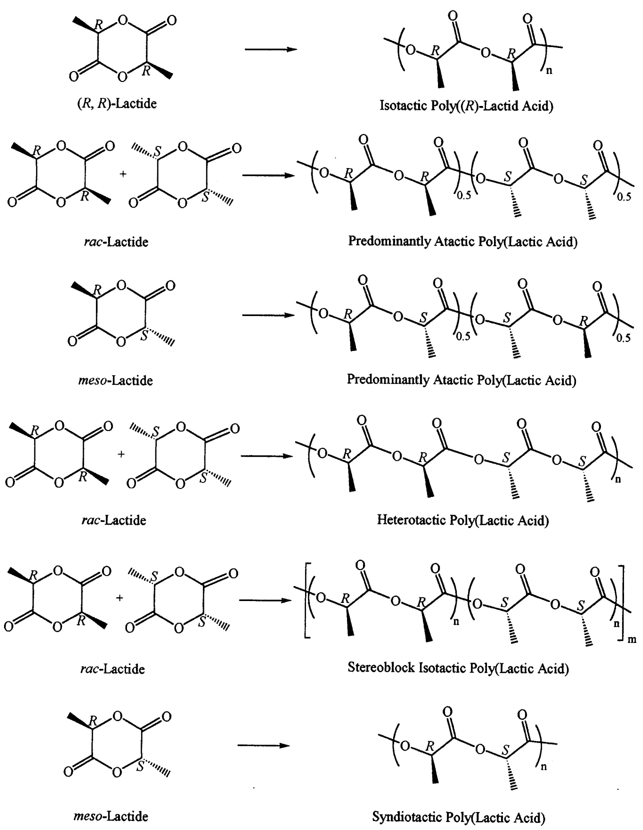
β-Diketiminatoplatinum complexes have received little attention. The cationic Pt(IV) complex of eq 6 was reported in 1976.[41] Recently the crystalline, five-coordinate, but thermally stable, platinum(IV) alkyl $[Pt\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Me_3]$ was preparedfrom the potassium β-diketiminate and $[\{PtMe_3(\mu\text{-}OTf)\}_4]$; variable-temperature ^1H NMR spectra showed it to be highly fluxional in solution down to

223 K.[31] It was light-sensitive in solution, but its thermal stability is noteworthy, as five-coordinate Pt(IV) alkyls are often highly labile intermediates in many reductive eliminations of Pt(IV) complexes.

4.5. Group 12 Metal β-Diketiminates

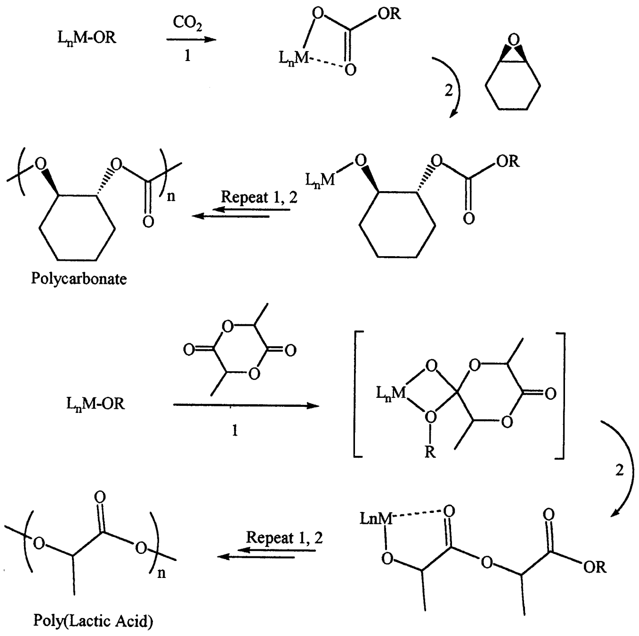
Early work on β-diiminates of zinc concerned the synthesis (from HL′ and $ZnCl_2$, in the presence of a base) and spectra of the complexes ZnL'_2 (L′ = [N(Et)C(H)C(H)C(Me)NEt],[10] $[\{N(Ph)C(H)\}_2CH]$,[12] and $[\{N(R^1)C(H)\}_2CPh]$ (R^1 = C_6H_4Cl-4, C_6H_4Me-4)[94]). Revival of interest in zinc β-diketiminates has largely been triggered by the disclosure that some are living single-site catalysts not only for the ring-opening polymerization of lactide (LA)[33,107,108] (see Scheme 19;[33] for a review of this topic using these and other catalysts, see ref 70) but also for the copolymerization of cyclohexene oxide (CHO) and carbon dioxide[35,109,110] [see Scheme 20, illustrated for a metal alkoxide, such as $[Zn(L)O^iPr]$.[35]

Scheme 19

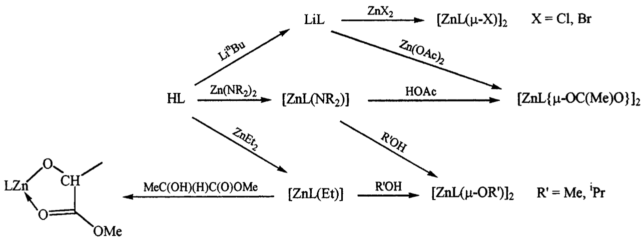


The heteroleptic β-diketiminatozinc complexes employed in these catalytic studies were prepared by the methods of Scheme 21, in which the ligand L = $[\{N(R^1)C(Me)\}_2CH]$ (R^1 = $C_6H_3R^2{}_2$-2,6 with R^2 = Me, Et, ^nPr, ^iPr; $C_6H_3{}^iPrR^3$-2,6 with R^3 = H, Me, Et, ^nPr; $C_6H_3Et^nPr$-2,6; $C_6H_2Me_3$-2,4,6) or $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(H)\}_2CH]$.[33,35] Representative examples were X-ray-characterized (see Table 1). Similar experiments yielded the complexes $[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}R']$ (R′ = Me, Ph, $^tBu(thf)$].[6b]

Scheme 20

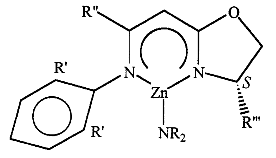


Scheme 21



Some significant observations on LA polymerization to PLA followed. (i) $[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}O^iPr)]_2$ (**21**) exhibited especially fast rates in CH_2Cl_2 and good control of polydispersity, and there was a linear relationship between the molecular weight of PLA and conversion, with the initiator as the end-group.[33] (ii) The importance of changing the 2,6-dialkylphenyl substituents was demonstrated by showing that **21** and *D,L*-LA yielded heterotactic PLA (especially at low temperatures), whereas 2,6-$Et_2C_6H_3$ or 2,6-$^nPr_2C_6H_3$ analogues were less selective.[33] (iii) With *meso*-LA, **21** yielded syndiotactic PLA, but at a lower rate than with *D,L*-LA.[33] Using the same β-diketiminato ligand as **21**, the corresponding thf adduct of the trimethylsiloxide was also an active catalyst, but less so than the crystallographically characterized isoleptic $[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(O^tBu)(thf)]$.[72]

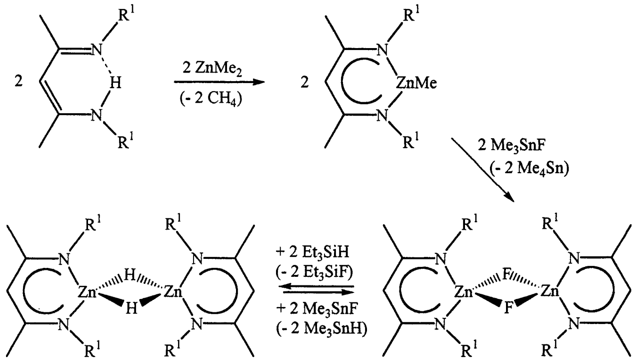
Active catalysts for the polymerization of CHO and CO_2 were of the formula $[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}X]$ (X = OR′, OCOR′, NR_2, but not with X = Cl, Br, Et), $[Zn\{(N(C_6H_3{}^iPr\text{-}2\text{-}Et\text{-}6)C(Me))_2CH\}(OMe)]$ (the most active), and $[Zn\{(N(C_6H_3Et_2\text{-}2,6)C(Me))_2CH\}X']$ (X′ = OMe, O^iPr, OAc, NR_2).[35] The polymers were atactic and of low polydispersity and contained *trans*-cyclohexane linkages in the main chain, consistent with backside attack of the epoxide during enchainment.[109,110] Restricted rotation about the *N*-aryl bond appeared to be important. Using an optically active complex **22** gave enantioselective copolymer, with R′ = ^iPr = R″ and R‴ = ^tBu the most active.[109]



22

The first examples of crystalline zinc compounds with bridging fluorine and hydrogen atoms were synthesized as represented in Scheme 22 ($R^1 = C_6H_3$-Me_2-2,6).[111]

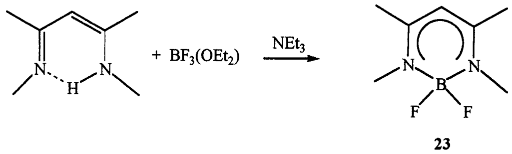
Scheme 22



The crystalline zinc and cadmium heterobimetallic complexes $[ML'(\mu\text{-}I)_2Li(OEt_2)]$ (M = Zn, Cd), isoleptic with the Mn(II) complex, were obtained from $[LiL'(OEt_2)]$ and MI_2, $L' = [\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]$;[6] $ZnCl_2$ and $[LiL'']_2$ gave the crystalline $[ZnL''(\mu\text{-}Cl)]_2$, $L'' = [\{N(R)C(Ph)\}_2CH]$.[112]

4.6. Group 13 Metal *β*-Diketiminates

The first simple group 13 metal *β*-diketiminates reported were boron complexes (1989−1992), prepared either from the *β*-diketimine and $BF_3(OEt_2)$, for example, to give **23** (eq 30);[113,114] or by heating a trialkylborane and a nitrile in an autoclave, for example, the crystalline $[B\{(N(H)C(Me))_2CCN\}Et_2]$ from BEt_3 and EtCN.[115] Reaction of **23** with $[Cr(CO)_3(NCMe)_3]$ gave crystalline $[B\{(N(Me)C(Me))_2CH\}F_2(Cr(CO)_3)]$ **24**, which has the ligand in bonding mode **B**, in contrast to the **A** in **23**.[113] Some geometrical parameters are compared in Figure 3.[113]



23 (30)

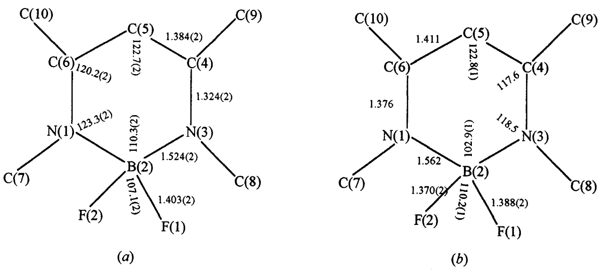
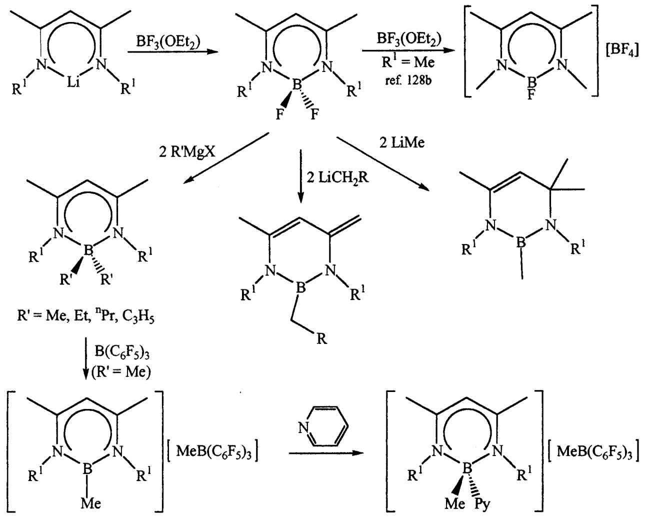


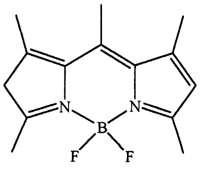
Figure 3. Selected geometrical parameters for **23** (a) and **24** (b).

Scheme 23

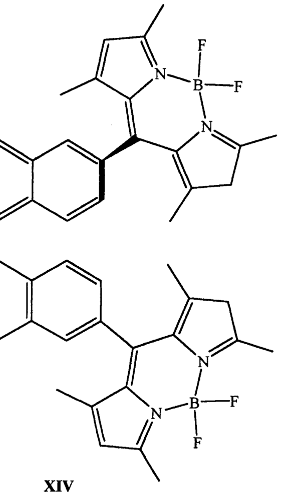


Data on *β*-diketiminatoboron complexes derived from the ligand $[\{N(C_6H_4Me\text{-}4)C(Me)\}_2CH]^-$, are summarized in Scheme 23 ($R^1 = C_6H_4Me$-4).[116a]

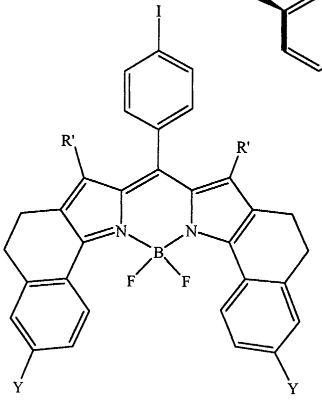
Predating these publications was a 1968 paper on fluorescent BF_2 complexes of di- and tripyrrylmethenes, using ligands of type **XI**, such as **XII**.[116b]



XII



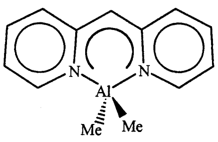
XIV



XIII

More recent studies have involved other boron dipyrromethane conjugates (BDP), including aryl-substituted 4,4′-difluoro-4-bora-3a,4a-diaza-5-indecene (BODIPY) dyes as fluorescent probes; examples are **XIII**[116c] and **XIV**[116d] (such complexes are not included in Table 1).

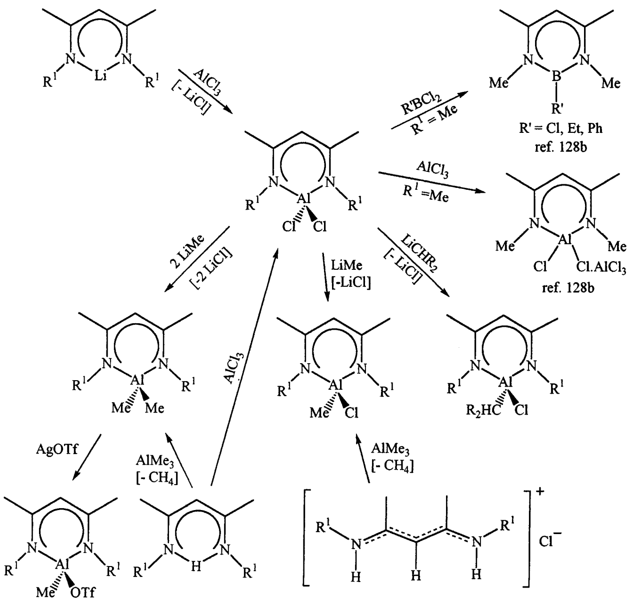
The first *β*-diketiminatoaluminum compound $[Al\{(N(Me)C(Me))_2CH\}Cl_2]$ was prepared in 1991 from $H[\{N(Me)C(Me)\}_2CH]$ and $AlCl_3/NEt_3$; with BCl_2R' it yielded $[B\{(N(Me)C(Me))_2CH\}R'][AlCl_4]$ (R′ = Cl, Et, Ph).[128b] One of the latter (R′ = Cl) with LiCl yielded $[B\{(N(Me)C(Me))_2CH\}Cl_2]$.[128b] The *β*-diketiminatoaluminum dimethyl **25** and its isostructural gallium complex were reported in 1994, prepared from the appropriate $MClMe_2$ (M = Al, Ga) and $[Li\{(2\text{-}NC_5H_4)_2\text{-}CH\}]$.[59]



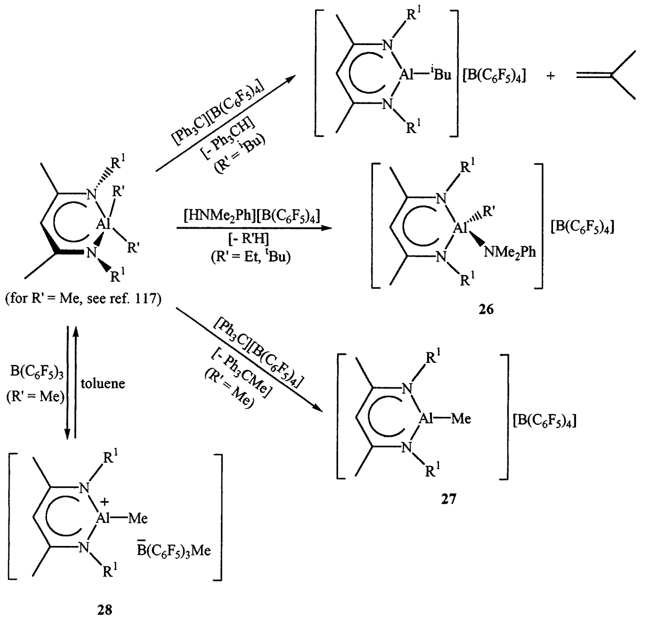
25

The next development, in 1998, related to the synthesis of a series of well-characterized complexes, as summarized in Scheme 24 ($R^1 = C_6H_4Me\text{-}4$).[117] The more hindered, crystalline $[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2\text{-}CH\}Me_2]$ was obtained from $AlMe_3$ and the β-diketimine.[117] The compounds $[Al\{(N(R^1)C(Ph))_2CH\}\text{-}R'_2]$ (R^1 = Ph, $C_6H_4Cl\text{-}4$; R′ = Me, Et) were prepared from PhC(O)N(R′)H and $AlMe_3$ or $AlEt_3$.[43]

Scheme 24

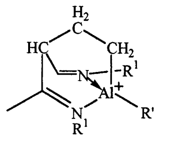


Scheme 25



Significant interest in this area was sparked by the disclosure that certain neutral and cationic *N*,*N*′-(chelate)aluminum alkyls were catalysts or procatalysts for the polymerization of olefins. The chelates have included β-diketiminates;[118,153] their preparation is summarized in Scheme 25 ($R' = C_6H_3{}^iPr_2\text{-}2,6$). Complexes **27** and **28** were structurally characterized. The former crystallizes as an ion pair in which the $[B(C_6F_5)_4]^-$ anion binds weakly to the Al atom of the cation through an *m*-fluorine, whereas the latter contains two cations and two anions that crystallize as $\{[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)]_2[B(C_6F_5)_3\text{-}Me]\}^+$ and $[B(C_6F_5)_3Me]^-$.

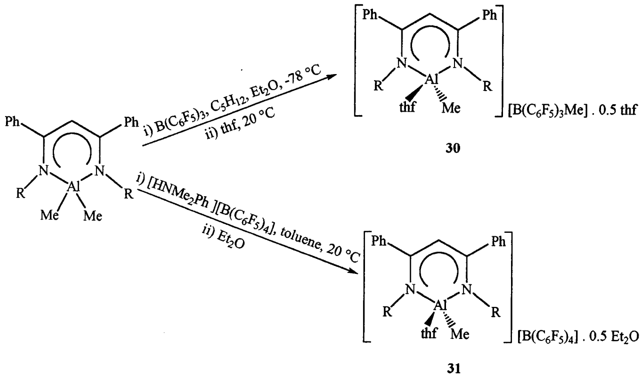
Treatment of salt **26** with C_2H_4 gave the salt containing the cation **29**, which with MeC≡CMe yielded C_2H_4 and the analogue in which the CH_2-CH_2 moiety was replaced by C(Me)=C(Me).[118]

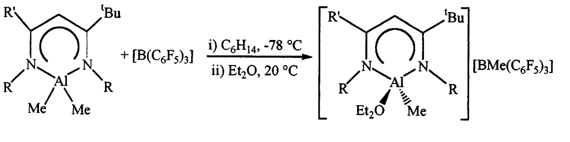


29

Results related to those of Scheme 25 were reported by our group, using the ligands $[N(R)C(R')C(H)C\text{-}(R'')NR]^-$ [R′ = R″ = Ph, $C_6H_4Me\text{-}4$, $C_6H_4OMe\text{-}4$; R′ = Ph; and R″ = $C_6H_4Me\text{-}4$, ${}^tBu$, 1-adamantyl (Ad); R′ = $C_6H_4Me\text{-}4$, R″ = ${}^tBu$].[46,119,120] The syntheses of selected crystalline examples are shown in Scheme 26[120] and eq 31 (R′ = $C_6H_4Me\text{-}4$);[46] the neutral precursors were obtained from $AlMe_3$ and the appropriate β-diketimine. The salts **30** and **31**, which were separated ion pairs, were the first such species to be structurally authenticated;[120] the Al atom is in a distorted monopyramidal environment, and the Al−N bond lengths are slightly longer and the N−Al−N′ bond angles slightly wider than in the neutral precursor.[120] Another dimethylaluminum β-diiminate, from the corresponding diimine and $AlMe_3$, was $[Al\{(N(PPh_2)C(H))_2CH\}Me_2]$.[49]

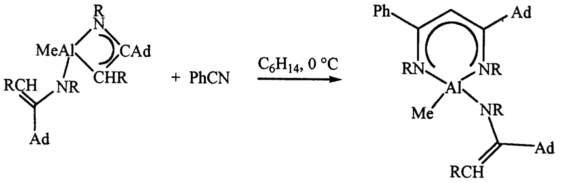
Scheme 26





(31)

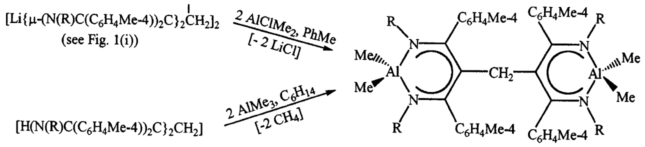
A crystalline β-diketiminato(1-azaallyl)aluminum methyl was prepared by the reaction of eq 32.[46] An



(32)

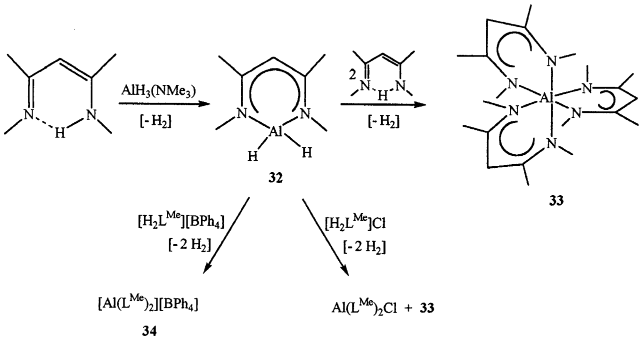
ansa-CH_2-bridged, crystalline (mode **B**), dinuclear complex was obtained, as shown in Scheme 27;[46] it is noteworthy that the isoleptic lithium (Figure 2i) and aluminum compounds have different structures.

Scheme 27



A number of interesting aluminum β-diketiminates derived from the ligands $[\{N(R^1)C(Me)\}_2CH]^-$ ($\equiv L^{R1-}$; R^1 = Me, ^iPr, Ph), including the X-ray-characterized compounds **32**,[121,122b] **33**,[122a,b] and **34**,[122b,123] were obtained as shown in Scheme 28; the *N,N'*-diisopropyl (X-ray) and -diphenyl analogues of **32** were also described.[121] The homoleptic complex **33** is a rare tris(β-diketiminato)metal complex (but see also **15** and Scheme 37).

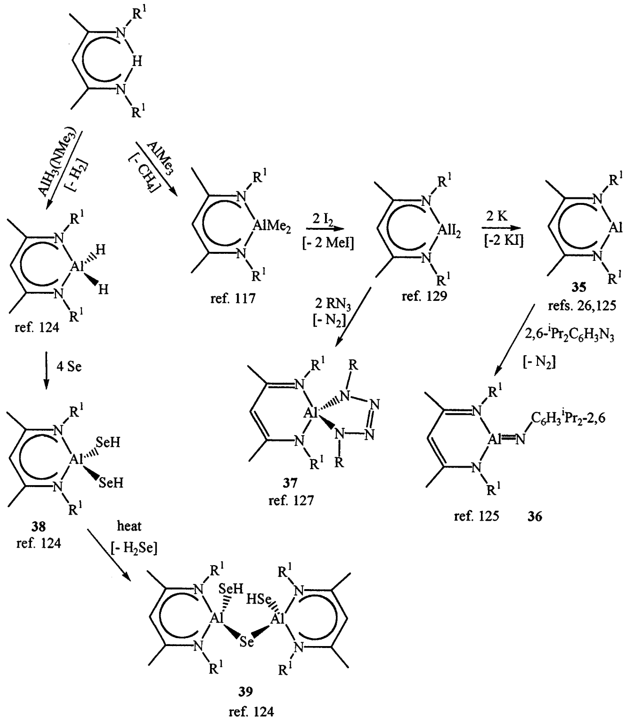
Scheme 28



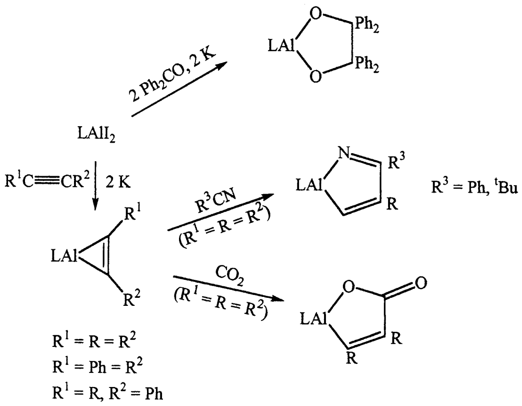
Using the bulkier ligand $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2\text{-}CH]^-$ ($\equiv L^-$), the derived β-diketiminato dihydride[124] and dimethyl[117] were precursors for further interesting complexes, the majority of which have been crystallographically authenticated, as summarized in Schemes 29 and 30. These data provide further examples of the role of a bulky β-diketiminato spectator ligand to stabilize unusual compounds, in this instance the aluminum(I) complex **35**,[26,125] the aluminum imide **36**,[125,126] the heterocycle **37**,[127] and the selenols **38** and **39**.[124]

Employing the same ligand L^-, the three crystalline β-diketiminatometal dichlorides were also (for Al and Ga, see ref 128a) prepared from $[LiL(OEt_2)]$ and $AlCl_3$, $GaCl_3$, and $InCl_3$, respectively, whereas using "GaI" yielded $GaLI_2$.[129] The similarly crystalline $[GaLMe_2]$ and $[InLMe_2]$ were obtained from HL

Scheme 29



Scheme 30



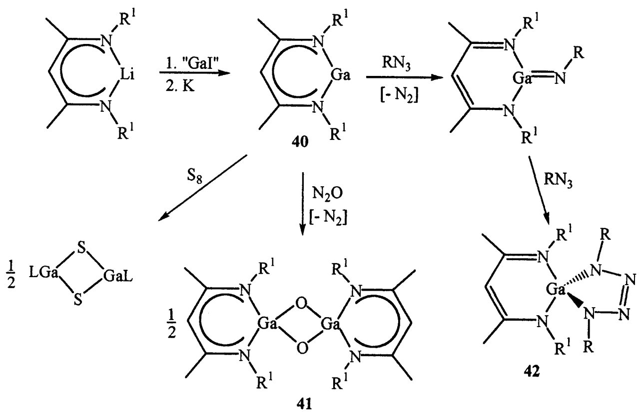
with $GaMe_3$ and $InLCl_2$ with MeMgBr, respectively.[129] However, with the ether-free LiL and "GaI", the product was the gallium(I) analogue **40**[27] of **35**, as shown, with further interesting reactions of **40** with N_2O,[130] S_8,[130] and trimethylsilyl azide,[131] in Scheme 31. Each of the crystalline products, except the gallium sulfide, was structurally established. Compound **41** is a unique dimeric gallium oxide,[130] and **41** and **42** are a structurally isomeric pair.

4.7 Group 14 Metal β-Diketiminates and a Phosphorus Analogue

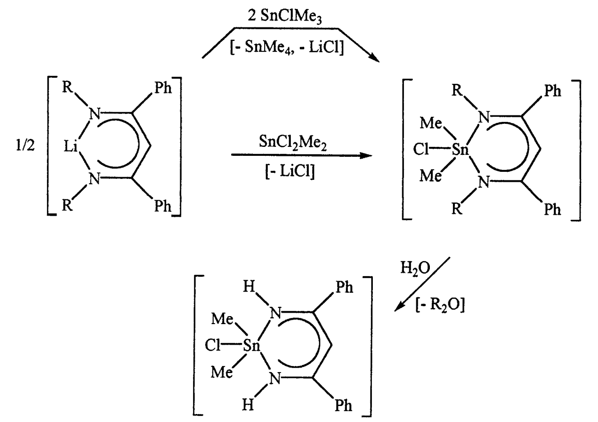
The first group 14 metal β-diketiminates $[Sn\{(N(R)C(Ph))_2CH\}Cl(Me)_2]$ (Figure 2c; mode **B**) and $[Sn\{(N(H)C(Ph))_2CH\}Cl(Me)_2]$ (Figure 2d; mode **A**) were obtained in 1994, as shown in Scheme 32. The reaction with $SnClMe_3$ is particularly surprising.[18]

Treatment of the appropriate potassium β-diketiminate with $SnCl_2$ or its hydrate yielded the crystalline $[Sn\{N(R)C(^tBu)C(H)C(Ph)N(R)\}Cl]$,[132] $[Sn\{N(H)C(^tBu)C(H)C(Ph)N(R)\}Cl]$,[24] and $[Sn\{N(H)C(^tBu)C(H)C(Ph)N(H)\}Cl]$.[132] The structure of each is

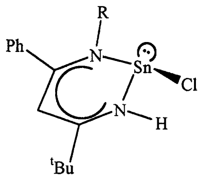
Scheme 31



Scheme 32



consistent with there being a stereochemically active lone pair, for example, **43**.[24] These reactions provide further illustrations that the N- and/or N'-$SiMe_3$ ($\equiv$ R) groups are not only of steric significance but also can be removable protecting groups.



43

The crystalline heteroleptic β-diketiminatotin(II) halides SnLX were prepared from SnX_2 and $[LiL]_2$, and it was noted that the second halide X^- was not displaceable by L^- (for related observations, see refs 133 and 134), L = $[\{N(R)C(Ph)\}_2CH]$.[91,95] This and further reactions of SnLCl are summarized in Scheme 33. X-ray data are available for SnLX′ (X′ = Cl, Br, NR_2) and **44**. The Sn(IV) compound **44** is particularly noteworthy, being only the third example of an Sn(IV) complex having a terminal sulfide and the first to have four-coordinate tin; selected geometric parameters are shown in Figure 4.[91,95] The exchange process between the chloride and the bromide, studied by 2D EXSY ^{119}Sn NMR spectroscopy, showed that they exchanged on the NMR time scale, believed to implicate a μ-Cl−μ-Br dinuclear transition state.[91]

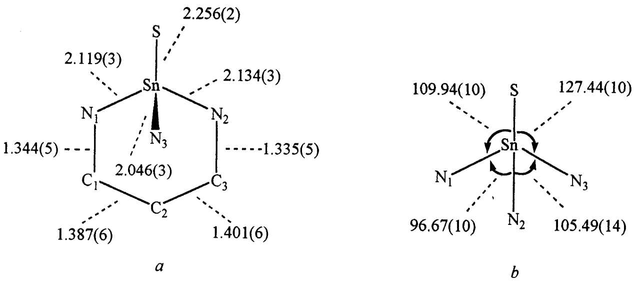
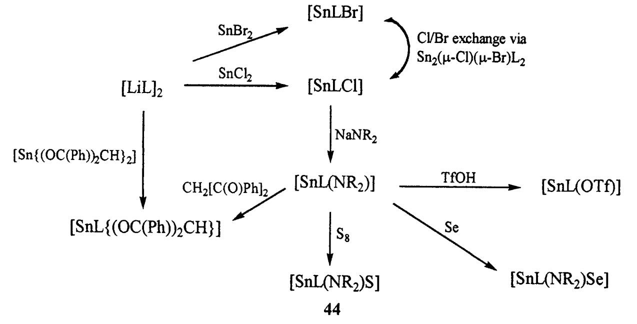
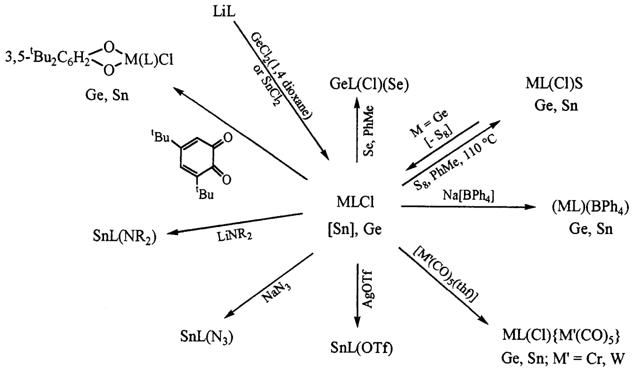


Figure 4. Selected bond lengths (angstroms) (a) and angles (degrees) (b) for **44**.

Scheme 33



Scheme 34



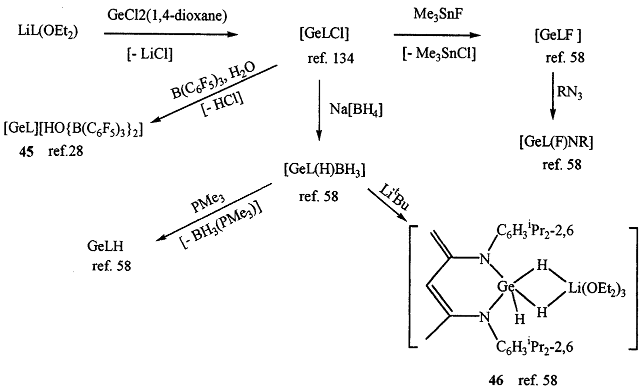
Reactions related to those of Scheme 33 and significant further extensions have been reported for germanium(II) β-diketiminates derived from the ligands $[\{N(R^1)C(Me)\}_2CH]^-$ [R^1 = Ph;[133] $C_6H_2Me_3$-2,4,6;[135] $C_6H_3{}^iPr_2$-2,6 (Ge,[28,58,134] Sn[34,134])], as summarized in Scheme 34 (L = $[\{N(Ph)C(Me)\}_2CH]$), eq 33 (L = $[\{N(C_6H_2Me_3\text{-}2,4,6)C(Me)\}_2CH])]$[135] and

$$\mathrm{LiL} \xrightarrow[\substack{\text{or SnCl}_2\\ [\text{- LiCl}]}]{\mathrm{GeCl_2(1,4\text{-}dioxane)}} \underset{\text{Ge, Sn}}{[\mathrm{MLCl}]} \xrightarrow[[\text{-NaCl}]]{\mathrm{NaN_3}} \underset{\text{Ge, Sn}}{[\mathrm{ML(N_3)}]} \tag{33}$$

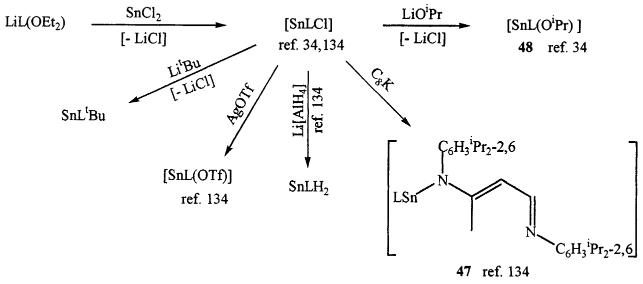
for L = $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]$ (Schemes 35[28,58,134] and 36,[34,134] respectively); X-ray data are available for those complexes shown in square brackets. Particularly noteworthy crystalline compounds are the two-coordinate β-diketiminatogermanium(II) cation of salt **45**,[28] the germanium(IV) hydride **46**, which can be regarded as a tautomer of a β-diketiminatogermanium(II) compound,[58] and the compound **47**,[134] which is an isomer of the unknown (and presumably too sterically hindered) SnL_2. The Sn(II) isopropoxide **48** was shown to be an initiator for the living ring-opening polymerization of *rac*-lactide to heterotactic-enriched poly(lactide) (for the more active isoleptic zinc complex, see section 4.5).[34]

Treatment of $LiL(OEt_2)$ with the appropriate tetrachloride $GeCl_4$ or SnX_4 in diethyl ether afforded

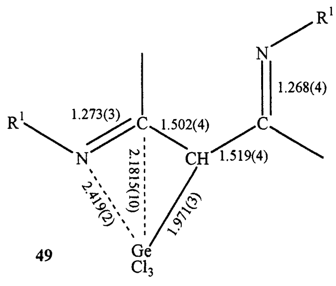
Scheme 35



Scheme 36



the metal trihalides [GeLCl$_3$] (**49**), SnLCl$_3$, and [SnLX$_3$] (X = Br, I).[52] Compound **49** is a thus far a unique example of *C*-bonded metal β-diketiminate (mode **E**); selected bond lengths (Å) are shown in Figure 5 (R^1 = C$_6$H$_3$^{i}Pr$_2$-2,6);[52] these data may be compared with those for the tin(IV) compounds of Figure 2c,d.[18] It may be, in our view, that an alternative interpretation of the X-ray data for compound **49** may be that it is a β-diketiminatogermanium 1,3-diazaallyl [GeL{N(R^1)=C(Me)NC(Me)=C(H)R^1}].



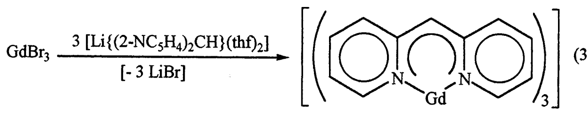
49

Figure 5.

Treatment of [P{W(CO)$_5$}$_2$(C$_5$Me$_5$)] with acetonitrile yielded the β-bis(iminato)phosphorus compound [P{N(H)C(C$_5$Me$_5$)C(H)C(H)NH} {W(CO)$_5$}$_2$].[136b]

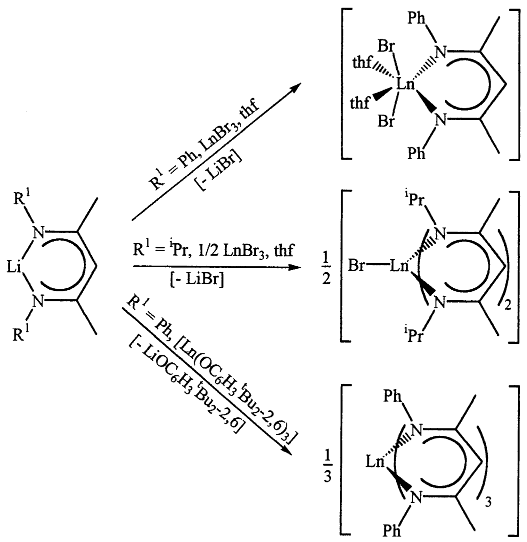
4.8. Lanthanide and Actinide β-Diketiminates

The first 4f-metal β-diketiminates were reported in 1994/1995, as shown in Schemes 37 (Ln = Sm, Gd; each was X-ray-characterized)[137,138] and 38[54,139] and eq 34.[140]

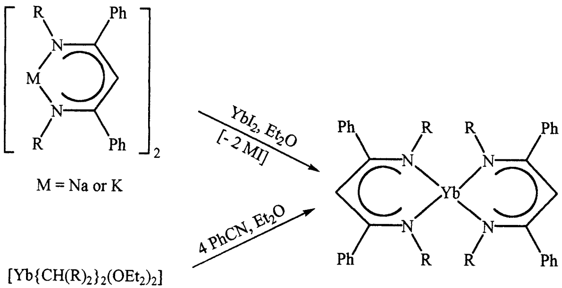


(34)

Scheme 37



Scheme 38



50

The structures of the crystalline homoleptic Yb(II) β-diketiminate **50** and of two analogues (see Table 1) have been investigated.[136a] The crystal structures show that in each three of the Yb–N bond distances are slightly shorter than the fourth and the variations in the endocyclic bond lengths, exemplified for [Yb{N(R)C(C$_6$H$_4$Me-4)C(H)C(Ad)NR}$_2$] in Figure 6,

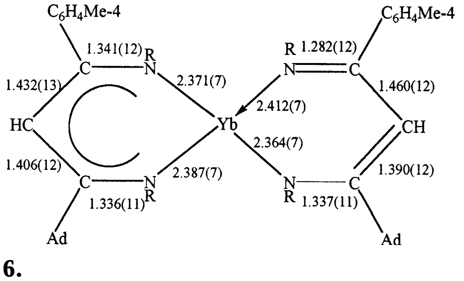


Figure 6.

are consistent with the notion that the canonical form [Yb(L){N(R)C(Ad)C(H)C(C$_6$H$_4$Me-4)=NR}] makes a contribution. Furthermore, in toluene-d_8 the ^{171}Yb-{^{1}H} chemical shift at 293 K is at the unexpected high frequency for a tetrahedral Yb(II) complex of δ 2634 for **50** (or 2624 and 2629 for the latter complex) (cf. ref 139 δ 820 and 830 for [Yb{N(R)C(^{t}Bu)C(H)R}$_2$].

The exceptionally large steric influence of the ligand [{N(R)C(Ph)}$_2$CH]$^-$ ($\equiv$ L$^-$) and various *N*,*N'*-bis(trimethylsilyl) analogues is further evident by the demonstration that (i) derived homoleptic Ln(III)

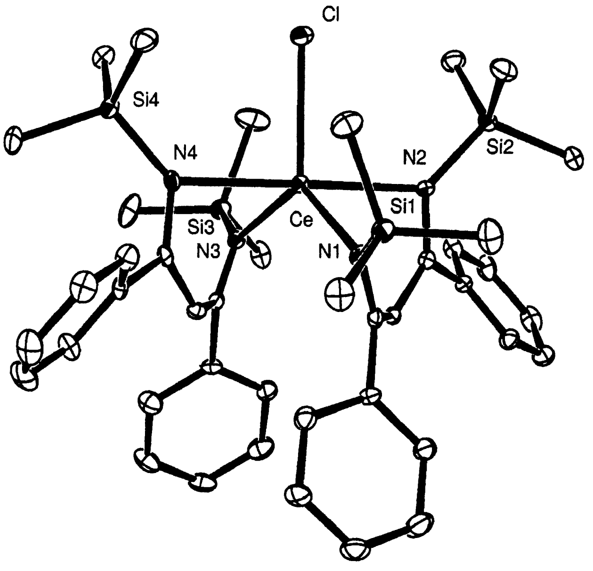
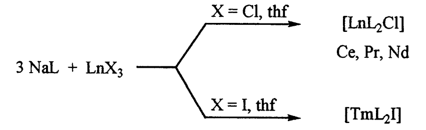


Figure 7.

β-diketiminates are not accessible (eq 35)[54] and (ii)



(35)

$$2\,\mathrm{LiCHR_2} + \underset{\mathbf{51}}{[\mathrm{CeL_2Cl}]} \xrightarrow{\mathrm{Et_2O}} \frac{1}{2}\,\underset{\mathbf{52}}{[\mathrm{CeL(CHR_2)_2}]} \qquad (36)$$

attempts to replace a halide from [LnL$_2$Hal] by a bulky alkyl led to the product of disproportionation (eq 36).[54] The crystal structures of **51** (Figure 7),[54] **52**,[141] and [CeL′(NR$_2$)$_2$] {obtained from [Ce(NR$_2$)$_3$] and HL′; L′ = [(N(R)C(C$_6$H$_4$^{t}Bu-4))$_2$CH]},[141] have been recorded.

Some remarkable, apparently subvalent, crystalline samarium and ytterbium β-diketiminates have been prepared recently and X-ray-characterized: [Sm$_2$L$_3$] [L = {N(R)C(Ph)}$_2$CH],[136a] [KSmL$_2$] (**53**),[136a] [Yb{LiL(thf)}$_2$] (**54**),[136a] [Yb{LiL′(thf)}$_2$],[136a] and [(YbL)$_3$(thf)] (**55**)[142] [L′ = {N(R)C(C$_6$H$_4$Ph-4)}$_2$CH]. If each of the L and L′ ligands is regarded as bearing a single negative charge (as has been assumed in all of the foregoing discussion in this review), then these complexes represent Sm and Yb in oxidation states 1^1/$_2$, 1, 0, 0, and 1, respectively. However, a more plausible interpretation is that the monoanionic β-diketiminato ligands L$^-$ and L′$^-$ have an accessible and hence partially occupied LUMO (e.g., L^{2-}). The syntheses of **53**, **54**, and **55** are illustrated by eqs 37,[136a] 38,[136a] and 39[142] and the structures of crystalline **53**[136a] and **55**[142] in Figures 8 and 9, respectively. Complex **53** is a centrosymmetric dimer; one of the ligands L of the monomeric binuclear moiety not only binds the Sm and K ions as shown in Figure 8 but also acts as a bridge by virtue of an η^6-Ph to the K′ ion of a second monomeric moiety.

$$\mathrm{SmI_2} + \mathrm{KL} \xrightarrow{\mathrm{Et_2O}} \underset{\mathbf{53}}{[\mathrm{KSmL_2}]} \qquad (37)$$

$$\mathrm{YbCl_3} \xrightarrow[\text{2. 2.3 Li}]{\text{1. 2 KL, thf}} \underset{\mathbf{54}}{[\mathrm{Yb\{LiL(thf)\}_2}]} \qquad (38)$$

$$\mathrm{YbL_2} + \mathrm{Yb(C_{10}H_8)(thf)_x} \xrightarrow[-\mathrm{C_{10}H_8}]{\mathrm{thf}} \underset{\mathbf{55}}{[\mathrm{(YbL)_3(thf)}]} \qquad (39)$$

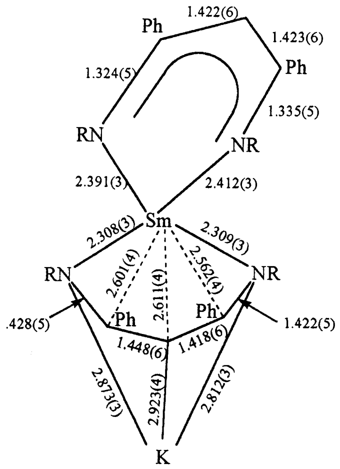


Figure 8.

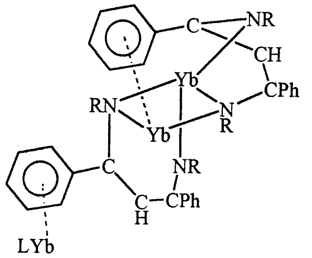
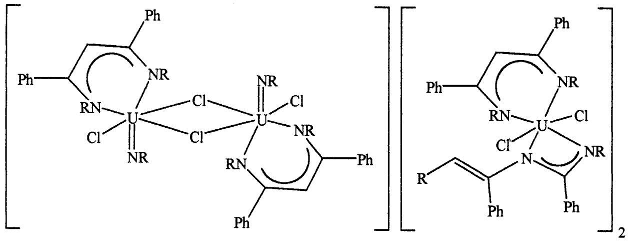
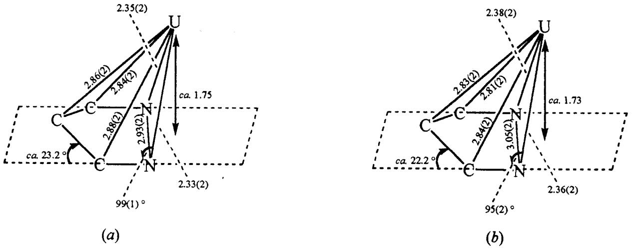


Figure 9.



56



(*a*)

(*b*)

Figure 10.

Only two 5f-metal β-diketiminates have been made. The reaction between UCl$_4$ and [LiL]$_2$ yielded the crystalline salt **56**, comprising the [{U^{VI}L(NR)(μ-Cl)}$_2$]$^{2+}$ cation and two dichloro-β-diketiminatouranium(III) 1,3-diazaallyl anions.[143] Selected geometric parameters of the UL moiety of the cation and anion are shown in parts a and b, respectively, of Figure 10.[143] By contrast, from ThCl$_4$ and [LiL]$_2$, the crystalline complex [ThL$_2$Cl$_2$] was obtained.[144]

Table 1. *β*-Diketiminatometal Complexes

complex	characterization	bonding mode	comments	ref
Group 1				
$[Li\{N(R)C(Ph)C(H)C(^tBu)N(R)\}]_2$	^1H, ^{13}C, and EA			19
$[Li\{(N(R)C(Ph))_2CH\}]_2$	^1H, ^{13}C, ^{29}Si, EA, and X-ray	C	central LiNLi′N′ ring	18
$[Li\{(N(R)C(C_6H_4Me\text{-}4))_2CH\}]_2$	^1H, ^{13}C, and EA			18
$[Li\{(N(R)C(C_6H_4OMe\text{-}4))_2CH\}]_2$	^1H, ^{13}C, MS, and EA			119
$[Li\{(N(H)C(C_6H_4OMe\text{-}4))_2CH\}]_2$	^1H, ^{13}C, MS and EA			119
$[Li\{(N(C_6H_3Me_2\text{-}2,6)C(R))_2CH\}]$	^1H, ^{13}C, and ^7Li			39, 40
$[Li\{\mu\text{-}(N(R)C(Ph))_2C\}]_2CH_2$	^1H, ^{13}C, ^7Li, ^{29}Si, MS, EA, and X-ray	H	from $CH_2[C\{C(Ph)NR\}_2H]_2$	46
$[Li\{N(R)C(Ph)C(H)(C_5H_4N\text{-}2)\}]_2$	^1H, ^{13}C, MS, and EA			36, 60
$[Li\{N(R)C(tBu)C(H)(C_5H_4N\text{-}2)\}]_2$	^1H, ^{13}C, MS, EA, and X-ray	C	central LiNLi′N′ ring	36
$[Li\{N(R)C(Ph)C(R)(C_5H_4N\text{-}2)\}]_2$	^1H, ^{13}C, MS, EA, and X-ray	C	central LiNLi′N′ ring	36, 60
$[Li\{N(R)C(Ph)C(H)(C_9H_6N\text{-}2)\}]_2$	^1H, ^{13}C, MS, and EA			36, 60
$[Li\{N(R)C(Ph)C(R)(C_9H_6N\text{-}2)\}]_2$	^1H, ^{13}C, MS, and EA			36, 60
$[Li\{N(R)C(Ph)C(R)(C_5H_4N\text{-}2)\}(OEt_2)(NCPh)]$	^1H, ^{13}C, and X-ray	B		36
$[Li\{(N(R)C(Ph))_2CH\}(tmen)]$	^1H, ^{13}C, EA, and X-ray	A		55
$[Li\{(N(R)C(Ph))_2CH\}(thf)(NCPh)]$	^1H and ^{13}C			55
$[Li\{(N(R)C(Ph))_2CH\}(thf)_2]$	^1H, ^{13}C, ^7Li, and X-ray	A		55
$[Li\{(N(R)C(Ph))_2CH\}(NEt_3)_2]$	^1H and ^{13}C			55
$[Li\{[N(C_6H_3Me_2\text{-}2,6)C(R)C(H)C(Ph)N(R)\}\text{-}(tmen)]$	^1H, ^{13}C, and ^7Li			39, 40
$[Li\{(2\text{-}NC_5H_4)_2CH\}(thf)_2]$	^1H, ^{13}C, ^7Li, MS, EA, and X-ray	A	from ligand **IV**	59
$[Li\{(2\text{-}NC_5H_4)_2CH\}((2\text{-}NC_5H_4)_2CH_2)]$	X-ray	A	solvated by free ligand (**IV**)H	59
$[Li\{(N(R)C(H))_2CH\}(OP(NMe_2)_3)]_2$	^1H, ^{13}C, ^7Li, ^{31}P, IR, EA,and X-ray	A	dimer with bridging $PO(NMe_2)_3$	61
$[Li\{(N(R)C(Ph))_2CH\}(OEt_2)(LiCHR_2)]$	^1H, ^{13}C, ^7Li, MS, EA, and X-ray	D	$LiCHR_2$ acts as acceptor	39, 40
$[Li\{(N(R)C(Ph))_2CH\}(thf)(LiCHR_2)]$	^1H, ^{13}C, ^7Li, EA, and X-ray	D	$LiCHR_2$ acts as acceptor	39, 40
$[Li(12\text{-}crown\text{-}4)_2][Li\{(2\text{-}NC_5H_4)_2CH\}_2]$	^7Li, CP/MAS, MS, and X-ray	A	lithiate anion; ligand **IV**	59
$[Li\{(N(^tBu)C(R))_2CH\}(CN^tBu)(LiCHR_2)]$	^1H, ^{13}C and ^7Li, and X-ray	D	$LiCHR_2$ acts as acceptor	39, 40
$[Li\{(N(PPh_2)C(H))_2CH\}(thf)_2]$	^1H and ^{13}C			49
$[Li\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(thf)]$	^1H, ^{13}C, ^7Li, and X-ray	A		37, 78
$[Li\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(OEt_2)]$	^1H, ^{13}C, ^7Li, and X-ray	A		37, 104
$[Li\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}]_n$	^1H, ^{13}C, ^7Li, and X-ray	$A+\mu\text{-}\kappa^3$	two forms: a dimer and a dodecamer	37
$[Li\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CCl\}(OEt_2)]$	^1H, EA, and X-ray	B		104
$[Li\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(^tBu))_2CH\}(thf)]$	^1H, ^{13}C, and X-ray	A		78
$[Li\{(N(R)C(C_6H_3Me_2\text{-}2,6))_2Si(R)\}(thf)_3]$	^1H, ^{13}C, ^7Li, and EA		3-sila-*β*-diketiminato complex	145
$[Li\{(N(R)C(C_6H_3Me_2\text{-}2,6))_2Si(R)\}\text{-}(NCC_6H_3Me_2\text{-}2,6)_3]$	^1H, ^{13}C, ^7Li, ^{29}Si, and EA	B	3-sila-*β*-diketiminato complex	145
$[Li\{(N(R)C(C_6H_3Me_2\text{-}2,6))_2Si(R)\}\text{-}(NCC_6H_3Me_2\text{-}2,6)_2]$	^1H, ^{13}C, ^7Li, EA, and X-ray	B	3-sila-*β*-diketiminato complex	145
$[Li\{(N(SiMe_2NMe_2)C(Ph))_2CH\}]$	^1H and ^{13}C			146
$[LiGe(R)\{C(Ph){=}N(R)\}_2]_2$	^1H, ^{13}C, ^7Li, EA, and X-ray		3-germa-*β*-diketiminato complex	145
$[Na\{(N(R)C(Ph))_2CH\}(thf)_2]$	^1H, ^{13}C, EA, and X-ray	A		45
$[K\{(N(R)C(Ph))_2CH\}]_2$	^1H, ^{13}C, and EA		from $PhCN + KCHR_2$ or $KO^tBu + Li(LL)$	18
$[K\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}]\cdot PhMe$	^1H, IR, EA, and X-ray	B	each monomeric unit has an $\eta^5\text{-}C_6H_3{}^iPr_2\text{-}2,6$ contact to a neighboring K	62b
$[K\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(^tBu))_2CH\}]_n$	^1H and ^{13}C			78
$[K\{(N(R)C(Ph))_2CH\}(thf)_2]_n$	^1H, ^{13}C, ^{29}Si, EA, and X-ray	H		45
$[K\{(N(H)C(Ph)C(H)C(Ph)N(R)\}(thf)_2]_2$	^1H, ^{13}C, ^{29}Si, EA, and X-ray	H		62a
$[K\{(N(H)C(Ph)C(H)C(Ph)N(R)\}(tmen)]_2$	^1H, ^{13}C, ^{29}Si, EA, and X-ray	H		45
$[K\{(N(H)C(Ph))_2CH\}(thf)_{0.5}]_n$	^1H and ^{13}C			62a
$[K\{(N(H)C(Ph))_2CH\}]n$	X-ray	H	insoluble in cold thf	62a
$[K\{NSi(Me)_2NC(Ph)C(H)C(Ph)\}(thf)_3]_2$	^1H, ^{13}C, ^{29}Si, EA and X-ray	H		62a, 146, 147
Group 2				
$[Mg\{(N(R)C(Ph))_2CH\}_2]$	^1H, ^{13}C, EA, and X-ray	A	from $MgBr_2 + Li(LL)$; tetrahedral metal center	53
$[Mg\{N(R)C(Ph)C(H)C(^tBu)N(R)\}_2]$	^1H, ^{13}C, and EA			53
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)(thf)]$	^1H, ^{13}C, EA, and X-ray	B		65
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}Me)]_2$	^1H, ^{13}C, EA, and X-ray	B		65, 66

Table 1. Continued

complex	characterization	bonding mode	comments	ref
Group 2 (Continued)				
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(Me)(thf)]$	^1H, ^{13}C, EA, and X-ray	B	distorted tetrahedral geometry around magnesium atom	67
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(Me)]$	^1H, ^{13}C, EA, and X-ray	B	trigonal planar geometry around Mg atom	67
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(CH_2CH{=}CH_2)(thf)]$	^1H, EA, and X-ray	B		68
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(\mu\text{-}CH_2CHCH_2)]_6$	^1H, EA, and X-ray	B		68
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)(OEt_2)]$	^1H, ^{13}C, and EA	B		66
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}({}^tBu)]$	^1H, ^{13}C, and EA	A		66
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(O{}^tBu)]$		A	review on polymerization of lactide and related cyclic esters	70
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}O{}^iPr)]_2$	^1H, ^{13}C, and X-ray	A	catalyst for living polymerization of lactide	33
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl(thf)]$	^1H			29a
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}({}^iPr)(OEt_2)]$	^1H, ^{13}C, IR, MS, EA, and X-ray	B		69
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}I(OEt_2)]$	^1H, ^{13}C, IR, MS, EA, and X-ray	B		69
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}H)_3(BH)(OEt_2)]$	^1H, ^{13}C, IR, MS, EA, and X-ray	B	first μ-H_3 bridged BH_4−Mg complex	69
$[Mg\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(O{}^tBu)(thf)]$	^1H and X-ray	B		72
$[Mg\{(N(Me)C(Me))_2CH\}_2]$	^1H, ^{13}C, MS, and EA			63
$[Mg(1,2\text{-}\overline{NC_6H_4NC(Me)C(H)C(Me)N}\}_2(thf)]$	^1H, EA, and X-ray	A		71
$[Ca\{(N(R)C(Ph))_2CH\}_2]$	^1H, ^{13}C, and EA			64
$[Sr\{(N(R)C(Ph))_2CH\}_2]$	^1H, ^{13}C, and EA			64
$[Ba\{(N(R)C(Ph))_2CH\}_2]$	^1H, ^{13}C, and EA			64
$[Ba_2\{(N(C_6H_{11}\text{-}c)C(Me))_2CH\}_3(NR_2)]$	^1H, EA, and X-ray	B, G, H	bridging $[-N(C_6H_{11}\text{-}c)C(Me)-C(H)C(Me){=}N(C_6H_{11}\text{-}c)]^-$	56
Group 3				
$[Sc\{(N(H)C(C_6H_4OMe\text{-}4))_2CH\}(Cp^*)_2]$	^1H, ^{13}C, IR, and EA		by insertion of RCN into Sc−Me bond	73
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl_2(thf)]$	^1H, ^{13}C, UV−vis, EA, and X-ray	B		74, 76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}Cl_2]$	^1H, ^{13}C, UV−vis, EA, and X-ray	B		74, 76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)_2(thf)]$	^1H, ^{13}C, UV−vis, EA, and X-ray	B		74, 76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(CH_2R)_2]$	^1H, ^{13}C, UV−vis, EA, and X-ray	B		74, 76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(CH_2R)_2]$	^1H, ^{13}C, UV−vis, EA, and X-ray	B		74, 76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(CH_2Ph)_2]$	^1H, ^{13}C, UV−vis, and EA			74, 76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(Me)_2]$	^1H, ^{13}C, UV−vis, EA, and X-ray	B		76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(Et)_2]$	^1H, ^{13}C, UV−vis, EA, and X-ray	B		76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(CH_2Ph)_2]$	^1H, ^{13}C, UV−vis, EA, and X-ray	B		76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(CH_2{}^tBu)_2]$	^1H, ^{13}C, UV−vis, and EA			76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(CH_2{}^tBu)_2]$	^1H, ^{13}C, UV−vis, and EA			76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}Cl(Me)]$	^1H, ^{13}C, and EA			76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(Me)(CH_2R)]$	^1H and ^{13}C			76
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(CH_2Ph)(\eta^6\text{-}C_6H_5CH_2B(C_6F_5)_3)]$	^1H, ^{13}C, and X-ray	B	zwitterionic Sc^+/B^-	74
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(TeCH_2R)_2]$	^1H, ^{13}C			75
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(TeCH_2R)_2]$	^1H, ^{13}C, ^{125}Te, EA, and X-ray	B		75
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}Te)]_2$	^1H, ^{13}C, EA, and X-ray	B		75
$[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu))_2CH\}(TeCH_2R)]_2(\mu\text{-}Te)$	^1H, ^{13}C, EA, and X-ray	B		75
$[\overline{Sc\{(N(CH_2CH_2N}Et_2)C(Me))_2CH\}Cl_2]$	^1H, ^{13}C, ^{45}Sc, MS, EA, and X-ray	B	six-coordinate Sc; Cl's axial	57
$[\overline{Sc\{(NCH_2CH_2N}Et_2)C(Me)C(H)(\mu\text{-}CH_2)N(CH_2CH_2Et_2)\}(NR_2)]_2$	^1H, ^{13}C, ^{29}Si, ^{45}Sc, MS, EA, and X-ray	B, I	five-coordinate Sc	57
Group 4				
$[Ti\{(N(Ph)C(Me))_2CH\}Cl_2(thf)_2]$	^1H, ^2H, μ_{eff}, EA, and X-ray		active procatalyst for ethylene polymerization and ethylene/α-olefin copolymerization	77, 80
$[Ti\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}Cl_3]$	^1H, ^{13}C, and EA			78, 79
$[Ti\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(NMe_2)_3]$	^1H, ^{13}C, EA, and X-ray	B		79
$[Ti\{(N(C_6H_2Me_3\text{-}2,4,6)C(Me))_2CH\}Cl_2]$	^1H, ^{13}C, EA, and X-ray	A		78
$[Ti\{(N(C_6H_2Me_3\text{-}2,4,6)C(Me))_2CH\}(Me)_2]$	EA and X-ray	A	with $B(C_6F_5)_3$, an active catalyst for ethylene polymerization and ethylene/α-olefin copolymerization	78

Table 1. Continued

complex	characterization	bonding mode	comments	ref
	Group 4 (Continued)			
[Ti{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}Cl$_2$]	X-ray	A		78
[Ti{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}(Me)$_2$]			active procatalyst for ethylene polymerization and ethylene/α-olefin copolymerization	78
[Ti{(N(C$_6$H$_2$Me$_3$-2,4,6)C(^{t}Bu))$_2$CH}Cl$_2$]				78
[Ti{(N(C$_6$H$_2$Me$_3$-2,4,6)C(^{t}Bu))$_2$CH}(Me)$_2$]	EA and X-ray	A	active procatalyst for ethylene polymerization and ethylene/α-olefin copolymerization	78
[Zr{N(H)C(Me)C(H)(2-NC$_5$H$_3$Me-3)}(Cp)$_2$]	^{1}H			82
[Zr{N(R)C(Ph)C(H)C(^{t}Bu)N(R)}Cl$_3$]	^{1}H, ^{13}C, EA, and X-ray	B	procatalyst for olefin polymerization	19−21
[Zr{η^2-C,N-CH$_2$[6-Me-pyrid-2-yl]}Cp$_2$][BPh$_4$]	^{1}H, IR		by insertion of MeCN into Zr−(1-azaallyl) bond	82
[Zr{(N(R)C(Ph))$_2$CH}Cl$_3$]	^{1}H, ^{13}C, EA, and X-ray	B		45
[Zr{N(R)C(Ph)C(H)(C$_5$H$_4$N-2)}$_2$Cl$_2$]	^{1}H, ^{13}C, and EA		ethylene polymerization procatalyst	83, 84
[Zr{N(R)C(Ph)C(R)(C$_5$H$_4$N-2)}$_2$Cl$_2$]	^{1}H, ^{13}C, MS, and EA		ethylene polymerization procatalyst	60, 83, 84
[Zr{N(R)C(^{t}Bu)C(R)(C$_5$H$_4$N-2)}$_2$Cl$_2$]	^{1}H, ^{13}C, EA, and X-ray	B	ethylene polymerization procatalyst	60, 83, 84
[Zr{N(R)C(Ph)C(H)(C$_9$H$_6$N-2)}$_2$Cl$_2$]	^{1}H, ^{13}C, MS, EA, and X-ray		ethylene polymerization procatalyst	60, 83, 84
[Zr{N(R)C(Ph)C(R)(C$_9$H$_6$N-2)}$_2$Cl$_2$]	^{1}H, ^{13}C, MS, and EA		ethylene polymerization procatalyst	60, 83, 84
[Zr{(N(Ph)C(Me))$_2$CH}(CH$_2$Ph)$_3$]	^{1}H, ^{13}C, MS, and EA		ethylene polymerization catalyst	85, 86
[Zr{(N(C$_6$H$_4$Me-4)C(Me))$_2$CH}(CH$_2$Ph)$_3$]	^{1}H, ^{13}C, IR, EA, and X-ray	B		87
[Zr{(η^3-N(C$_7$H$_6$))C(Me)C(H)C(Me)N(C$_6$H$_4$Me-4)}-(η^2-CH$_2$Ph)(η^1-CH$_2$Ph)]	^{1}H, ^{13}C, EA, and X-ray	B	five-coordinate Zr; cyclometalated	87
[Zr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}(Me)$_3$]	^{1}H, ^{13}C, EA, and X-ray	B		87
[Zr{(N(Ph)C(Me))$_2$CH}(NMe$_2$)$_3$]	^{1}H, ^{13}C, EA, and X-ray	B		85
[Zr{(N(C$_6$H$_4$CF$_3$-4)C(Me))$_2$CH}(NMe$_2$)$_3$]	^{1}H, ^{13}C, IR, and EA			85
[Zr{(N(Ph)C(Me))$_2$CH}Cl$_3$]	^{1}H, ^{13}C, IR, and EA		ethylene polymerization procatalyst	85, 86
[Zr{(N(C$_6$H$_4$CF$_3$-4)C(Me))$_2$CH}Cl$_3$]·NHMe$_2$	^{1}H, ^{13}C, IR, and EA			85
[Zr{(N(Ph)C(Me))$_2$CH}$_2$(NMe$_2$)$_2$]	^{1}H, ^{13}C, IR, and EA			85
[Zr{(N(Ph)C(Me))$_2$CH}$_2$Cl$_2$]	^{1}H, ^{13}C, IR, EA, and X-ray	B	ethylene polymerization procatalyst	85, 86
[Zr{(N(Ph)C(Me))$_2$CH}$_2$(Me)$_2$]	^{1}H, ^{13}C, IR, EA, and X-ray	B	ethylene polymerization procatalyst	85, 86
[Zr{(N(Ph)C(Me))$_2$CH}$_2$(Bn)$_2$]	^{1}H, ^{13}C, IR, and EA		ethylene polymerization procatalyst	85, 86
[Zr{(N(Ph)C(Me))$_2$CH}(η^5-Cp)Cl$_2$]	^{1}H, ^{13}C, IR, and EA		ethylene polymerization procatalyst	85, 86
[Zr{(N(Ph)C(Me))$_2$CH}$_2$(η^5-C$_9$H$_7$)Cl$_2$]	^{1}H, ^{13}C, IR, EA, and X-ray	B		85
[Zr{(N(C$_6$H$_4$CF$_3$-4)C(Me))$_2$CH}(η^5-Cp)Cl$_2$]	^{1}H, ^{13}C, IR, and EA		ethylene polymerization procatalyst	85, 86
[Zr{(N(Ph)C(Me))$_2$CH}(η^5-Cp)(Me)$_2$]	^{1}H, ^{13}C, IR, and EA		ethylene polymerization procatalyst	85, 86
[Zr{(N(C$_6$H$_4$CF$_3$-4)C(Me))$_2$CH}(η^5-Cp)(Me)$_2$]	^{1}H, ^{13}C, IR, and EA			85
[Zr{(N(Ph)C(Me))$_2$CH}(η^5-Cp)(Me)][B(C$_6$F$_5$)$_4$]	^{1}H, ^{13}C, IR, EA, and X-ray		ethylene polymerization catalyst	86
[Zr{(N(C$_6$H$_4$Me-4)C(Me))$_2$CH}(η^5-Cp)(μ-Cl)]$_2$[B(C$_6$F$_5$)$_4$]$_2$·4C$_6$H$_5$Cl	EA and X-ray	B	dicationic dinuclear complex	86
[Zr{(N(C$_6$H$_4$Me-4)C(Me))$_2$CH}(NMe$_2$)$_3$]	^{1}H, ^{13}C, EA, and X-ray	B		79
[Zr{(N(C$_6$H$_4$Me-4)C(Me))$_2$CH}Cl$_3$]	^{1}H, ^{13}C, and EA			79
[Zr{(N(C$_6$H$_4$Me-4)C(Me))$_2$CH}$_2$Cl$_2$]	^{1}H, ^{13}C, EA, and X-ray	B		79
[Zr{(N(C$_6$H$_4$Me-4)C(Me))$_2$CH}$_2$(OMe)$_2$]	^{1}H, ^{13}C, and EA			79
[Zr{(N(C$_6$H$_4$Me-4)C(Me))$_2$CH}(OMe)$_3$]	^{1}H, ^{13}C, and EA			79
[Zr{(N(C$_6$H$_4$Me-4)C(Me))$_2$CH}$_2$(OC$_6$H$_4$Me-4)$_2$]	^{1}H, ^{13}C, and EA			79
[Zr{(N(C$_6$H$_4$Me-4)C(Me)) $_2$CH}$_2$-(OCH$_2$C$_6$H$_4$^{t}Bu-4)$_2$]	^{1}H, ^{13}C, and EA			79
[Zr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}(NMe$_2$)$_2$Cl]	^{1}H, ^{13}C, EA, and X-ray	A		79
[Zr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}Cl$_3$(thf)]	^{1}H, ^{13}C, and EA			79
[Zr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}Cl$_3$]	^{1}H, ^{13}C, EA, and X-ray	A		79
[Zr{(N(R^1)C(Me))$_2$CH}Cl$_3$(thf)] R^1 = Me, Ph, C$_6$H$_4$Me-2, C$_6$H$_3$Me$_2$-2,6 R = C$_6$H$_3$^{i}Pr$_2$-2,6	^{1}H, ^{13}C, and EA ^{1}H, ^{13}C, EA, and X-ray	 B	procatalysts for ethylene polymerization (R^1 = Me, most active)	7

Table 1. Continued

complex	characterization	bonding mode	comments	ref
	Group 4 (Continued)			
[Zr{(N(H)C(Ph)C(H)C(Ph)N)(Si(Me)$_2$NC(Ph)-C(H)C(Ph)N)$_3$SiMe$_2$}Cl]	^{1}H, ^{13}C, EA, and X-ray		24-membered macrocycle (**15**)	62a
[Hf{N(R)C(Ph)C(H)C(^{t}Bu)N(R)}Cl$_3$]	^{1}H, ^{13}C, and EA			19
[Hf{N(R)C(^{t}Bu)C(H)(C$_5$H$_4$N-2)}$_2$Cl$_2$]	^{1}H, ^{13}C, EA, and X-ray	B	procatalyst for ethylene polymerization	83, 84
	Group 5			
[V{(N(Ph)C(Me))$_2$CH}Cl$_2$(thf)$_2$]	^{1}H, ^{2}H, μ_{eff}, EA, and X-ray		active procatalyst for ethylene polymerization and ethylene/α-olefin copolymerization	77, 80
[V{(N(C$_6$H$_2$Me$_3$-2,4,6)C(Me))$_2$CH}Cl$_2$]				77, 78
[V{(N(C$_6$H$_2$Me$_3$-2,4,6)C(Me))$_2$CH}(Me)$_2$]	EA			78
[V{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}Cl$_2$]	EA			78
[V{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}(Me)$_2$]	EA and X-ray			78
[V{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}(^{n}Bu)$_2$]	EA and X-ray			78
[V{(N(C$_6$H$_2$Me$_3$-2,4,6)C(^{n}Bu))$_2$CH}Cl$_2$]	X-ray			78
[V{(N(Ph)C(Me))$_2$CH}(Me)$_2$]	μ_{eff}, EA, and X-ray			78, 80
[V{(N(Ph)C(Me))$_2$CH}(Me)(OEt$_2$)]-[B{C$_6$H$_5$(CF$_3$)$_2$-3,5}$_4$]	μ_{eff}, EA, and X-ray			80
	Group 6			
[Cr{(N(H)C(Me))$_2$CH}(Cp*)Cl]	^{1}H, IR, MS, μ_{eff}, and EA		by insertion of MeCN into Cr−Me bond	88
[Cr{(N(H)C(Et))$_2$CH}(Cp*)Cl]	^{1}H, IR, and EA		by insertion of EtCN into Cr−Et bond	88
[Cr{N(H)(C(Me))$_2$C(Et)N(H)}(Cp*)Cl]	^{1}H, IR, and EA		by insertion of EtCN into Cr−Me bond	88
[Cr{(N(H)C(Et))$_2$CMe}(Cp*)Cl]	^{1}H, MS, μ_{eff}, and EA		by insertion of EtCN into Cr−Me bond	88
[Cr{(N(Ph)C(Me))$_2$CH}Cl$_2$(thf)$_2$]	MS, μ_{eff}, EA, and X-ray	B	procatalyst for ethylene polymerization	80, 90
[Cr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}Cl(μ-Cl)]$_2$	MS, μ_{eff}, EA, and X-ray	B	procatalyst for ethylene polymerization	30, 90
[Cr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}(Me)(μ-Cl)]$_2$	MS, EA, and X-ray	B	procatalyst for ethylene polymerization	30, 90
[Cr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}(μ-Cl)$_2$(thf)]$_2$·thf	MS, μ_{eff}, EA, and X-ray	B	procatalyst for ethylene polymerization	90
[Cr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}Cl(O$_2$CMe)(thf)]	MS, μ_{eff}, EA, and X-ray	B	procatalyst for ethylene polymerization	90
[Cr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}Cl(O$_2$CPh)(thf)]	MS, μ_{eff}, and EA		procatalyst for ethylene polymerization	90
[Cr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}-Cl({OC(Me)}$_2$CH)]	MS, μ_{eff}, EA, and X-ray	B	procatalyst for ethylene polymerization	90
[Cr{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}-Cl({OC(Ph)}$_2$CH)]	^{1}H, ^{2}H, μ_{eff}, and X-ray	B	procatalyst for ethylene polymerization	90
[W{N(H)C(Me)(C(H))$_2$N(Et)}(Cp*)(CO)$_2$]	^{1}H, ^{13}C, IR, MS, EA, and X-ray	B	by insertion of MeCN into a W−(1-azaallyl) bond	89
[W{N(H)C(Ph)(C(H))$_2$N(Et)}(Cp*)(CO)$_2$]	^{1}H, ^{13}C, IR, MS, and EA		by insertion of PhCN into a W−(1-azaallyl) bond	89
	Group 7			
[Mn{N(H)(C$_6$H$_3$Me-2)6-C(H)N(^{t}Bu)}$_2$] (see eq 7)	IR, MS, ESR, μ_{eff}, EA, and X-ray	A	tetrahedral Mn(II)	42
[Mn{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}(μ-I)$_2$Li-(OEt$_2$)$_2$]	IR, MS, EA, and X-ray	B		6a
[Mn{(N(R)C(Ph))$_2$CH}$_2$]	^{1}H, MS, μ_{eff}, and EA			91
	Group 8			
[Fe{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(^{t}Bu))$_2$CH}Cl]	^{1}H, μ_{eff}, and X-ray	A	three-coordinate Fe(II)	29a
[(Fe{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(^{t}Bu))$_2$CH})(μ-N$_2$)]	resonance Raman, UV−vis, μ_{eff}, and X-ray	A	long N−N bond	29b
M$_2$[(Fe{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(^{t}Bu))$_2$CH})$_2$(μ-N$_2$)] (M = Na, K)	UV−vis, μ_{eff}, and X-ray	A		29b
[Fe{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}(μ-Cl)$_2$Li(thf)$_2$]	^{1}H, μ_{eff}, and X-ray	A		29a
[Fe{(N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me))$_2$CH}-Cl(μ-Cl)]$_2$[Mg(thf)$_4$]	^{1}H and X-ray	A	ClMgCl core	29a
[Fe{(N(R)C(Ph))$_2$CH}$_2$]	^{1}H, MS, μ_{eff}, EA, and X-ray	A	pseudo-tetrahedral	91, 95
	Group 9			
[Co{(2-NC$_4$Me$_3$)(2′-N′C$_4$H$_3$)CH}$_2$]	IR, UV−vis, and EA			93
[Co{N(Et)(C(H))$_2$C(Me)N(Et)}$_2$]	^{1}H, IR, MS, UV−vis, μ_{eff}, and EA			9, 10
[Co{(2-NC$_4$HMe$_2$-3,5)$_2$CH}$_2$]	^{1}H, IR, UV−vis, and EA			92, 93
[Co{(2-NC$_4$Me$_3$)$_2$CH}$_2$]	IR, UV−vis, and EA			93
[Co{(N(Ph)C(H))$_2$CMe}$_2$]	IR, UV−vis, and EA			13, 16, 17
[Co{(N(Ph)C(H))$_2$CH}$_2$]	IR, UV−vis, μ_{eff}, and EA			13, 16, 17
[Co{(N(C$_6$H$_4$Me-4)C(H))$_2$CH}$_2$]	IR, UV−vis, and μ_{eff}			148
[Co{(N(C$_6$H$_4$Me-3)C(H))$_2$CH}$_2$]	IR, UV−vis, and μ_{eff}			148

Table 1. Continued

complex	characterization	bonding mode	comments	ref
Group 9 (Continued)				
$[Co\{N(Ph)C(Ph)(C(H))_2N(Ph)\}_2]$	IR, EA, and μ_{eff}			48b
$[Co\{N(C_6H_4Me\text{-}4)C(Ph)(C(H))_2N(C_6H_4Me\text{-}4)\}_2]$	IR, EA ,and μ_{eff}			48b
$[Co\{N(C_6H_4OMe\text{-}4)C(Ph)(C(H))_2N(C_6H_4OMe\text{-}4)\}_2]$	IR, EA, and μ_{eff}			48b
$[Co\{N(C_6H_4Br\text{-}4)C(Ph)(C(H))_2N(C_6H_4Br\text{-}4)\}_2]$	IR, EA, and μ_{eff}			48b
$[Co\{N(Ph)C(C_6H_4Br\text{-}4)(C(H))_2N(Ph)\}_2]$	IR, EA, and μ_{eff}			48b
$[Co\{N(C_6H_4Br\text{-}4)C(C_6H_4Br\text{-}4)(C(H))_2N(C_6H_4Br\text{-}4)\}_2]$	IR, EA, and μ_{eff}			48b
$[Co\{(N(Ph)C(H))_2CPh\}_2]\cdot 0.5C_6H_6$	UV−vis and EA			94
$[Co\{(N(C_6H_4Cl\text{-}4)C(H))_2CPh\}_2]$	UV−vis and EA			94
$[Co\{(N(C_6H_4Me\text{-}4)C(H))_2CPh\}_2]$	UV−vis and EA			94
$[Co\{(N(H)C(Me))_2CH\}_2]$	MS, UV−vis, and μ_{eff}			8a
$[Co\{(N(Me)C(Me))_2CH\}_2]$	EA, UV−vis, and μ_{eff}			8a
$[Co\{(N(Et)C(Me))_2CH\}_2]$	EA, UV−vis, and μ_{eff}			8a
$[Co\{(N(Ph)C(Me))_2CH\}_2]$	EA, UV−vis, and μ_{eff}			8a
$[Co\{(N(R)C(Ph))_2CH\}_2]$	MS, EA, and X-ray	A	tetrahedral Co(II)	22, 24
$[Co\{(N(H)C(Ph))_2CH\}_2]$	MS, EA, and X-ray	A	square planar Co(II)	22, 24
$[Co\{(N(CH_2C{\equiv}CH)C(H))_2CH\}(OCOCMe_3)_2\text{-}2(NH_2CH_2C{\equiv}CH)_2]$	IR, EA, and X-ray	A	octahedral Co(III), amines apical, carboxylates *cis*	44
$[Co\{N(H)C(^{t}Bu)C(H)C(NMe_2)N(R)\}(OR)]$	^{1}H, ^{13}C, EA, and X-ray	A	three-coordinate Co(II)	149
$[Co\{(N(H)C(NMe_2))_2CH\}(\mu\text{-}OR)]_2$	^{1}H, ^{13}C, EA, and X-ray	A		149
$[Rh\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(1,5\text{-}COD)]$	^{1}H, ^{13}C, EA, and X-ray			150, 151
$[Rh\{(N(C_6H_3Cl_2\text{-}2,6)C(Me))_2CH\}(1,5\text{-}COD)]$	^{1}H, ^{13}C, and EA			151
$[Rh\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(C_2H_4)_2]$	^{1}H, ^{13}C, EA, and X-ray	A		151
$[Rh\{(N(C_6H_3Cl_2\text{-}2,6)C(Me))_2CH\}(C_2H_4)_2]$	^{1}H, ^{13}C, and EA			151
$[Rh\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(COE)]$	^{1}H, ^{13}C, EA, and X-ray	B	three-coordinate Rh	150, 151
$[Rh\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(C_2Me_4)_2]$	^{1}H and ^{13}C			151
$[Rh\{(N(C_6H_3Cl_2\text{-}2,6)C(Me))_2CH\}(COE)]$	^{1}H, ^{13}C, EA, and X-ray	A		151
$[Rh\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(NBE)]$	^{1}H, ^{13}C, EA, and X-ray	A	three-coordinate Rh + agostic	151
$[Rh\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(COE)(NCMe)]$	^{1}H, ^{13}C, EA, and X-ray	A		151
$[Rh\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(COE)(N_2)]$	^{1}H, ^{13}C, and IR			151
$[Rh\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(H_2)]_2$	^{1}H and ^{13}C			151
$[Rh\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(COE)(H_2)]$	^{1}H and ^{13}C		dihydrogen complex	151
$[Rh\{(N(H)C(Me))_2CH\}(CO)_2][BF_4]$	^{1}H, ^{13}C, EA, and X-ray	A		105
$[Rh\{(N(CH)(Me)(Ph)\text{-}R)C(H))_2CH\}(COD)]$	^{1}H and EA		catalyst for enantioselective hydrosilylation	106
$[Ir\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(COE)(H)_2]$	^{1}H, ^{13}C, and X-ray	A	dihydrido−Ir(III) complex	151
Group 10				
$[Ni\{(N(R)C(Ph))_2CH\}_2]$	MS, EA, and X-ray	A	planar Ni(II)	45
$[Ni\{(N(H)C(Ph))_2CH\}_2]\cdot 2Et_2O$	^{1}H, ^{13}C, IR, MS, EA, and X-ray	A	an Et_2O, H-bonded to each *trans*-NH group	91, 95
$[Ni\{(2\text{-}NC_4Me_3)(2'\text{-}N'C_4H_3)CH\}_2]$	IR, EA, and UV−vis			93
$[Ni\{(2\text{-}NC_4HMe_2\text{-}3,5)_2CH\}_2]$	^{1}H, IR, μ_{eff}, EA, and UV−vis			92, 93
$[Ni\{(2\text{-}NC_4HMe_2\text{-}3,5)_2CH\}_2]$	X-ray	A	D_2 symmetry	14
$[Ni\{(2\text{-}NC_4Me_2\text{-}3,5(CO_2C_2H_5)\text{-}4)_2CH\}_2]$	^{1}H and μ_{eff}			92
$[Ni\{(2\text{-}NC_4Me_3)_2CH\}_2]$	IR, EA, and UV−vis			93
$[Ni\{(N(Ph)C(H))_2CPh\}_2]\cdot 0.5C_6H_6$	EA and UV−vis			94
$[Ni\{(N(C_6H_4Me\text{-}4)C(H))_2CPh\}_2]$	EA and UV−vis			94
$[Ni\{(N(C_6H_4Me\text{-}3)C(H))_2CH\}_2]$	IR, μ_{eff}, and UV−vis			148
$[Ni\{(N(C_6H_4Me\text{-}4)C(H))_2CH\}_2]$	IR, μ_{eff}, and UV−vis			148
$[Ni\{N(Ph)C(Ph)(C(H))_2N(Ph)\}_2]$	IR, μ_{eff}, and EA			48b
$[Ni\{N(C_6H_4Me\text{-}4)C(Ph)(C(H))_2N(C_6H_4Me\text{-}4)\}_2]$	IR, μ_{eff}, and EA			48b
$[Ni\{N(C_6H_4OMe\text{-}4)C(Ph)(C(H))_2N(C_6H_4OMe\text{-}4)\}_2]$	IR, μ_{eff}, and EA			48b
$[Ni\{N(C_6H_4OEt\text{-}4)C(Ph)(C(H))_2N(C_6H_4OEt\text{-}4)\}_2]$	IR, μ_{eff}, and EA			48b
$[Ni\{N(C_6H_4Br\text{-}4)C(Ph)(C(H))_2N(C_6H_4Br\text{-}4)\}_2]$	IR, μ_{eff}, and EA			48b
$[Ni\{N(Ph)C(C_6H_4Br\text{-}4)(C(H))_2N(Ph)\}_2]$	IR, μ_{eff}, and EA			48b
$[Ni\{N(C_6H_4Br\text{-}4)C(C_6H_4Br\text{-}4)(C(H))_2N(C_6H_4Br\text{-}4)\}_2]$	IR, μ_{eff}, and EA			48b
$[Ni\{(N(Ph)C(H))_2CMe\}_2]$	IR, UV−vis, and EA			13, 16, 17
$[Ni\{(N(Ph)C(H))_2CH\}_2]$	IR, UV−vis, μ_{eff}, and EA			12, 13, 16, 17
$[Ni\{(N(C_6H_4Cl\text{-}4)C(H))_2C(Ph)\}_2]\cdot 0.5C_6H_6$	UV−vis, EA, and X-ray	A		94, 97
$[Ni\{(N(Ph)C(H))_2C(Ph)\}_2]\cdot 0.5C_6H_6$	UV−vis and EA			94
$[Ni\{(N(C_6H_4Me\text{-}4)C(H))_2CH\}_2]$	UV−vis and EA			94
$[Ni\{(N(H)C(Me))_2CH\}_2]$	^{1}H, UV−vis, μ_{eff}, and EA			8a
$[Ni\{(N(Me)C(Me))_2CH\}_2]$	UV−vis, μ_{eff}, and EA			8a
$[Ni\{(N(Et)C(Me))_2CH\}_2]$	UV−vis, μ_{eff}, and EA			8a
$[Ni\{(N(Ph)C(Me))_2CH\}_2]$	^{1}H, ^{13}C, UV−vis, EA, and X-ray	A		8a, 11, 96
$[Ni\{(N(C_6H_4Me\text{-}2)C(Me))_2CH\}_2]$	^{1}H, UV−vis, μ_{eff}, and EA			11

Table 1. Continued

complex	characterization	bonding mode	comments	ref
Group 10 (Continued)				
$[\mathrm{Ni\{(N(C_6H_4Me\text{-}3)C(Me))_2CH\}_2}]$	^{1}H, UV−vis, μ_{eff}, and EA			11
$[\mathrm{Ni\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}_2}]$	^{1}H, UV−vis, μ_{eff}, and EA			11
$[\mathrm{Ni\{(N(C_6H_4C_6H_5\text{-}4)C(Me))_2CH\}_2}]$	^{1}H, UV−vis, μ_{eff}, and EA			11
$[\mathrm{Ni\{(N(CH_2C_6H_5)C(Me))_2CH\}_2}]$	^{1}H, UV−vis, μ_{eff}, and EA			11
$[\mathrm{Ni\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH_2\}Br_2}]$	^{1}H, ^{13}C, MS, EA, and X-ray	B	β-diketimine acts as base; active α-olefin polymerization procatalyst; first use of $\mathrm{H[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]}$	25
$[\mathrm{Pd\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2C(H)Pd(NCMe)_3\}(NCMe)_2][BF_4]_3}$	^{1}H, ^{13}C, EA, MS, and X-ray	F	bridging β-diketimine; active α-olefin polymerization procatalyst	25
$[\mathrm{Pd\{(N(R)C(Ph))_2CH\}_2}]$	^{1}H, ^{13}C, EA, MS, and X-ray	B	square planar Pd(II); ligands *trans*-boat	45
$[\mathrm{Pd\{(N(R)C(Ph))_2CH\}(\eta^3\text{-}CH_2CHCH_2)}]$	^{1}H, ^{13}C, EA, MS, and X-ray	B		45
$[\mathrm{Pt\{(N(H)C(Me))_2CH\}(NH_3)_4][ClO_4]_3}$	^{1}H and EA		cationic Pt(IV)	41
$\mathrm{Pt\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)_3}]$	^{1}H,^{13}C, EA, and X-ray	A	first stable, coordinatively unsaturated Pt(IV) five-coordinate complex	31
Group 11				
$[\mathrm{Cu\{(2\text{-}NC_4Me_3)(2'\text{-}N'C_4H_3)CH\}_2}]$	IR, UV−vis, and EA			93
$[\mathrm{Cu\{(N(Ph)C(H))_2CH\}_2}]$	IR, UV−vis, μ_{eff}, ESR, and EA			12, 13, 94
$[\mathrm{Cu\{(N(Ph)C(H))_2CMe\}_2}]$	UV−vis and ESR			94
$[\mathrm{Cu\{(N(C_6H_4Me\text{-}3)C(H))_2CH\}_2}]$	IR, UV−vis, and μ_{eff}			148
$[\mathrm{Cu\{(N(Ph)C(H))_2CMe\}_2}]$	IR, UV−vis, and EA			13
$[\mathrm{Cu\{(N(Ph)C(H))_2CH\}_2]\cdot 0.5C_6H_6}$	UV−vis, ESR, and EA			94
$[\mathrm{Cu\{(N(C_6H_4Me\text{-}4)C(H))_2CPh\}_2}]$	UV−vis, ESR, and EA			94
$[\mathrm{Cu\{(N(C_6H_4Cl\text{-}4)C(H))_2CPh\}_2]\cdot 0.5C_6H_6}$	UV−vis, ESR, and EA			94
$[\mathrm{Cu\{(N(Ph)C(Ph)(C(H))_2N(C_6H_4Me\text{-}4)\}_2}]$	IR, μ_{eff}, and EA			48b
$[\mathrm{Cu\{(N(C_6H_4Me\text{-}4)C(Ph)(C(H))_2N(C_6H_4Me\text{-}4)\}_2}]$	IR, μ_{eff}, and EA			48b
$[\mathrm{Cu\{(N(C_6H_4OMe\text{-}4)C(Ph)(C(H))_2N(C_6H_4OMe\text{-}4)\}_2}]$	IR, μ_{eff}, and EA			48b
$[\mathrm{Cu\{(N(C_6H_4OEt\text{-}4)C(Ph)(C(H))_2N(C_6H_4OEt\text{-}4)\}_2}]$	IR, μ_{eff}, and EA			48b
$[\mathrm{Cu\{(N(C_6H_4Br\text{-}4)C(Ph)(C(H))_2N(C_6H_4Br\text{-}4)\}_2}]$	IR, μ_{eff}, and EA			48b
$[\mathrm{Cu\{(N(C_6H_4Br\text{-}4)C(C_6H_4Br\text{-}4)(C(H))_2N(C_6H_4Br\text{-}4)\}_2}]$	IR, μ_{eff}, and EA			48b
$[\mathrm{Cu\{((2\text{-}NC_4Me_2\text{-}3,5)(CO_2Et\text{-}4))_2CH\}_2}]$	EA and X-ray	A		15
$[\mathrm{Cu\{(2\text{-}NC_4HMe_2\text{-}3,5)_2CH\}_2}]$	IR, UV−vis, and EA			93
$[\mathrm{Cu\{(2\text{-}NC_4Me_3)_2CH\}_2}]$	IR, UV−vis, and EA			93
$[\mathrm{Cu\{(N(H)C(Me))_2CH\}_2}]$	UV−vis, μ_{eff}, and EA			8a
$[\mathrm{Cu\{(N(Me)C(Me))_2CH\}_2}]$	UV−vis, μ_{eff}, and EA			8a
$[\mathrm{Cu\{(N(Et)C(Me))_2CH\}_2}]$	UV−vis, μ_{eff}, and EA			8a
$[\mathrm{Cu\{(N(Ph)C(Me))_2CH\}_2}]$	UV−vis, μ_{eff}, ESR, EA, and X-ray	A		8a, 94, 152
$[\mathrm{Cu\{(N(C_6H_4Me\text{-}4)C(H))_2CH\}Cl}]$	IR, UV−vis, and μ_{eff}			148
$[\mathrm{Cu\{H(N(C_5H_4N)C(Me))_2CH\}_2(NCS)_2}]$	UV−vis, ESR, EA, and X-ray	A		102
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl}]$	UV−vis, ESR, EA, and X-ray	B		102, 103
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(SCPh_3)}]$	UV−vis, ESR, MCD, resonance Raman, EA, and X-ray		three-coordinate Cu(II) (model for Cu protein active site)	102, 103
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(SC_6H_3Me_2\text{-}2,6)}]$	UV−vis, ESR, MCD, resonance Raman, EA, and X-ray	B		103
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}\{SC(Ph)_2CH_2OMe\}}]$	UV−vis, ESR, CV, EA, and X-ray	B		32
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}\{SC(Ph)_2CH_2SMe\}}]$	UV−vis, ESR, CV, EA, and X-ray	B	structural model for Cu protein active site	32
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}OC_6H_3Me_2\text{-}2,6)}]$	UV−vis, ESR, EA, and X-ray	A		104
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(OC_6H_4OMe\text{-}4)}]$	UV−vis, ESR, CV, EA, and X-ray	A		104
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(OC_6H_4{}^tBu\text{-}4)}]$	UV−vis, ESR, Raman, CV, EA, and X-ray	A		104
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(CNC_6H_3Me_2\text{-}2,6)}]$	UV−vis, EA, and X-ray	A		104
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CCl\}(OC_6H_4{}^tBu\text{-}4)}]$	UV−vis, ESR, and X-ray	A		104
$[\mathrm{Cu\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CCl\}Cl}]$	UV−vis, ESR, and X-ray	A		104
$[\mathrm{Cu\{(N(C_6H_2Me_3\text{-}2,4,6)C(H))_2C(NO_2)\}]_\infty}$	IR, MS, EA, and X-ray	A	polymer chain: Cu−O bridges	51

Table 1. Continued

complex	characterization	bonding mode	comments	ref
	Group 11 (Continued)			
$[Cu\{(N(C_6H_2Me_3\text{-}2,4,6)C(H))_2\text{-}C(NO_2)\}(PPh_3)]$	^1H, UV−vis, MS, and EA			51
$[Cu\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(\eta^2\text{-}CH_2CH_2)]$	^1H and X-ray	A		101
$[Cu\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(\eta^2\text{-}CH_2CHPh)]$	^1H and X-ray	A		101
$[Cu\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}OH)]_2$	IR, UV−vis, μ_{eff}, and X-ray	A	possibly via $[Cu^{III}(\mu\text{-}O)]_2$ complex	101
$[Cu\{(N(R)C(Ph))_2CH\}_2]$	^1H, MS, μ_{eff}, EA, and X-ray	A	pseudo-tetrahedral	91, 95
$[Cu\{(N(H)C(Ph))_2CH\}_2]\cdot 2Et_2O$	^1H, IR, MS, μ_{eff}, and X-ray	A	square planar: an Et_2O molecule H-bonded to each *trans*-NH group	91, 95
	Group 12			
$[Zn\{N(Et)(C(H))_2C(Me)N(Et)\}_2]$	^1H, IR, MS, and UV−vis			9
$[Zn\{(N(Ph)C(H))_2CH\}_2]$	^1H and EA			12
$[Zn\{(N(Ph)C(H))_2CPh\}_2]\cdot 0.5C_6H_6$	UV−vis and EA			94
$[Zn\{(N(C_6H_4Me\text{-}4)C(H))_2CPh\}_2]$	UV−vis and EA			94
$[Zn\{(N(C_6H_4Cl\text{-}4)C(H))_2CPh\}_2]$	UV−vis and EA			94
$[Zn\{(N(C_6H_3Et_2\text{-}2,6)C(Me))_2CH\}(Et)]$	^1H			107
$[Zn\{(N(C_6H_3Et_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}OMe)]_2$			active catalyst for co-polymerization of CO_2 and cyclohexene oxide	107, 110
$[Zn\{(N(C_6H_3Et_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}OAc)]_2$	^1H and X-ray	A	active catalyst for co-polymerization of CO_2 and cyclohexene oxide	111
$[Zn\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}F)]_2$	^1H, ^{19}F, MS, EA, and X-ray	B	first Zn compound with bridging F atoms	111
$[Zn\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}H)]_2$	^1H, MS, EA, and X-ray	A	first Zn compound with bridging H atoms	111
$[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}\text{-}(OSiMe_3)(thf)]$			review on polymerization of lactide and related esters	70
$[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}I)_2\text{-}Li(OEt_2)]$	^1H, ^{13}C, MS, EA, and X-ray	B		6a
$[Zn\{(N(C_6H_3Et_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}O^iPr)]_2$	^1H, ^{13}C, and X-ray	A	catalyst for living polymerization of lactide	33
$[Zn\{(N(C_6H_3{}^nPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}O^iPr)]_2$	^1H, ^{13}C, and X-ray	A	catalyst for living polymerization of lactide	33, 35, 108
$[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(NR_2)]$	^1H and X-ray	A	catalyst for alternating copolymerization of cyclohexene oxide and CO_2	35
$[Zn\{(N(C_6H_3{}^iPr\text{-}2\text{-}{}^nPr\text{-}6)C(Me))_2CH\}(NR_2)]$	^1H			35
$[Zn\{(N(C_6H_3{}^nPr_2\text{-}2,6)C(Me))_2CH\}(NR_2)]$	^1H		catalyst for living polymerization of lactide	33, 35, 108
$[Zn\{(N(C_6H_3Et_2\text{-}2,6)C(Me))_2CH\}(NR_2)]$	^1H, ^{13}C		catalyst for living polymerization of lactide	33, 35
$[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Et]$	^1H, ^{13}C		inactive	33, 35
$[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}\text{-}\{OC(H)(Me)CO_2Me\}]$	^1H, ^{13}C, and X-ray	A	catalyst for living polymerization of lactide	33
$[Zn\{(N(C_6H_3Me_3\text{-}2,4,6)C(Me))_2CH\}(\mu\text{-}O^iPr)]_2$			catalyst for living polymerization of lactide	108
$[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(OR)(thf)]$	^1H		catalyst for living polymerization of lactide	72
$[Zn\{(N(C_6H_3R^3{}_2\text{-}2,6)C(R^1))\text{-}C(H)C\{OC(H)_2[C(H)R^2]N\}\{NR_2\}]$			catalyst for enantioselective alternating copolymerization of cyclohexene oxide and CO_2	109
$R^1 = Me, R^2 = Ph\text{-}R, R^3 = {}^iPr$				
$R^1 = CF_3, R^2 = Ph\text{-}R, R^3 = {}^iPr$				
$R^1 = {}^iPr, R^2 = Ph\text{-}R, R^3 = {}^iPr$				
$R^1 = {}^iPr, R^2 = {}^iPr\text{-}S, R^3 = {}^iPr$				
$R^1 = {}^iPr, R^2 = {}^tBu\text{-}S, R^3 = {}^iPr$				
$R^1 = {}^iPr, R^2 = {}^tBu\text{-}S, R^3 = Et$	X-ray	A	the most active catalyst	
$R^1 = CF_3, R^2 = {}^tBu\text{-}S, R^3 = {}^iPr$				
$[Zn\{(N(C_6H_3R^1{}_2\text{-}2,6)C(Me))_2CH\}_2\{\mu\text{-}OC(O)Me\}]_2$			catalyst for alternating copolymerization of cyclohexene oxide and CO_2	35
$R^1 = Et$	^1H and X-ray	A		
$R^1 = {}^iPr$	^1H and X-ray	A		
$R^1 = {}^nPr$	^1H and X-ray	A		
$[Zn\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}\{\mu\text{-}OC(O)Me\}]_2$	^1H and X-ray	Å		35
$[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}X)]_2$				35
$X = Cl$	^1H		inactive	
$X = Br$	^1H and X-ray	A	inactive	
$[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}OMe)_2Na(thf)_3]$	^1H and X-ray	A		35

Table 1. Continued

complex	characterization	bonding mode	comments	ref
Group 12 (Continued)				
$[Zn\{(N(C_6H_3Et_2\text{-}2,6)C(Me))_2CH\}_2(\mu\text{-}OH)]_2$			inactive	35
$[Zn\{(N(R)C(Ph))_2CH\}_2(\mu\text{-}Cl)]_2$	^1H, ^{13}C, ^{29}Si, MS, and X-ray	B		112
$[Zn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}R']$	^1H, ^{13}C, IR, MS, and X-ray			6b
$R' = Me$		A		
$R' = Ph$		B		
$R' = {}^tBu(thf)$		B		
$[Cd\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}I)_2\text{-}Li(OEt_2)_2]$	^1H, IR, MS, EA, and X-ray	B		6a
Group 13				
$[B\{(N(H)C(Me))_2C(CN)\}(Et)_2]$	^1H, ^{13}C, ^{11}B, IR, MS, EA, and X-ray	A, B	zwitterionic	115
$[B\{(N(H)C(Me))_2C(CN)\}(Pr)_2]$	^1H, ^{13}C, ^{11}B, IR, MS, and EA			115
$[B\{(N(H)C(Me))_2C(CN)\}(1,5\text{-}C_8H_{14})]$	^1H, ^{13}C, ^{11}B, IR, MS, and EA			115
$[B\{N(H)C(Me)(C(H))_2N(H)\}(Pr)_2]$	^1H, ^{13}C, ^{11}B, and GC/MS			115
$[B\{(N(H)C(Me))_2CH\}(Pr)_2]$	GC/MS		liquid	115
$[B\{(N(H)C(Et))_2CMe\}(Et)_2]$	^1H, ^{13}C, ^{11}B, IR, and MS			115
$[B\{(N(H)C(Pr))_2CEt\}(Et)_2]$	^1H, ^{13}C, ^{11}B, IR, and MS			115
$[B\{(N(H)C(Me))_2CH\}(1,5\text{-}C_8H_{14})]$	^1H, ^{13}C, ^{11}B, and MS			115
$[B\{N(H)C(Me)(C(H))_2N(H)\}(1,5\text{-}C_8H_{14})]$	^1H, ^{13}C, ^{11}B, and GC/MS			115
$[B\{(N(Me)C(Me))_2CH\}F_2]$	^1H, ^{13}C, ^{19}F, ^{11}B, and X-ray			113, 114
$[B\{(N(Me)C(Me))_2CH\}(F)_2\{Cr(CO)_3\}]$	^1H, ^{13}C, ^{19}F, ^{11}B, and X-ray	B		113
$[B\{(N(Me)C(Me))_2CH_2\}F_2][BF_4]$	^1H, ^{13}C, ^{11}B, and EA			114
$[B\{(N(Me)C(Me))_2CH_2\}F_2][PF_6]$	X-ray	B		114
$[B\{(N(Me)C(Me))_2CH\}F][BF_4]$	^1H, ^{13}C, ^{11}B, and EA			128b
$[B\{(N(Me)C(Me))_2CH\}Cl_2]$	^1H, ^{13}C, ^{11}B, and EA			128b
$[B\{(N(Me)C(Me))_2CH\}R'][AlCl_4]$	^1H, ^{13}C, ^{11}B, and EA			128b
$R' = Cl$				
$R' = Et$				
$R' = Ph$				
$[B\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}F_2]$	^1H, ^{13}C, ^{11}B, ^{19}F, MS, EA, and X-ray	A		116a
$[B\{(C_6H_4Me\text{-}4)C(Me)C(H)C(Me)_2\text{-}N(C_6H_4Me\text{-}4)\}(Me)]$	^1H, ^{13}C, ^{11}B, MS, EA, and X-ray	A		116a
$[B\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(Me)_2]$	^1H, ^{13}C, ^{11}B, MS, EA, and X-ray	A		116a
$[B\{N(C_6H_4Me\text{-}4)C(Me)C(H)C(Me)_2\text{-}N(C_6H_4Me\text{-}4)\}(CH_2SiMe_3)]$	^1H, ^{13}C, ^{11}B, MS, EA, and X-ray	A		116a
$[B\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}({}^nPr)_2]$	^1H, ^{13}C, ^{11}B, and EA			116a
$[B\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(C_2H_3)_2]$	^1H, ^{13}C, ^{11}B, and EA			116a
$[B\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(C_3H_5)_2]$	^1H, ^{13}C, ^{11}B, and EA			116a
$[B\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(Me)]\text{-}[BMe(C_6F_5)_3]$	^1H, ^{13}C, ^{11}B, ^{19}F, and EA			116a
$[B\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(Me)(py)]\text{-}[BMe(C_6F_5)_3]$	^1H, ^{13}C, ^{11}B, ^{19}F, and EA			116a
$[Al\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}Cl_2]$	^1H, ^{13}C, ^{27}Al, MS, EA, and X-ray	A		117
$[Al\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(Me)(OTf)]$	^1H, ^{13}C, ^{19}F, IR, MS, EA, and X-ray	B		117
$[Al\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(Me)_2]$	^1H, ^{13}C, ^{27}Al, MS, EA, and X-ray	B		117
$[Al\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(Me)Cl]$	^1H, ^{13}C, ^{27}Al, MS, and EA			117
$[Al\{(N(C_6H_4Me\text{-}4)C(Me))_2CH\}(CHR_2)Cl]$	^1H, ^{13}C, ^{27}Al, MS, and EA			117
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)_2]$	^1H, ^{13}C, ^{27}Al, MS, EA, and X-ray	B		117, 118
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Et)_2]$	^1H and ^{13}C			118
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}({}^iBu)_2]$	^1H and ^{13}C			118
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Et)\text{-}(NMe_2Ph)][B(C_6F_5)_4]$	^1H and ^{13}C			118
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}({}^iBu)]\text{-}[B(C_6F_5)_4]$	^1H and ^{13}C			118
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)]\text{-}[B(C_6F_5)_4]$	^1H, ^{13}C, ^{19}F, and X-ray	A	ion pair	153
$([Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)]_2\text{-}[BMe(C_6F_5)_3])^+[BMe(C_6F_5)_3]^-$	^1H, ^{13}C, ^{19}F, ^{11}B, and X-ray	A	“triple ion” + free anion	153
$[Al\{(N(R)C(Ph))_2CH\}(Me)_2]$	^1H, ^{13}C, EA, and X-ray	B		120
$[Al\{(N(R)C(Ph))_2CH\}(Me)(thf)]\text{-}[BMe(C_6F_5)_3]\cdot 0.5thf$	^1H, ^{13}C, ^{11}B, MS, EA, and X-ray	B	well-separated ion pair	120
$[Al\{(N(R)C(Ph))_2CH\}(Me)(OEt_2)]\text{-}[B(C_6F_5)_4]\cdot 0.5OEt_2$	^1H, ^{13}C, ^{11}B, MS, EA, and X-ray	B	well-separated ion pair	120
$[Al\{(N(R)C(C_6H_4OMe\text{-}4))_2CH\}(Me)_2]$	^1H, ^{13}C, MS, and EA			119
$[Al\{(N(R)C(C_6H_4Me\text{-}4))_2CH\}(Me)_2]$	^1H, ^{13}C, ^{29}Si, ^{27}Al, MS, and EA			46
$[Al\{N(R)C(Ph)C(H)C(C_6H_4Me\text{-}4)N(R)\}(Me)_2]$	^1H, ^{13}C, ^{29}Si, ^{27}Al, and MS		from 1-azaallyl-$AlMe_2$ + PhCN	46
$[Al\{(N(R)C(C_6H_4Me\text{-}4)C(H)C({}^tBu)N(R)\}(Me)_2]$	^1H, ^{13}C, ^{29}Si, ^{27}Al, MS, and EA			46
$[Al\{(N(R)C(C_6H_4Me\text{-}4)C(H)C({}^tBu)N(R)\}\text{-}(Me)(OEt_2)][BMe(C_6F_5)_3]$	^1H, ^{13}C, ^{29}Si, ^{27}Al, ^{11}B, and MS			46
$[Al\{N(R)C(Ph)C(H)C(Ad)N(R)\}(Me)_2]$	^1H, ^{13}C, ^{29}Si, ^{27}Al, and X-ray	B		46
$[Al\{N(R)C(Ph)C(H)C(Ad)N(R)\}(Et)_2]$	^1H, ^{13}C, ^{29}Si, and ^{27}Al			46
$[Al\{(N(R)C(C_6H_4Me\text{-}4)C(H)C({}^tBu)N(R)\}(Me)Cl]$	^1H, ^{13}C, ^{29}Si, ^{27}Al, and MS			46
$[Al\{N(R)C(Ph)C(H)C(Ad)N(R)\}\{N(R)C(Ad)\text{-}{=}CH(R)\}(Me)]$	^1H, ^{13}C, ^{29}Si, ^{27}Al, MS, EA, and X-ray	B	mixed β-diketiminato/ 1-azaallylaluminum methyl	46
$[\{Al(Me)_2(N(R)C(C_6H_4Me\text{-}4))_2C\}_2CH_2]$	^1H, ^{13}C, ^{29}Si, ^{27}Al, MS, EA, and X-ray	B		46

Table 1. Continued

complex	characterization	bonding mode	comments	ref
Group 13 (Continued)				
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}H_2]$	^{1}H, ^{13}C, IR, MS, and EA			124
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(SeH)_2]$	^{1}H, ^{13}C, ^{27}Al, IR, MS, EA, and X-ray	A	first structurally characterized M-SeH compound	124
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(SeH)]_2Se$	^{1}H, ^{27}Al, ^{77}Se, IR, MS, EA, and X-ray	A		124
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}]$	^{1}H, ^{13}C, IR, MS, EA, and X-ray	B	first stable monomeric Al(I) compound	26, 125
$[Al\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(N(R)N_2N(R)]$	^{1}H, ^{13}C, ^{29}Si, MS, EA, and X-ray	B		127
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}I_2]$	^{1}H, ^{13}C, MS, EA, and X-ray	B		26, 129
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl_2]$	^{1}H, ^{13}C, EA, and X-ray	B		129
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}\text{-}(NC_6H_2{}^iPr_3\text{-}2,4,6)]$	^{1}H, ^{13}C, ^{27}Al, MS, and EA		aluminum imide	125
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(LL')]$				126
LL′ = $[C(R)]_2$	^{1}H, ^{13}C, ^{27}Al, ^{29}Si, MS, IR, UV−vis, and X-ray	A		
LL′ = $[C(Ph)]_2$	^{1}H, ^{13}C, ^{27}Al, ^{29}Si, MS, IR, UV−vis, and X-ray	A		
LL′ = $C(R)CPh$	^{1}H, ^{13}C, ^{27}Al, ^{29}Si, MS, and IR			
LL′ = $[OC(Ph)_2]_2(OEt_2)$	^{1}H, ^{13}C, ^{27}Al, ^{29}Si, MS, IR, and X-ray	A		
LL′ = $OC(O)[C(R)]_2$	^{1}H, ^{13}C, ^{27}Al, and ^{29}Si			
LL′ = $OC(Ph)_2[C(R)]_2(OEt_2)$	^{1}H, ^{13}C, ^{27}Al, ^{29}Si, and X-ray	A		
LL′ = $NC(Ph)[C(R)]_2$	^{1}H, ^{13}C, ^{27}Al, ^{29}Si, and X-ray	A		
LL′ = $[NC({}^tBu)]_2$	^{1}H, ^{13}C, ^{27}Al, and ^{29}Si			
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(NR)]$	^{1}H, ^{13}C, MS, and EA		first aluminum imide	126
$[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}\text{-}(NC_6H_3{}^iPr_2\text{-}2,6)]$	^{1}H, ^{13}C, MS, and EA		aluminum imide	126
$[Al\{(N(Me)C(Me))_2CH\}_3]$	^{1}H, ^{13}C, ^{27}Al, MS, EA, and X-ray	B	rare tris(β-diketiminato)metal complex	123
$[Al\{(N(Ph)C(Ph))_2CH\}(Me)_2]$	^{1}H, ^{13}C, IR, and EA		from benzanilide + aluminum alkyl	43
$[Al\{(N(Ph)C(Ph))_2C(Me)\}(Et)_2]$	^{1}H, ^{13}C, IR ,and EA		from benzanilide + aluminum alkyl	43
$[Al\{(N(C_6H_4Cl\text{-}4)C(Ph))_2C(Me)\}(Et)_2]$	^{1}H, ^{13}C, EA, and X-ray	A	from benzanilide + aluminum alkyl	43
$[Al\{(N(C_6H_4Cl\text{-}4)C(Ph))_2CH\}(Me)_2]$	^{1}H, ^{13}C, EA, and X-ray	A	from benzanilide + aluminum alkyl	43
$[Al\{(N(C_6H_4Me\text{-}4)C(Ph))_2CH\}(Me)_2]$	^{1}H, ^{13}C, and EA		from benzanilide + aluminum alkyl	43
$[Al\{(N(C_6H_4Me\text{-}4)C(Ph))_2C(Me)\}(Et)_2]$	^{1}H, ^{13}C, ^{31}P, and EA		from benzanilide + aluminum alkyl	43
$[Al\{(N(PPh_2)C(H))_2CH\}(Me)_2]$	^{1}H, ^{13}C, ^{31}P, and EA			49
$[Al\{(N(Me)C(Me))_2CH\}H_2]$	^{1}H, ^{13}C, ^{27}Al, MS, EA, and X-ray	B	from diketimine + $AlH_3(NMe_3)$	121
$[Al\{(N({}^iPr)C(Me))_2CH\}H_2]$	^{1}H, ^{13}C, ^{27}Al, MS, EA, and X-ray	B	from diketimine + $AlH_3(NMe_3)$	121
$[Al\{(N(Ph)C(Me))_2CH\}H_2]$	^{1}H, ^{13}C, ^{27}Al, MS, and EA		from diketimine + $AlH_3(NMe_3)$	121
$[Al\{(N(Me)C(Me))_2CH\}_2][BPh_4]$	^{1}H, ^{13}C, ^{27}Al, ^{11}B, EA, and X-ray	A	cationic spirocyclic Al complex	121, 122a,b
$[Al\{(N(Me)C(Me))_2CH\}_2Cl]$	^{1}H, ^{13}C, ^{27}Al, MS, and EA		cationic spirocyclic Al complex	122a,b
$[Al\{(N(Me)C(Me))_2CH\}Cl_2]$	^{1}H, ^{13}C, ^{27}Al, MS, EA, and X-ray	B		122b, 128a,b
$[Al\{(N(Me)C(Me))_2CH\}_2Br]$	^{1}H, ^{13}C, ^{27}Al, MS, and EA			122b
$[Al\{(N(Me)C(Me))_2CH\}Cl_2{\cdot}AlCl_3]$	^{1}H, ^{13}C, ^{27}Al, and EA			128b
$[Al\{(N(Et)C(Me))_2CH\}Cl_2]$	^{1}H, ^{13}C, ^{27}Al, MS, EA, and X-ray	B		128a
$[Al\{(N({}^iPr)C(Me))_2CH\}Cl_2]$	^{1}H, ^{13}C, ^{27}Al, MS, and EA			128a
$[M\{(2\text{-}NC_5H_4)_2CH\}(Me)_2]$ (M = Al or Ga)	^{1}H, ^{13}C, EA, and X-ray	A	from ligand **IV**	59
$[Ga\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}]$	^{1}H, ^{13}C, IR, UV−vis, EA, and X-ray	A	Ga(I) carbene analogue	27
$[Ga\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}\text{-}(NC_6H_2{}^iPr_3\text{-}2,4,6)]$	^{1}H, ^{13}C, MS, UV−vis, EA, and X-ray	B	gallium imide	125
$[Ga\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl_2]$	^{1}H, ^{13}C, EA, and X-ray	B		129
$[Ga\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}I_2]$	^{1}H, ^{13}C, EA, and X-ray	B		129
$[Ga\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)_2]$	^{1}H, ^{13}C, EA, and X-ray	B		131
$[Ga\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}\text{-}(N(R)N_2N(R))]$	^{1}H, ^{13}C, EA, and X-ray	B	1-gallatetraazacyclopentane complex	131
$[Ga\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(N_3)(NR_2)]$	^{1}H, ^{13}C, EA, and X-ray	B		131
$[Ga\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(\mu\text{-}O)]_2$	^{1}H, EA, and X-ray	B	first $(GaO)_2$ ring	130
$[Ga\{(N(Me)C(Me))_2CH\}Cl_2]$	^{1}H, ^{13}C, ^{71}Ga, MS, EA, and X-ray	B		128a
$[Ga\{(N(Et)C(Me))_2CH\}Cl_2]$	^{1}H, ^{13}C, ^{71}Ga, MS, and EA			128a
$[Ga\{(N({}^iPr)C(Me))_2CH\}Cl_2]$	^{1}H, ^{13}C, ^{71}Ga, MS, EA, and X-ray	B		128a
$[In\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl_2]$	^{1}H, ^{13}C, EA, and X-ray	B		129
$[In\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}I_2]$	^{1}H, ^{13}C, EA, and X-ray	B		129
$[In\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(Me)_2]$	^{1}H, ^{13}C, EA, and X-ray	B		129
$[Tl\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}]$	^{1}H, ^{13}C, and EA			101

Table 1. Continued

complex	characterization	bonding mode	comments	ref
	Group 14			
$[Ge\{(N(Ph)C(Me))_2CH\}Cl]$	^1H, ^{13}C, MS, and EA			133
$[Ge\{(N(Ph)C(Me))_2CH\}I]$	^1H, ^{13}C, MS, and EA			133
$[Ge\{(N(Ph)C(Me))_2CH\}Cl(1,2\text{-}O,O'C_6H_2{}^tBu_2\text{-}3,5)]$	^1H, ^{13}C, MS, and EA			133
$[Ge\{(N(Ph)C(Me))_2CH\}(Cl)S]$	^1H, ^{13}C, MS, and EA			133
$[Ge\{(N(Ph)C(Me))_2CH\}(Cl)Se]$	^1H, ^{13}C, MS, and EA			133
$[Ge\{(N(Ph)C(Me))_2CH\}][BPh_4]$	^1H, ^{13}C, MS, and EA			133
$[Ge\{(N(Ph)C(Me))_2CH\}(NR_2)]$	^1H, ^{13}C, MS, and EA			133
$[Ge\{(N(Ph)C(Me))_2CH\}Cl(Cr(CO)_5)]$	^1H, ^{13}C, IR, MS, and EA			133
$[Ge\{(N(Ph)C(Me))_2CH\}Cl(W(CO)_5)]$	^1H, ^{13}C, IR, MS, and EA			133
$[Ge\{(N(C_6H_2Me_3\text{-}2,4,6)C(Me))_2CH\}Cl]$	^1H, ^{13}C, IR, EA, and X-ray	B		135
$[Ge\{(N(C_6H_2Me_3\text{-}2,4,6)C(Me))_2CH\}(N_3)]$	^1H, ^{13}C, ^{14}N, IR, EA, and X-ray	B		135
$[Ge\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl]$	^1H, MS, EA, and X-ray	B		58, 134
$[Ge\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}]\text{-}[\{B(C_6F_5)_3\}_2(\mu\text{-}OH)]$	^1H, ^{13}C, ^{11}B, ^{19}F, IR, and X-ray	A		28
$[Ge\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me){=}C(H)C(Me)\text{-}{=}N(C_6H_3{}^iPr_2\text{-}2,6)\}Cl_3]$	1H, IR, MS, EA, and X-ray	B	five-coordinate Ge, part of a four-membered ring, Ge−C(H) 1.971(3) Å	52
$[Ge\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}Cl]$	^1H, MS, and EA			58
$[Ge\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}F]$	^1H, ^{19}F, IR, MS, EA, and X-ray	B		58
$[Ge\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}H(BH_3)]$	^1H, ^{11}B, IR, MS, EA, and X-ray	B		58
$[Ge\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}F]$	^1H, ^{19}F, MS, and EA			58
$[Ge\{(N(C_6H_3Me_2\text{-}2,6)C(Me))_2CH\}H(BH_3)]$	^1H, ^{11}B, IR, MS, and EA			58
$[Ge\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}F(NR)]$	^1H, ^{19}F, ^{29}Si, and MS			58
$[Ge\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}H]$				58
$[Ge\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)C(H)C({=}CH_2)N\text{-}C_6H_3{}^iPr_2\text{-}2,6\}H\{BH(\mu\text{-}H)_2Li(OEt_2)_3\}]$	^1H, ^7Li, ^{11}B, MS, EA, and X-ray		tautomer of a β-diketiminato-germanium compound	58
$[Sn\{N(R)C(Ph)C(H)C({}^tBu)N(R)\}Cl]$	^1H, ^{13}C, ^{119}Sn, MS, EA, and X-ray	A	localized metallacycle	24, 132
$[Sn\{N(R)C(Ph)C(H)C({}^tBu)N(H)\}Cl]$	^1H, ^{13}C, ^{119}Sn, MS, EA, and X-ray	A		22, 24, 132
$[Sn\{N(H)C(Ph)C(H)C({}^tBu)N(H)\}Cl]$	^1H, ^{13}C, ^{119}Sn, MS, EA, and X-ray	A	delocalized metallacycle	24, 132
$[Sn\{N(R)C(C_6H_4Me\text{-}4)C(H)C(tBu)N(R)\}Cl]$	^1H, ^{13}C, ^{29}Si, ^{119}Sn, MS, EA, and X-ray	A		46
$[Sn\{N(H)C(C_6H_4Me\text{-}4)C(H)C(tBu)N(H)\}Cl]$	^1H, ^{13}C, ^{119}Sn, MS, and EA			46
$[Sn\{(N(R)C(Ph))_2CH\}Cl]$	^1H, ^{13}C, ^{29}Si, ^{119}Sn, MS, EA, and X-ray	B	trigonal pyramidal at Sn	24, 91
$[Sn\{(N(H)C(Ph))_2CH\}Cl]$	^1H, ^{13}C, ^{119}Sn, MS, and EA			132
$[Sn\{(N(R)C(Ph))_2CH\}Br]$	^1H, ^{13}C, ^{29}Si, ^{119}Sn, MS, EA, and X-ray	B	trigonal pyramidal at Sn	24, 91
$[Sn\{(N(R)C(Ph))_2CH\}(NR_2)]$	^1H, ^{13}C, ^{29}Si, ^{119}Sn, MS, EA, and X-ray	B	trigonal pyramidal at Sn	91, 95
$[Sn\{(N(R)C(Ph))_2CH\}(OSO_2CF_3)]$	^1H, ^{13}C, ^{29}Si, ^{119}Sn, MS, and EA		probably (^{119}Sn) four-coordinate Sn(II)	91
$[Sn\{(N(R)C(Ph))_2CH\}\{(OC(Ph))_2CH\}]$	^1H, ^{13}C, ^{29}Si, ^{119}Sn, MS, and EA			91
$[Sn\{(N(R)C(Ph))_2CH\}(NR_2)S]$	^1H, ^{13}C, ^{29}Si, ^{119}Sn, MS, EA, and X-ray	B	four-coordinate Sn(II) terminal sulfide	91, 95
$[Sn\{(N(R)C(Ph))_2CH\}(NR_2)Se]$	^1H, ^{13}C, ^{29}Si, ^{119}Sn, MS, and EA		spectra suggest structural analogue to sulfide	91
$[Sn\{(N(R)C(Ph))_2CH\}(Me)_2Cl]$	^1H, ^{13}C, ^{119}Sn, EA, and X-ray	B		18
$[Sn\{(N(H)C(Ph))_2CH\}(Me)_2Cl]$	^1H, ^{13}C, ^{119}Sn, EA, and X-ray	A		18
$[Sn\{(N(Ph)C(Me))_2CH\}Cl]$	^1H, ^{13}C, ^{119}Sn, MS, EA, and X-ray	A		133
$[Sn\{(N(Ph)C(Me))_2CH\}I]$	^1H, ^{13}C, ^{119}Sn, MS, and EA			133
$[Sn\{(N(Ph)C(Me))_2CH\}Cl(1,2\text{-}O,O'C_6H_2{}^tBu_2\text{-}3,5)]$	^1H, ^{13}C, ^{119}Sn, MS, and EA			133
$[Sn\{(N(Ph)C(Me))_2CH\}Cl(S)]$	^1H, ^{119}Sn, and MS		unstable	133
$[Sn\{(N(Ph)C(Me))_2CH\}][BPh_4]$	^1H, ^{13}C, ^{119}Sn, MS, and EA			133
$[Sn\{(N(Ph)C(Me))_2CH\}(NR_2)]$	^1H, ^{13}C, ^{29}Si, ^{119}Sn, MS, and EA			133
$[Sn\{(N(Ph)C(Me))_2CH\}(OSO_2CF_3)]$	^1H, ^{19}F, ^{119}Sn, MS, and EA			133
$[Sn\{(N(Ph)C(Me))_2CH\}(N_3)]$	^1H, ^{119}Sn, MS, and EA			133
$[Sn\{(N(Ph)C(Me))_2CH\}Cl(Cr(CO)_5)]$	^1H, ^{13}C, ^{119}Sn, IR, MS, and EA			133
$[Sn\{(N(Ph)C(Me))_2CH\}Cl(W(CO)_5)]$	^1H, ^{13}C, ^{119}Sn, IR, MS, and EA			133
$[Sn\{(N(C_6H_2Me_3\text{-}2,4,6)C(Me))_2CH\}Cl]$	^1H, ^{13}C, IR, EA, and X-ray	B		135
$[Sn\{(N(C_6H_2Me_3\text{-}2,4,6)C(Me))_2CH\}(N_3)]$	^1H, ^{13}C, ^{14}N, IR, EA, and X-ray	A	weak intermolecular Sn...N contacts	135
$[Sn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl]$	^1H, ^{119}Sn, MS, EA, and X-ray	B		34, 134
$[Sn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(OSO_2CF_3)]$	^1H, ^{119}Sn, ^{19}F, MS, and X-ray	B		134
$[Sn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(N_3)]$	^1H, ^{119}Sn, MS, and EA			134
$[Sn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me){=}C(H)C(Me){=}N(C_6H_3{}^iPr_2\text{-}2,6)\}]$	^1H, ^{119}Sn, MS, EA, and X-ray	B, I	one chelated β-diketiminato + one monodentate ligand	134
$[Sn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}(O{}^iPr)]$	^1H, EA, and X-ray	B	catalyst for living polymerization of *rac*-lactide	34
$[Sn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl_3]$	^1H, ^{119}Sn, IR, MS, and EA		five-coordinate Sn atom	52
$[Sn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Br_3]$	^1H, ^{13}C, IR, MS, EA, and X-ray	B	five-coordinate Sn atom	52
$[Sn\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}I_3]$	^1H, ^{13}C, IR, MS, EA, and X-ray	B	five-coordinate Sn atom	52

Table 1. Continued

complex	characterization	bonding mode	comments	ref
Group 15				
$[\overline{\mathrm{P\{N(H)C(C_5Me_5)C(H)C(H)N}}\mathrm{H\}\text{-}\{W(CO)_5\}_2]}$	^{1}H, ^{31}P, IR, MS, EA, and X-ray	B		136b
Lanthanides				
$\mathrm{[Ce\{(N(R)C(Ph))_2CH\}_2Cl]}$	^{1}H, ^{13}C, MS, EA, and X-ray	B		54, 141
$\mathrm{[Ce\{(N(R)C(Ph))_2CH\}(CHR_2)_2]}$	^{1}H, ^{13}C, EA, and X-ray	B		54, 141
$\mathrm{[Ce\{(N(R)C(C_6H_4{}^tBu\text{-}4))_2CH\}(NR_2)_2]}$	^{1}H, ^{13}C, ^{29}Si, IR, MS, and X-ray	B		141
$\mathrm{[Pr\{(N(R)C(Ph))_2CH\}_2Cl]}$	^{1}H, ^{29}Si, MS ,and EA			54
$\mathrm{[Nd\{(N(R)C(Ph))_2CH\}_2Cl]}$	^{1}H, ^{13}C, ^{29}Si, MS, EA, and X-ray	B		54
$\mathrm{[Sm\{(N(R)C(Ph))_2CH\}_2Cl]}$	^{1}H, ^{13}C, ^{29}Si, MS, and EA			54
$\mathrm{[Sm\{(N(R)C(Ph))_2CH\}_2(thf)_2]}$	^{1}H and MS			54
$\mathrm{[Sm\{(N(Ph)C(Me))_2CH\}_3]\cdot 2thf}$	IR and X-ray	A		137
$\mathrm{[Sm\{(N({}^iPr)C(Me))_2CH\}_2Br]}$	IR and X-ray	B		138
$\mathrm{[Sm\{N(R)C(C_6H_4Me\text{-}4)C(H)C(Ad)\text{-}N(R)\}_2]}$	X-ray	B		136a
$\mathrm{[(Sm\{(N(R)C(C_6H_4Ph\text{-}4))_2CH\})_2(\mu\text{-}\{(N(R)C(C_6H_4Ph\text{-}4))_2CH\})]}$	X-ray	B, D	subvalent Sm?	136a
$\mathrm{[KSm\{(N(R)C(Ph))_2CH\}_2]_2}$	X-ray	B, D	dimer has one *N*,*N′*-bridging ligand to K, and the other has an η^6-contact to neighboring K atom; subvalent Sm?	136a
$\mathrm{[Gd\{(NC_5H_4)_2CH\}_3]}$	X-ray	A		140
$\mathrm{[Gd\{(N(Ph)C(Me))_2CH\}_3]}$	X-ray	A		137
$\mathrm{[Gd\{(N(Ph)C(Me))_2CH\}Br_2(thf)_2]}$	IR and X-ray	A		137
$\mathrm{[Gd\{(N({}^iPr)C(Me))_2CH\}_2Br]}$	IR and X-ray	B		137
$\mathrm{[Tm\{(N(R)C(Ph))_2CH\}_2I]}$	MS and EA			54
$\mathrm{[Yb\{(N(R)C(Ph))_2CH\}_2]}$	^{1}H, ^{13}C, ^{171}Yb, ^{29}Si, MS, EA, and X-ray	B		54, 136a, 139
$\mathrm{[Yb\{N(R)C(Ph)C(H)C({}^tBu)N(R)\}_2]}$	^{1}H, ^{13}C, ^{171}Yb, ^{29}Si, MS, and EA			54, 154
$\mathrm{[Yb\{(N(R)C(Ph))_2CH\}_2(thf)_2]}$	^{1}H, ^{13}C, and ^{29}Si			54
$\mathrm{[Yb\{(N(R)C(Ph))_2CH\}_2Cl]}$	^{1}H, MS, and EA			54
$\mathrm{[Yb\{(N(R)C(C_6H_4Ph\text{-}4))_2CH\}_2]}$	^{1}H, ^{13}C, ^{171}Yb, EA, and X-ray	B (but one longer Yb−N bond)	in solution may (^{171}Yb NMR) have planar, three-coordinate Yb	136a
$\mathrm{[Yb\{N(R)C(C_6H_4Me\text{-}4)C(H)\text{-}C(Ad)N(R)\}_2]}$	^{1}H, ^{13}C, ^{171}Yb, EA, and X-ray	B (but one longer Yb−N bond)	in solution may (^{171}Yb NMR) have planar, three-coordinate Yb	136a
$\mathrm{[(Yb\{(N(R)C(Ph))_2CH\}(\mu\text{-}I)(thf)]_2}$	^{1}H, ^{13}C, ^{171}Yb, and X-ray	B		136a
$\mathrm{[Yb\{(N(R)C(C_6H_4Ph\text{-}4))_2CH\}Cl(\mu\text{-}Cl)_2\text{-}Li(thf)(OEt_2)]\cdot OEt_2}$	X-ray	B		136a
$\mathrm{[Yb\{(N(R)C(Ph))_2CH\}_2\{Li(thf)\}_2]}$	X-ray	D	subvalent Yb?	136a
$\mathrm{[Yb\{(N(R)C(C_6H_4Ph\text{-}4))_2CH\}_2\{Li(thf)\}_2]}$	X-ray	D	subvalent Yb?	136a
Actinides				
$\mathrm{[Th\{(N(R)C(Ph))_2CH\}_2Cl_2]}$	^{1}H, ^{13}C, MS, EA, and X-ray	B		144
$\mathrm{[U\{(N(R)C(Ph))_2CH\}Cl(\mu\text{-}Cl)(NR)]_2\text{-}[UCl_2\{(N(R)C(Ph))_2CH\}\text{-}\{N(R)C(Ph)NC(Ph)CHR\}]_2}$	^{1}H, EA, and X-ray	B	dinuclear U(VI) cation, U(III) anions (one β-diketiminate, one 1,3-diazaallyl)	22

5. β-Diketiminatometal Complexes

Table 1 provides a summary of data on β-diketiminatometal complexes (and aldiminato analogues) [MS = mass spectrometry; EA = elemental analyses; ^{x}M corresponds to NMR-active nucleus; UV−vis = electronic spectroscopy; IR = infrared spectroscopy; El = electrochemistry; ESR = electron paramagnetic resonance; MCD = magnetic circular dichroism; μ_{eff} = magnetic moment; R = $\mathrm{SiMe_3}$; R′ = $\mathrm{Si^tBu_3}$; Ad = adamantyl; Cp = η^5-$\mathrm{C_5H_5}$; Cp* = η^5-$\mathrm{C_5Me_5}$; tmen = $\mathrm{(Me_2NCH_2)_2}$; pmdeta = $\mathrm{(Me_2NCH_2CH_2)_2NMe}$; HMPA = $\mathrm{OP(NMe_2)_3}$; COD = 1,5-cyclooctadiene; COE = cyclooctene; NBE = norbornene].

6. Concluding Remarks

The field of β-diiminatometal (largely β-diketiminatometal) complexes is now very extensive and surely has reached maturity. Of the 166 citations in section 5, 150 deal with original findings. The topic has witnessed rapid growth, as evident from the 38 papers published in 2001, the 20 in 2000, the 49 in 1994−1999, the 14 dealing with unpublished work, and only 32 publications before 1990. Of the 63 natural metals, β-diiminates have been reported for all but Rb, Cs, Y, La, Nb, Ta, Re, Ru, Os, Ag, Au, Hg, Pb, As, Sb, Bi, Eu, Dy, Ho, and Lu. Data for 475 metal β-diiminates are shown in Table 1.

β-Diketiminates have an important role as spectator ligands, by virtue of their strong binding to metals, their tunable and extensive steric demands, and their diversity of bonding modes. They are often able to stabilize complexes in unusually low metal oxidation states, as cations, and others containing multiply bonded (to metal) coligands. Many such complexes are coordinatively unsaturated and this and other features are the key to their ability to function as catalysts for processes as varied as olefin oligo-, poly-, and copolymerization, ring-opening polymerization of lactide or related monomers, and copolymerization of expoxides and carbon dioxide.

The β-diketiminates are structurally related to ligands such as porphyrins and corrins. Appropriate Cu(II) β-diketiminates are biomimetic analogues of Cu(II) protein active sites, for example, Cu(II) phenolates as intermediates in the catalytic cycles of metalloenzymes such as galactose oxidase.

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8. Appendix (Added in Proof): 2002 Publications up to End of June

We are aware of 27 papers in the above category. They have contributed to the following areas, using the numbering system of the list of contents. Abbreviations used: R = $SiMe_3$, L^1 = $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]$, L^2 = $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C({}^tBu)\}_2CH]$, L^3 = $[\{N(CH_2CH_2NEt_2)C(Me)\}_2CH]$.

Section 3. The compounds $[YbL^4\{\mu\text{-}Li(thf)\}_2]$ [L^4 = $\{N(R)C(R')\}_2CH$, R′ = Ph or C_6H_4Ph-4] have been formulated as Yb(II) complexes with a *dianionic* β-diketiminato ligand.[155]

Section 4.1. The compounds $[M\{(N(R)C(C_6H_3Me_2\text{-}2,6))_2SiR\}]_2$ have been described.[156]

Section 4.2. $[Mg(L^1){}^iPr]$ is an initiator for the living syndioselective polymerization of methyl methacrylate.[157] $[Mg(L^1)(\mu\text{-}F)(thf)]_2$ has been reported.[158] The compounds $[Mg(L^1)(N^iPr_2)(thf)]$ and $[Mg(L^1)(O^tBu)(thf)]$ have been compared with Zn analogues.[159]

Section 4.3. DFT studies on early transition metal complexes have been described.[160]

Seciton 4.3.1. $[Sc(L^2)Me_2]$ has been converted into cationic Sc complexes, which are procatalysts for ethylene polymerization.[161] The complex $[ScBr(\mu\text{-}L^3MgBr)_2]$ has been formulated as a Sc(I) complex.[162]

Section 4.3.2. Chiral C_2-symmetric Zr(IV) β-diketiminates have been described.[163]

Section 4.3.3. Various β-diketiminato Cr(III) complexes are procatalysts for ethylene polymerization.[164]

Section 4.4. Mössbauer and EPR spectra of some planar high spin Fe(II) β-diketiminates have been analyzed.[165] Further reactions of $[Rh(L^1)(COE)]$[166] and $[Pt(L^1)Me_3]$[167] have been described. Transient superoxocopper and bis(μ-oxo)dicopper β-diketiminates have been identified.[168] $[Cu\{(N(C_6H_2Me_3\text{-}2,4,6)C(Me))_2CH\}(OAc)]$ underwent oxidative degradation yielding $\{N(C_6H_2Me_3\text{-}2,4,6)C(Me)\}_2CO$.[169]

Section 4.5. $[Zn(L^1)X]$ [X = N^iPr_2, O^tBu, $OSiPh_3(thf)$] complexes have been reported.[159] An MO study of $[Zn(L^1)(OMe)]$-catalyzed copolymerization of CO_2 and cyclohexene oxide has been reported,[170] as has a review of stereoselective metal (including Zn)-catalyzed polymerizations.[171]

Section 4.6. Further studies of BODIPY dyes,[172] and a review of Al(I) complexes[173] have been published. $[Al(L^5)I_2]$ and a higher homologue,[174] as well as $[\{Al(L^5)Cl\}_2(\mu\text{-}O)]$,[175] L^5 = $[\{N(Me)C(Me)\}_2CH]$ have been reported. Data on $[Ga(L^1)(PPh_2)\{OSO_2CF_3\}]$,[176] $[In(L^1)Cl]_2$,[177] and $[In(L^1)(Cl)(\mu\text{-}OH)]_2$ have appeared.

Seciton 4.8. A review of nonclassical organolanthanide chemistry provided data on $[\{K(\mu\text{-}L^4)SmL^4\}_2]$ and $[YbL^4\{\mu\text{-}Li(thf)\}_2]$ (see also ref. 155).[178] The compounds $[Pr(L^3)X_2]$ (X = Cl, Br, BH_4) have a pseudooctahedral Pr environment.[179] The compounds $[Yb(L^1)Cl_2(thf)_2]$, $[Yb(L^1)Cl(\eta^5\text{-}C_5H_4Me)]$, $[Yb(L^1)(NR'_2)(\eta^5\text{-}C_5H_4Me)]$ (R′ = ^{i}Pr, Ph) have been characterized[180] and mentioned in a review.[181]

Note Added After ASAP Posting

An earlier version of this article posted ASAP August 24, 2002 had an incorrect N−N bond length on p 3044 (second full paragraph). The correct bond length appears in this version posted September 11, 2002.

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