

Bis(imino)pyridines: Surprisingly Reactive Ligands and a Gateway to New Families of Catalysts

Vernon C. Gibson,^{*,†} Carl Redshaw,^{*,‡} and Gregory A. Solan^{*,§}

Department of Chemistry, Imperial College, South Kensington Campus, London, SW7 2AZ, United Kingdom, Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, The University of East Anglia, Norwich, NR4 7TJ, United Kingdom, and Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, United Kingdom

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1. Introduction and Scope

It has been almost a decade since sterically demanding bis(arylimino)pyridine ligands, [2,6-(ArN=CR)₂C₅H₃N] (**1**) (Figure 1), were found to impart late transition metals, especially iron and cobalt,^{1–7} with very high (unprecedented for these metals) catalytic activities for ethylene polymerization, in some cases as high as those of the most efficient metallocenes. Since these initial developments, numerous reports have appeared in the literature concerning the effects of ligand modifications, and structure–activity relationships have become apparent. However, the reason why this particular ligand set is able to promote such catalytic activity, where many other ligands fail, remains largely a mystery. This review focuses on the development of the chemistry of tridentate **1** and its associated metal complexation chemistry and reveals how this ligand system is capable of accepting or donating negative charge, thereby influencing the redox potential of coordinated metals. Furthermore, the variety of chemistry displayed by this ligand system is truly amazing, best illustrated by the varied points of attack available to common alkylating agents (*vide infra*). The chemistry developed on **1** and its relatives has facilitated entry into a host of new ligand families which are currently being investigated around the world for their potential use in a variety of metal-mediated transformations. Indeed, the explosion in coordination chemistry for this class of ligand has now led to the catalytic screening of many transition metals as well as lanthanides and main-group elements (see Chart 1). Herein, we discuss the latest developments on the iron/cobalt system following the Brookhart–Gibson–Dupont discovery^{1–7} before highlighting the rich chemistry displayed by this ligand and its close relatives.

For more general overviews of post-metallocene α -olefin polymerization catalysts, the reader is referred to a series of

* To whom correspondence should be addressed. E-mail: v.gibson@ic.ac.uk, carl.redshaw@uea.ac.uk, and gas8@le.ac.uk.

[†] Imperial College.

[‡] The University of East Anglia.

[§] University of Leicester.



Vernon Gibson received his B.Sc. degree from the University of Sheffield in 1980 followed by his D.Phil degree in 1984 from the University of Oxford, where he studied with Malcolm Green. He was a NATO postdoctoral fellow with John Bercaw at Caltech from 1984 to 1986 before being appointed to a lectureship in Inorganic Chemistry at the University of Durham, England. He was promoted to Full Professor at Durham in 1992 and in 1995 moved to Imperial College, where he now holds the Sir Edward Frankland BP Chair of Inorganic Chemistry. His research interests include fundamental studies on metal coordination and organometallic complexes and their catalytic applications.



Carl Redshaw entered university after a promising career with Hull City was cut short through injury. He received his B.Sc. (Hons, 1985) and Ph.D. (1989, with John Errington) degrees from the University of Newcastle. He was a Robert A. Welch Fellow at the University of Texas, Austin (1989–90), and a postdoctoral fellow with the late Professor Sir G. Wilkinson at Imperial College, London (1990–92), and at the IRC, Durham (1993–95). He then returned to Imperial College in 1995 with Vernon Gibson. In 1998, he was awarded a Leverhulme Fellowship and moved to the University of East Anglia in 1999, where he was appointed as a lecturer in Inorganic Chemistry, and was promoted to Senior Lecturer in March 2007. His interests include the coordination chemistry of calixarenes, main-group macrocyclic chemistry, and use of metal agents in the battle against cancer and leukemia.

recent reviews,^{8–12} while simple derivatization of the iron/cobalt bis(imino)pyridine system has recently been reviewed by Bianchini and co-workers.¹³

2. 2,6-Bis(imino)pyridine Ligands

2.1. Ligand Synthesis

The first example of a ligand of this class to be reported was bis(hydrazone)pyridines by Busch and Stoufer,¹⁴ while Lions and Martin¹⁵ and later Figgins and Busch¹⁶ prepared and characterized a series of bis(alkylimino)pyridines. The bis(arylimino)pyridine ligands, [2,6-(ArN=CR)₂C₅H₃N] (**1**, R = H or Me, Ar = aryl group), as first reported by Alyea



Greg Solan was born in Redhill, England, in 1966. He attended the University of Sussex, where he received his B.Sc. (Hons, 1988) degree in Chemistry with European studies. He carried out his doctoral work at the University of Cambridge in organometallic chemistry under the supervision of Martin Mays. After finishing his Ph.D. degree (1992), he was a postdoctoral fellow at the Université de Lausanne with the late Carlo Floriani, at the University of Edinburgh with Richard Winpenny, and at Imperial College with Vernon Gibson. In 1999, he was appointed to a lectureship in Inorganic Chemistry at the University of Leicester. His research interests cover coordination and organometallic chemistry and their use in catalysis and new inorganic materials synthesis.

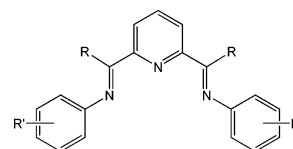


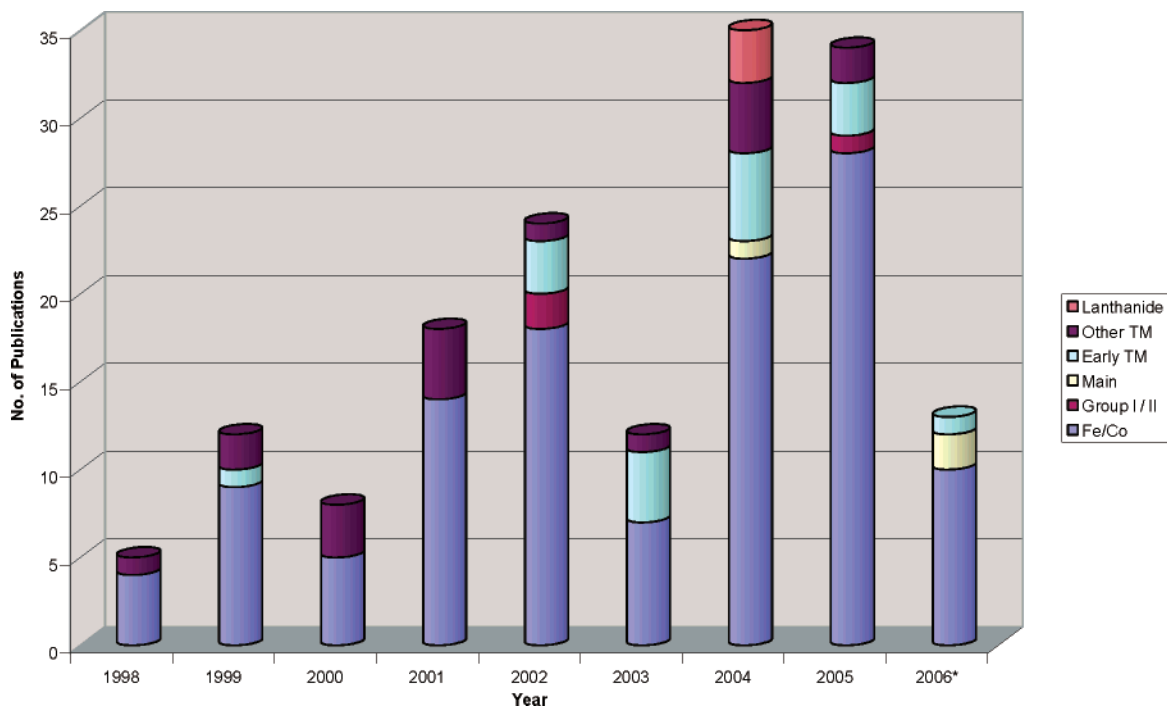
Figure 1. Bis(arylimino)pyridine **1** (R = H or Me, R' = H, hydrocarbyl, fluorohydrocarbyl, halo, alkoxy, hydroxyl).

and Merrel,¹⁷ are readily accessible from the condensation reaction of either 2,6-pyridinedicarboxaldehyde or 2,6-diacetylpyridine with two equivalents of the corresponding aniline in an alcohol (e.g., ethanol, propanol, methanol) at elevated temperature, and the reaction is often catalyzed by an acid (e.g., formic acid, acetic acid, *p*-toluene sulfonic acid) (Scheme 1). In general, for a given aniline, the condensation reaction occurs more readily for 2,6-pyridinedicarboxaldehyde than for 2,6-diacetylpyridine, while 2,6-dibenzoylpyridine is almost unreactive under these conditions. Using this simple approach a rich variety of symmetrical examples of **1** have been prepared, many of which are included in Table 1. In addition, a number of bis(imino)pyridine ligands containing *N*-aryl groups fused to cyclic-aryl^{11,19–21} groups have been reported.

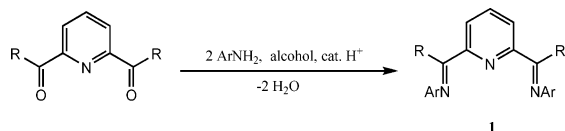
The less reactive 2,6-dibenzoylpyridine can be activated toward condensation by templating it with anhydrous nickel dichloride: two equivalents of the aniline in acetic acid under reflux react to afford the nickel complex [2,6-(ArN=CPh)₂C₅H₃N]NiCl₂ (**2**, Ar = 2,4,6-Me₃C₆H₂) in 89% yield (Scheme 2). Demetalation of **2** with aminopropyl silica gel in dichloromethane provides [2,6-(ArN=CPh)₂C₅H₃N] (**3**, Ar = 2,4,6-Me₃C₆H₂) in 51% yield.⁴³ Alternatively, **3** is available via acid-catalyzed condensation of the 2,6-dibenzoylpyridine, the latter being formed from the acid chloride by a phenylcuprate coupling reaction.⁵⁶

Bis(imino)pyridines containing non-hydrocarbyl substituents on the imino carbons can also be readily prepared. For example, ether and thioether groups can be attached to afford **4** by treating pyridine-2,6-dicarboxyimidoil dichloride with the respective NaER (R = Me, 2,6-Me₂C₆H₃; E = O, S; Scheme 3).⁵⁷ Alternatively, methoxy groups can be appended

Chart 1. Number of Publications Per Year on Bis(imino)pyridyl–metal Precatalysts (as of 09/25/06)



Scheme 1



to the ligand backbone by treatment of the pyridine-2,6-diacetyl chloride with aniline to give the carboxylic acid amide, which is then further reacted with Meerwein's reagent $[\text{Me}_3\text{O}][\text{BF}_4]$ to give the bis(imino)pyridine **5** (Scheme 4).⁵⁶

Introduction of a *tert*-butyl group into the 4 position of the peripheral pyridine ring in **1** can be realized in two steps.⁵⁸ First, radical substitution in 2,6-diacetylpyridine with *t*-Bu \cdot radicals using Minisci conditions gives the *tert*-butyl-substituted 2,6-diacetylpyridine (Scheme 5). Second, conversion to the novel bis(arylimino)pyridines [2,6-(ArN=CMe)₂-4-*t*-Bu-C₅H₂N] (**6**, Ar = 2,6-Me₂C₆H₃, 4-*t*-BuC₆H₄) can be achieved using standard condensation chemistry protocol (see Scheme 1).

Derivatization of the *N*-aryl substituents in **1** is also possible. For example, Ionkin et al. employed a palladium-catalyzed Suzuki cross-coupling of a tetrabromide-containing bis(arylimino)pyridine and a fluorinated boronic acid to give the 3,5-(*p*-FC₆H₄)-4-MeC₆H₂ member of the family (CF₃ groups can be introduced in a similar fashion) (Scheme 6).⁴⁷

Unsymmetrical 2,6-bis(arylimino)pyridines (Figure 2), [2-(ArN=CMe)-6-(Ar'N=CMe)C₅H₃N] (**7**), are prepared by the successive condensation reactions of 2,6-diacetylpyridine with two different anilines.^{31,43,48,59–61} For example, Esteruelas et al. prepared a family of unsymmetrical bis(arylimino)pyridines by, first, treating 2,6-diacetylpyridine with 2,4,6-trimethylaniline and, second, addition of the second aniline.⁴³

While the main emphasis has been on preparing bis(arylimino)pyridine ligands, there have also been a number of reports involving alkyl substituents, viz. bis(alkylimino)pyridine ligands.^{43,62,63} For example, the bis(cyclohexylimino)pyridine, [2,6-((C₆H₁₁)N=CMe)₂C₅H₃N] (**8**), has been prepared from the catalytic condensation of two equivalents

of cyclohexylamine with one equivalent of 2,6-diacetylpyridine by Esteruelas et al. (Figure 3).⁴³ Unsymmetrical 2-(arylimino)-6-(alkylimino)pyridines have also been reported in the case of **9** containing a stereogenic center (Figure 3).⁶¹

Condensation chemistry, via the use of hydrazines, allows access to bis(hydrazone)pyridines of the form **10** (Chart 2); the pyrrolyl-substituted derivative requires extended reaction times (5 days) to obtain good yields.^{64,65} Similarly, the ligands **11–14** have been prepared from the corresponding *N*-amino-*N*-heterocycle and 2,6-diacetyl(or diformyl)pyridine.⁶⁶

More elaborate bis(imino)pyridines belonging to the *N*-aryl family **1** that contain alkoxy groups (R' = long chain alkyl group) in the 3-, 4-, and 5-aryl positions have also been prepared (Chart 3) with a view to forming metallomesogens (liquid-crystalline metal complexes). Extension of this work to bis(imino)pyridines incorporating N–N linkages has also been reported (**15**).^{67–69}

In general, X-ray structures of **1** reveal that in the solid state the imino nitrogen atoms prefer to be disposed *trans* with respect to the central pyridine nitrogen.^{31,70–73} The molecular structure of the 2,6-dimethylphenyl-substituted example of **1** is depicted in Figure 4.

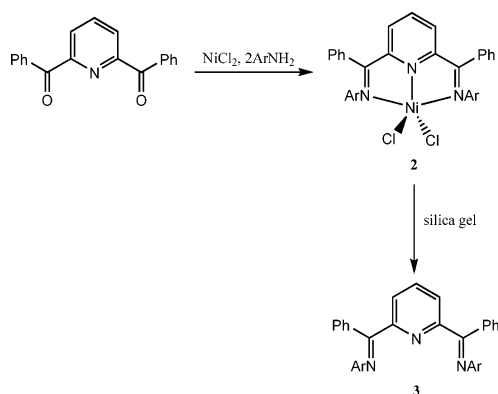
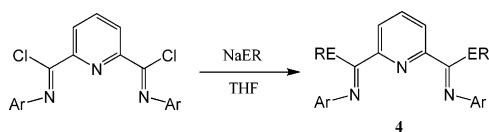
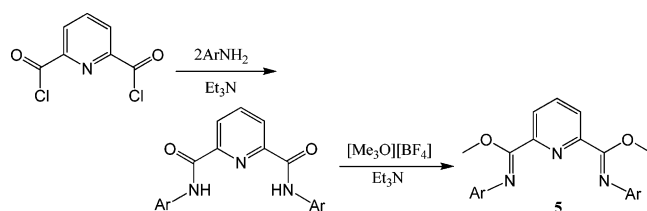
Structural frameworks related to **1** and its derivatives will be discussed in sections 3 and 4. Pybox ligands^{74–76} and macrocyclic ligand systems⁷⁷ have been reviewed elsewhere.

2.2. Iron and Cobalt Complexes/Precatalysts

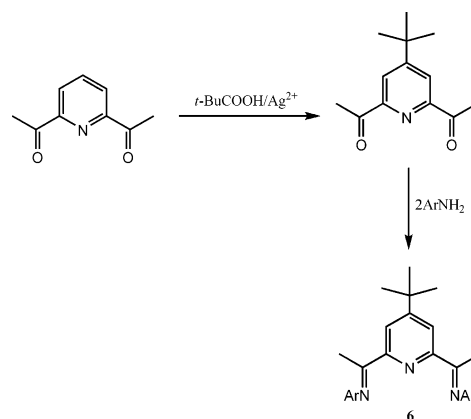
The first reports concerning the complexation of bis(imino)pyridine to iron and cobalt date back to the 1950s when Busch and Stoufer reported bis(hydrazone)pyridine complexes of iron(II), cobalt(II), and nickel(II),¹⁴ and the series was later extended by Curry, Robinson, and Busch⁷⁸ with subsequent spectroscopic studies carried out by Krumholz.⁷⁹ Bis(alkylimino)pyridine complexes of iron, cobalt, and copper were reported about the same time by Lions and Martin¹⁵ and by Figgins and Busch.⁸⁰ The paper by Lions and Martin also included the bis(phenylimino)pyridine ligand, which proved to give highly crystalline, deep red bis-

Table 1. Aryl Group Substitution Patterns Reported for 1

substitution pattern	R	refs ^a	substitution pattern	R	refs ^a
2-methyl	Me	1,18	2-(trifluoromethyl)	Me	43,44
4-methyl	Me	22	4-(trifluoromethyl)	Me	45
2,3-dimethyl	Me	18,23,24	2-(trifluoromethyl)-4-fluoro	Me	44
2,4-dimethyl	Me	18,25	2-(trifluoromethyl)-6-fluoro	Me	44
2,5-dimethyl	Me	26,27	3-bromo-2,4,6-trimethyl	Me	27,29
2,6-dimethyl	Me	6,25	4-bromo-2,6-dimethyl	Me	46
2,4,6-trimethyl	Me	6	3,5-dibromo-4-methyl	Me	47
2,6-dimethyl-4-ferrocenyl	Me	28	2-chloro-4-methyl	Me	41
2-ethyl	Me	1	2-fluoro-4-methyl	Me	41
2,6-diethyl	Me	29	2-methoxy-6-methyl	Me	43
2-isopropyl	Me	1	4-bromo-2,6-diisopropyl	Me	30
2,6-diisopropyl	Me	6	2-bromo-4,6-diisopropyl	Me	30
2,4,6-triisopropyl	Me	30	2-methyl-4-nitro	Me	48
2,6-diisopropyl-4-ferrocenyl	Me	28	2-methyl-3-nitro	Me	48
2,6-diisopropyl-4-allyl	Me	159	2-methyl-4-hydroxy	Me	49
2-isopropyl-6-methyl	Me	31	2-methyl-4-diethylamine	Me	48
2- <i>tert</i> -butyl	Me	6,22,25	4-methoxy	Me	50,51
2,5-di- <i>tert</i> -butyl	Me	32,33	2-methyl	H	18
2,6-dicycloalkyl	Me	34–36	4-methyl	H	52
2-bromo	Me	37,38	2,6-dimethyl	H	1
2,6-dibromo	Me	39	2,4,6-trimethyl	H	1,53
2-chloro	Me	35,37	2,6-diethyl	H	1
2,6-dichloro	Me	38	2,6-diisopropyl	H	1,54
2-fluoro	Me	37,38,40	2,6-diphenyl	H	18
2,4-difluoro	Me	41	4-methoxy	H	50,55
2,6-difluoro	Me	37,40,42			

^a Only original reports given.**Scheme 2****Scheme 3****Scheme 4**

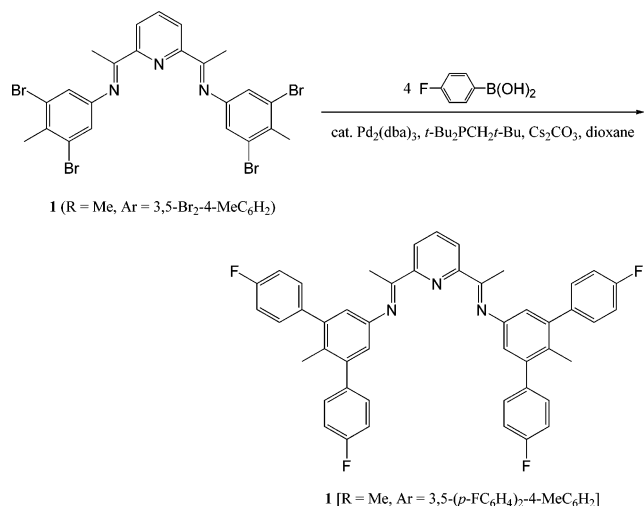
chelate perchlorate salts of iron(II). Other early examples were concerned with its coordination chemistry toward copper(II) and nickel(II).^{81,82} The group of Nelson, as well as working on macrocyclic ligand systems containing the bis(imino)pyridine motif,^{83,84} also studied the interaction of bis(imino)pyridine ligands with pendant olefinic, ethers, or thioether groups with a range of transition metals including

Scheme 5

complexes of copper, rhodium, and palladium.^{85–87}

Following these early reports, which were restricted to relatively small *N*-imino substituents, research into bis(imino)pyridine coordination chemistry was somewhat limited. In the mid-to-late 1980s, a number of reports were concerned with the binding capacity (both tridentate and bidentate modes observed) of the ligand with metal carbonyls,^{88,89} but it was not until 1998 with the discovery of polymerization-active iron and cobalt complexes stabilized by sterically hindered derivatives that a proliferation of well-characterized examples appeared in the literature. Typically, the synthesis of the iron and cobalt halide systems proceeds by treatment of a suitable divalent iron or cobalt halide (e.g., $\text{MX}_2 \cdot x\text{H}_2\text{O}$ or MX_2 ; X = Cl or Br) source with **1** in tetrahydrofuran or *n*-butanol giving complexes of composition $[\text{2,6-(ArN=CR)}_2\text{C}_5\text{H}_3\text{N}]\text{MX}_2$ (**16**, M = Fe; **17**, M = Co; R = H or Me, Ar = aryl, X = Cl or Br) (Scheme 7).^{1–7} Qian and co-workers noted that it is important to use a solvent of lower polarity than acetonitrile to encourage formation of five-coordinate complexes.³⁷ If the aryl groups are insufficiently bulky, bis(ligand) salts of the type $[\text{2,6-(ArN=CR)}_2\text{C}_5\text{H}_3\text{N}]_2\text{M}[\text{MX}_4]$ (**18**, Ar = Ph) can be formed.

Scheme 6



Crystal structure analyses of [2,6-(ArN=CMe)₂C₅H₃N]-MCl₂ [**16**, M = Fe, Ar = 2,6-*i*-Pr₂C₆H₃ or 2,4,6-Me₃C₆H₂; **17**, M = Co, Ar = 2-*t*-BuC₆H₄] revealed a distorted square-pyramidal geometry at the metal with the arylimino groups almost perpendicular to the plane of the bis(imino)pyridine backbone [Figure 5 depicts the molecular structure of **16** (R = Me, Ar = 2,4,6-Me₃C₆H₂, X = Cl)].⁶ The overall result is that the metal center is protected both above and below the M–N–N–N plane by the bulky *ortho* substituents on the imino aryl rings. When the aryl group is 2,3-dimethylphenyl or biphenyl (M = Fe), the geometry at the metal center is a distorted trigonal bipyramid with the pyridyl nitrogen and two halides forming the equatorial plane. This same geometry is also adopted at cobalt for the 2,6-Me₂C₆H₃ derivative.⁹⁰ For 2,4- or 2,6-difluoro-phenyl-derived ligands, complexation with iron dichloride in acetonitrile yielded only the ion-pair complexes [{2,6-(2,4-F₂C₆H₃N=CMe)₂C₅H₃N}]₂-Fe][Cl₃FeOCl₃] (**19**) and [{2,6-(2,6-F₂C₆H₃N=CMe)₂C₅H₃N}]₂-Fe][FeCl₄] (**20**), respectively.⁴²

The capacity of bis(arylimino)pyridine–iron and –cobalt halides to act as precatalysts for the polymerization and oligomerization of ethylene was first shown when toluene solutions of **16** or **17** were treated with excess MAO (or MMAO) to form the active catalyst (Scheme 8). In general, the productivities of the iron catalysts are an order of magnitude higher than for cobalt. Many of the initial reports were concerned with derivatization of the iminoaryl group, with particular emphasis on the steric influence of the 2,6-*ortho* substituents (Charts 4 and 5).^{1–7} Indeed, in these

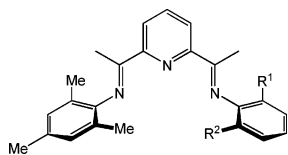


Figure 2. Unsymmetrical **7** (R¹ = R² = *i*-Pr; R¹ = *t*-Bu, R² = H; R¹ = CF₃, R² = H).

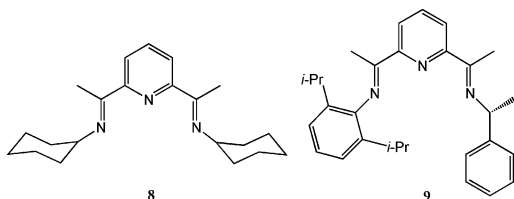


Figure 3. *N*-Alkyl-substituted bis(imino)pyridines.

systems it became evident that simply changing the size of the aryl substituents allows for control over not only catalyst activity, but also polymer molecular weight. With 2,6-R'₂ [R' = *i*-Pr (**a**), Me (**b**)] as the substitution pattern, access to strictly linear, high molecular weight polyethylene was achievable.^{2,4,5} In the case of **16b**, the activity of the polymerization catalyst could be enhanced by introducing a methyl group in the *para* position (**16c**).² On changing from the ketimine (R = Me) to the aldimine (R = H) derivative (for a given aryl group) of **16** and **17**, a reduction in polymer molecular weight was observed along with a lowering in the activity of the catalyst (e.g., **16c** vs **16d**).² Introduction of a single *ortho* substituent (e.g., R' = 2-Me) onto the imino-aryl group gives almost exclusively linear α -olefins (**16e**).^{1,18} The influence of electronic properties of the aryl groups has since been the subject of a number of investigations, and structure/activity trends have been identified. Studies on iron systems with different combinations of H, halide, and methyl in the *ortho*, *meta*, and *para* positions have established that optimal activities are obtained when a chloro substituent is *ortho* and a methyl is either *meta* or *para* (**16f**); all are oligomerization catalysts affording mostly linear α -olefins.⁴¹ Difluoro-substituted ligands (**g**, one F always *ortho*) have also been screened (with MMAO) for both iron and cobalt, and high oligomerization activities were found for the iron systems (**16g**), whereas the cobalt systems (**17g**) were inactive.^{41,42} Introduction of a *para*-bromo group (**16h**) raises the activity from 3750 to 5900 g/mmol·h·bar with a concomitant decrease in polymer molecular weight.⁴⁶ The effect of the *para*-bromo group has been compared to that of *para*-isopropyl, and results suggest electronic effects are beneficial for increased activity for iron systems, whereas steric effects appear to be more dominant for cobalt.³⁰

The Dupont group noted that a trifluoromethyl (CF₃) substituent in the *para* position of the aryl ring had little effect on catalyst productivity,^{3,4} though it was later found that the use of an *ortho*-aryl CF₃ group in the cobalt systems can lead to large increases in activity (and catalyst lifetimes) upon activation with MAO.⁴⁴ Notably, the system containing an *ortho*-CF₃ group in combination with an *ortho*-F substituent (**i**) possesses an activity >100 000 g/mmol·h·bar for the cobalt-based catalyst (**17i**), a figure of merit comparable to the most active iron catalysts. This same system will also oligomerize propene, 1-butene, and 1-hexene, yielding predominantly highly linear dimer products through 1,2- followed by 2,1-insertions. A number of substitution patterns involving *ortho*-methyl groups and *meta*-fluorinated aryls (F or CF₃ groups) have been investigated by Ionkin et al.⁴⁷ Ligands involving a 2,3-pattern of *ortho*-methyl and *meta*-aryl (**j**) or with two *meta*-aryls on one side and two *ortho*-methyls (**k** and **k'**) on the other yield highly active iron oligomerization systems with more ideal Schulz–Flory distributions than related systems containing no *meta*-aryl groups.⁴⁷ In the absence of *ortho*-methyl substituents but with two *meta*-fluorinated aryl groups on each imino aryl ring, inactive ion-pair complexes of the form [L₂Fe][FeCl₄] are generated.

Incorporating *ortho*-benzyl groups (**l**) has been reported to give a very high activity iron catalyst (40 800 g/mmol·h·bar cf. 1655 g/mmol·h·bar for the original 2,6-diisopropylphenyl derivative under the same catalytic conditions), producing linear polyethylene. Related ligands possessing either an *ortho*-phenyl or *ortho*-myrtanyl group are far less

Chart 2

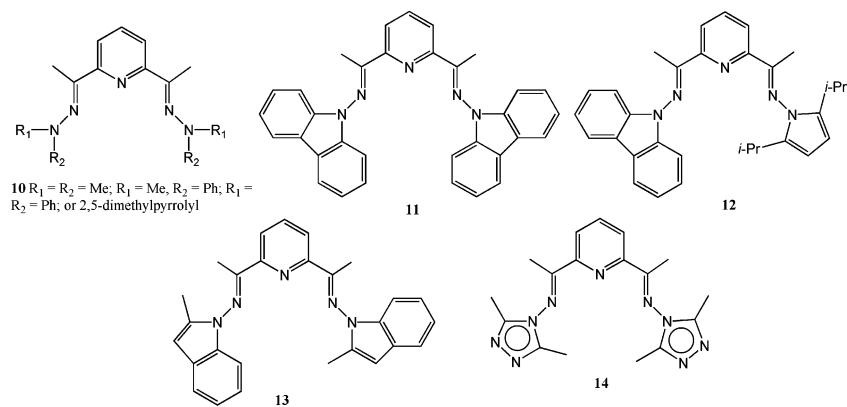
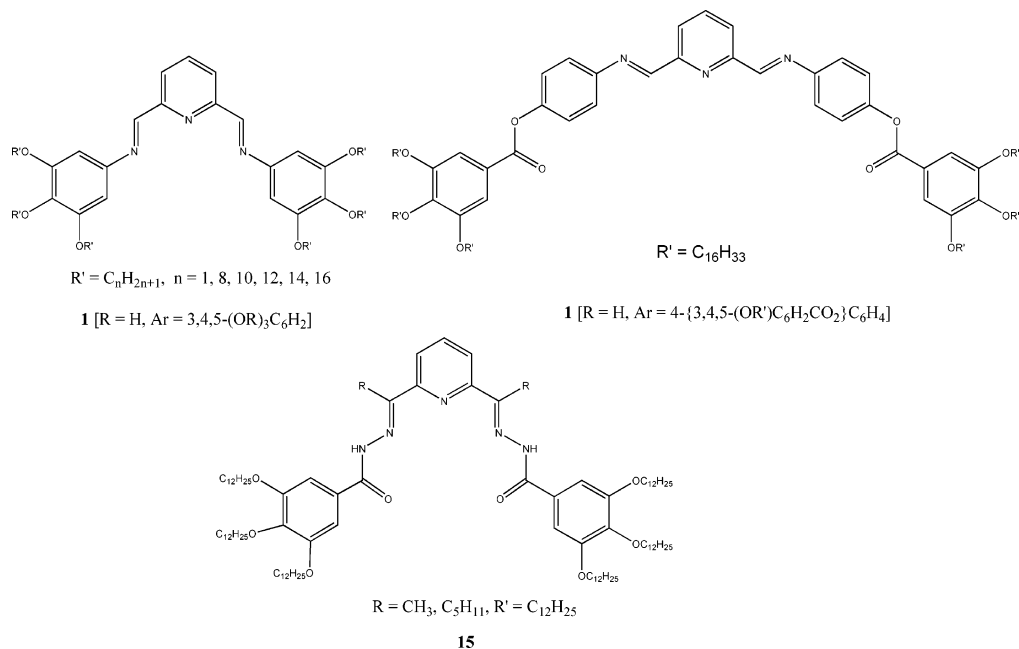
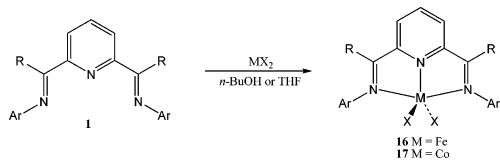


Chart 3



Scheme 7



active.²⁰ Use of a pyrenyl group (**m**) gave an iron catalyst exhibiting an activity of 13 480 g/mmol·h·bar and is reported to yield branched polyethylene.²⁰ For iron systems based on naphthyl groups, introduction of an *ortho*-methyl group (**n**) greatly enhances the activity of the system.¹⁹

Introduction of an electrochemically active ferrocenyl group at the para position has also been reported;²⁸ the iron

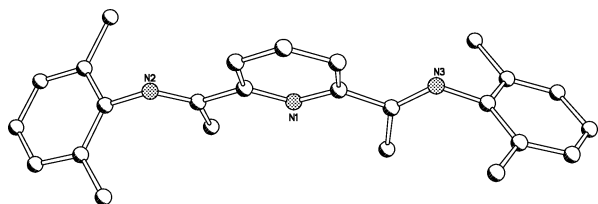
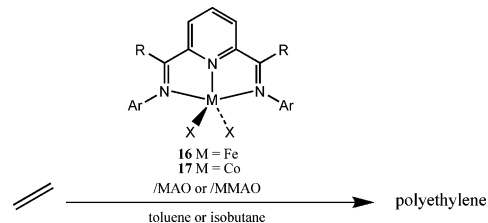


Figure 4. Molecular structure of **1** ($R = \text{Me}$, $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$). Drawing based on published structural data.⁷²

Scheme 8



system (**16o**) displays an activity of 6300 g/mmol·h·bar [440 g/mmol·h·bar for the cobalt analogue (**17o**)], affording a polymer with a molecular weight of 900 000. Such iron and cobalt systems when oxidized with ferrocenium hexafluoro-

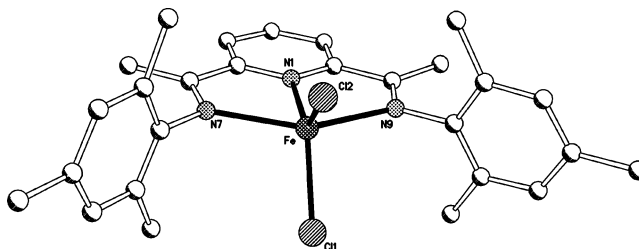


Figure 5. Molecular structure of **16** ($R = \text{Me}$, $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$). Drawing based on published structural data.⁶

Chart 4

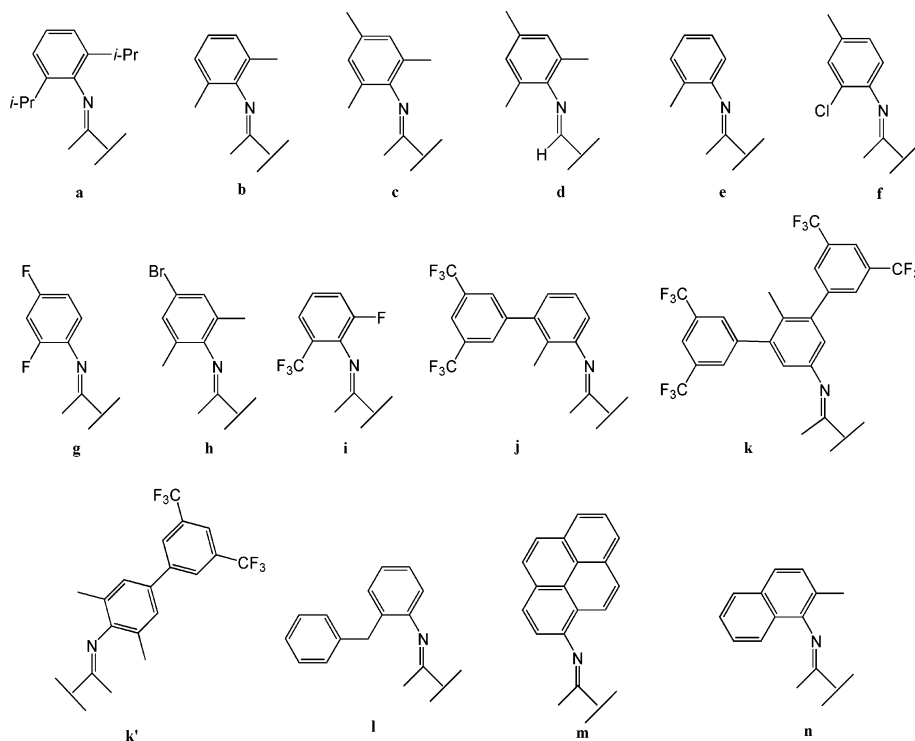
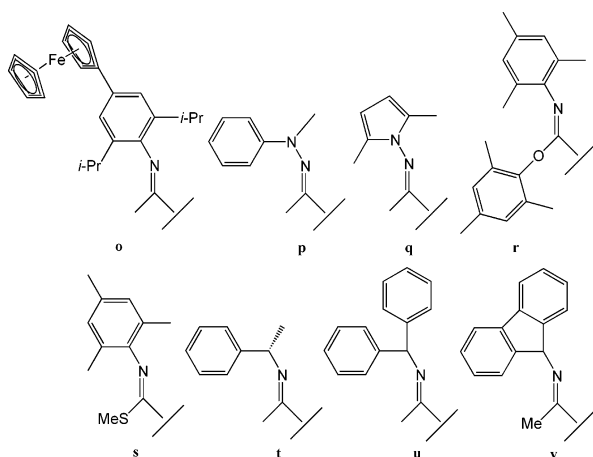


Chart 5

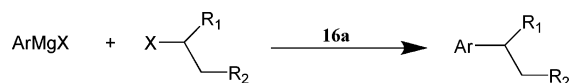


rophosphate afford cleanly $[\{2,6-(2,6-i\text{-Pr}_2-4\text{-FcArNCMe})_2\text{-C}_5\text{H}_3\text{N}\}]\text{MCl}_2(\text{PF}_6)_2$ (**21o**, M = Fe; **22o**, M = Co). However, no difference is observed in polymerization performance between **21o** and **22o** when compared with the reduced species when treated with MAO; this has been attributed to reduction of the dicationic ferrocenium species by the alkylaluminum cocatalyst.

Bis(hydrazone)pyridyl complexes $[2,6-(\text{R}'\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}]\text{-FeCl}_2$ [**23p**, $\text{R}' = \text{NPhMe}$; $\text{R}' = \text{NPh}_2$, NMe_2 ; **23q**, $\text{R}' = 2,5$ -dimethylpyrrolyl] have been tested in combination with MAO.^{64–66} For small R' groups, toluene-soluble α -olefins are obtained, whereas larger R' groups afford low molecular weight solid polyethylene; the catalytic activity of the 2,5-dimethylpyrrolyl derivative (up to ca. 3000 g/mmol·h·bar) is at least an order of magnitude greater than those of the other hydrazones.⁶⁴

Complexes $[2,6-\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}=\text{CR}\}_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ [**24r**, $\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{O}$; **25q**, $\text{R} = \text{MeS}$], possessing ether and thioether groups as the imino carbon substituents, are highly active catalysts for ethylene polymerization on treat-

Scheme 9

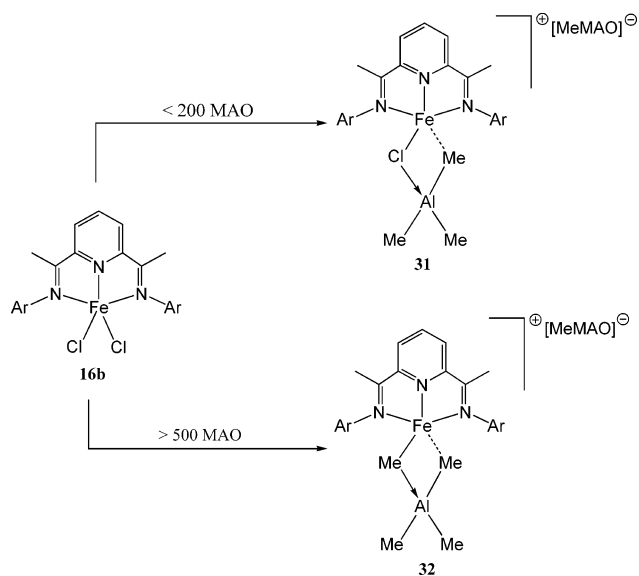


ment with MAO. Interestingly, replacement of the mesityl aryloxy in **24r** with an O–Me group leads to an inactive system.⁵⁷ The C_1 -symmetric complexes $[2-\{2,6-i\text{-Pr}_2\text{C}_6\text{H}_3\}\text{N}=\text{CMe}\}_6\text{-}\{(\text{PhCH}(\text{Me}))\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ (**26t**) reported by Bianchini et al. upon activation with MAO promote simultaneous polymerization and oligomerization (Schulz–Flory distribution) of ethylene.⁶¹ Complexes $[2,6-(\text{R}'\text{N}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ (**27u**, $\text{R}' = \text{Ph}_2\text{CH}$; **27v**, $\text{R}' = \text{fluorenyl}$) exhibit contrasting behavior, with **27u** being inactive but **27v** forming a highly active iron system for ethylene oligomerization.⁹¹

The parent bis(imino)pyridine–iron precatalyst $[2,6-\{(2,6-i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ (**16a**) is finding other uses in organic synthesis. For example, Bedford et al. have shown its sacrificial use in the cross-coupling of aryl Grignard reagents with primary and secondary halides bearing β -hydrogens (Scheme 9).⁹²

Other derivatives supported by **1** are also finding new applications; for example, iron(II) and cobalt(II) complexes bearing weakly bound triflate groups or with noncoordinated SbF_6^- anions have been prepared and screened as catalysts in the oxidation of cyclohexane with H_2O_2 . Only the iron(II) complexes exhibited activity, assigned to Fenton-type free-radical auto-oxidation. Crystal structures of the bis(imino)pyridyl complexes $[2,6-(\text{ArN}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}]\text{Fe}(\text{OTf})_2$ (**28**, $\text{Ar} = 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3$), $[\{2,6-(\text{ArN}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}\}\text{Fe}(\text{OTf})(\text{CH}_3\text{CN})](\text{SbF}_6)$ (**29**, $\text{Ar} = 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3$), and $[\{2,6-(\text{RN}=\text{CMe})_2\text{C}_5\text{H}_3\text{N}\}\text{Fe}(\text{CH}_3\text{CN})_3](\text{SbF}_6)_2$ (**30**, $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) were reported.⁹³ A number of iron(II) bis(imino)pyridine complexes have been evaluated for the atom transfer radical polymerization (ATRP) of styrene. Four-

Scheme 10



coordinate complexes derived from alkyl amines proved to be the most effective for ATRP.⁹⁴

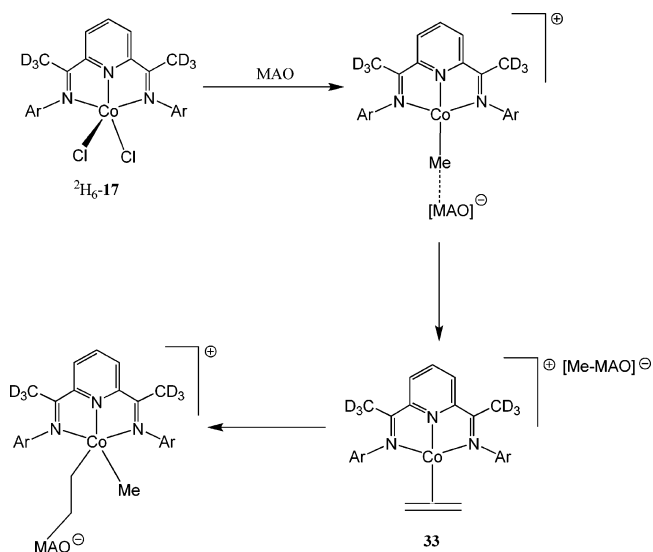
2.3. Characterization of the “Active Species”

By analogy with metallocene catalysts, the active species of MAO-activated bis(arylimino)pyridine–iron (**16**) and –cobalt (**17**) complexes was initially considered to be a highly reactive mono-methylated cobalt(II) or iron(II) cation of the form $[LM-Me]^+$ bearing a weakly coordinating counteranion such as $[X-MAO]^-$ ($X = \text{halide, Me}$). To probe this theory a number of spectroscopic investigations have been directed toward identifying the active species and serve to illustrate the difficulties in unequivocally determining their precise nature (vide infra).

Talsi et al. employed ^1H NMR and ^2H NMR spectroscopy to study intermediates formed via activation of ferrous-based polymerization catalysts with not only MAO but also AlMe_3 , $\text{AlMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$, and $\text{AlMe}_3/\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$.⁹⁵ With regard to **16b**/MAO, the data suggests ion pairs of the type $[2,6\text{-}\{(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}\text{Fe}^{\text{II}}(\mu\text{-Cl})(\mu\text{-Me})\text{AlMe}_2]^+[\text{Me-MAO}]^-$ (**31**) (at $\text{Al/Fe} < 200$) and $[2,6\text{-}\{(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}\text{Fe}^{\text{II}}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{Me-MAO}]^-$ (**32**) (at $\text{Al/Fe} > 500$) (Scheme 10), whereas the (**16b**)/ AlMe_3 system leads to neutral species of the type $[2,6\text{-}\{(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}\text{Fe}^{\text{II}}(\text{Cl})(\mu\text{-Me})_2\text{AlMe}_2]$ or $[2,6\text{-}\{(2,6\text{-Me}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}\text{Fe}^{\text{II}}(\text{Me})(\mu\text{-Me})_2\text{AlMe}_2]$.^{95–97} An electron paramagnetic resonance (EPR) spectroscopic study by the same group indicated that the iron center remains in the ferrous state throughout the activation.⁹⁷ The latter result contrasts with an investigation by Gibson et al. using Mössbauer and EPR spectroscopy of the **16a**/MAO system which was interpreted as 100% conversion to a species exhibiting a +3 oxidation state.⁹⁸

Using electrospray ionization tandem mass spectrometry (ESI-MS) to study the activation of **16a** with MAO in THF, the four-coordinate $[2,6\text{-}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}\text{FeMe}]^+$ cation was identified along with the iron hydride species $[2,6\text{-}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}\text{FeH}]^+$.⁹⁹ Under low Fe/MAO ratios, the activation reaction of **16a** by MAO is not complete with a cationic monochloride complex $[2,6\text{-}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}\text{FeCl}]^+$ detected. Furthermore, UV–visible spectroscopic studies revealed that the

Scheme 11



alkyl and hydride cations exist as THF adducts. UV–visible spectral changes associated with an MAO-activated bis(imino)pyridine–iron complex have also been investigated by Schmidt et al. In this study it was observed that changes in the spectra are strongly dependent on the elapsed time after MAO addition and MAO concentration.¹⁰⁰

The operational details of MAO-activated bis(imino)pyridine cobalt systems have also been studied. With regard to **17a**/MAO, initial reduction of the cobalt(II) precatalyst to cobalt(I) halide is followed by conversion to a cobalt(I) methyl and ultimately to a cobalt(I) cationic species (see section 2.6).^{101,102} Addition of ethylene affords an ethylene adduct $[\{2,6\text{-}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}\text{Co}(\eta^2\text{-C}_2\text{H}_4)\text{Me}\text{MAO}\}]^+$ (**33**), which is considered as the immediate precursor to the active species (Scheme 11). Using ^1H NMR and ^2H NMR spectroscopy it has been shown that the “non-coordinating” $[\text{Me-MAO}]^-$ anions are incorporated at the saturated ends of the polymers, consistent with an activation mechanism that involves nucleophilic attack by an abstracted alkyl group on the cationic ethylene species.¹⁰²

2.4. Theoretical Studies

In an initial full ab initio study on the diisopropylphenyl catalysts derived from **16a**, Gould and co-workers¹⁰³ computed the key structures operating for the first monomer insertion and showed that intermediates along the reaction coordinate have low-spin ($S = 0$) configurations. Ziegler et al. carried out DFT and DFT/molecular mechanics for an ethylene polymerization process initiated by cationic alkyl species based on the bis(imino)pyridine–iron model system **34** (Figure 6), and the iron–alkyl cation derived from **16a**. In this study they find that the rate-determining step for both termination and propagation is the capture of ethylene by the iron alkyl cation. The sterics imposed by the $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$ group was found to suppress ethylene capture for

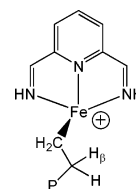


Figure 6. Cationic alkyl model system **34**.

Table 2. Range of Non-MAO Cocatalysts Employed To Activate Bis(imino)pyridine–iron Dihalides (16)

cocatalyst	refs
AlMe ₃	95,96,110,113
AlEt ₃	111,112
Al(<i>i</i> -Bu) ₃	96,110,112–114
Al(<i>n</i> -octyl) ₃	111,96
AlEt ₂ Cl	110
Al(<i>n</i> -hexyl) ₃	111
AlMe ₃ /Al(<i>i</i> -Bu) ₃	111
AlMe ₃ /B(C ₆ F ₅) ₃	95
AlMe ₃ /CPh ₃ B(C ₆ F ₅) ₄	95
AlEt ₃ /CPh ₃ B(C ₆ F ₅) ₄	115
Al(<i>i</i> -Bu) ₃ /CPh ₃ B(C ₆ F ₅) ₄	115
Et ₂ AlOAlEt ₂	112
(<i>i</i> -Bu) ₂ AlOAl(<i>i</i> -Bu) ₂	110,112

the termination step and increase the rate of insertion.¹⁰⁴ Using the cationic alkyl complex derived from **16a**, similar calculations reveal that the activity is inhibited by steric crowding.¹⁰⁵

Musaeu, Morokuma, and co-workers carried out a study on the mechanisms of chain propagation and β -hydride transfer termination for a series of iron precatalysts.¹⁰⁶ By using small and highly bulky systems, it is found that two axial ligands are required in order for the d_{z^2} orbital to be destabilized (with the trichelating ligand defining the equatorial xy plane) and for the singlet to be the ground state, a situation found for the β -hydride termination species. In contrast, only one axial ligand is present for chain propagation. The calculations for the two extremes of steric bulk are in agreement with the observed suppression of β -hydride transfer termination upon increasing the steric bulk of the ligand **1**. For cobalt(I) alkyl complexes, experimental results and theory have also been shown to be in agreement and support a stepwise pathway for reaction of the alkyl complexes with 1-alkenes, reacting by β -hydride transfer via a cobalt hydride intermediate.¹⁰⁴ Such cobalt alkyls have also been shown to contain low-spin cobalt(II) antiferromagnetically coupled to a ligand radical anion. The lowest triplet state is thermally accessible and accounts for observed ¹H NMR chemical shifts at room temperature.¹⁰⁸ Calculations have also been conducted on iron(II) precatalysts containing bis(imino)pyridines with cycloaliphatic substituents. Enhanced effects for the aliphatic derivatives (cf. alkyl) were found to be due to relatively higher thermal stabilities. However, there is no effect on the process of transforming the alkyl into the active cationic species.¹⁰⁹

2.5. Cocatalysts/Activators

While use of MAO (or MMAO = MAO containing 25% isobutyl groups) to activate bis(imino)pyridine–iron dihalide (**16**) and –cobalt dihalide (**17**) precatalysts for alkene polymerization has led the way, alternative activators have also been screened. Indeed, the important role played by the cocatalyst on the performance of the system was recognized early on. For example, it was shown for iron catalysts that the polyethylene molecular weight distribution depends on the MAO/Fe molar ratio with bimodal distributions sometimes achievable with large excesses of MAO.^{6,10} Table 2 shows some examples of alternative activators that have been employed.

Using the catalytic system [2,6-((2,6-*i*-Pr₂C₆H₃)N=CMe)₂C₅H₃N]FeCl₂ (**16a**)/AlMe₃, high activities comparable with an MAO-activated system can be obtained with

polyethylene displaying a bimodal molecular weight distribution containing large fractions of low molar mass products.¹¹⁰ Cramail et al. also reported a bimodal distribution with this precatalyst–cocatalyst combination but with much lower activities.¹¹¹ Indeed, it was found in their study that the catalytic activity followed the order AlMe₃ < Al(*n*-Oct)₃ < Al(*i*-Bu)₃ < AlEt₃ < Al(*n*-Hex)₃, with MAO-based systems still displaying the highest activity. Unlike the primary trialkylaluminum compounds, the Al(*i*-Bu)₃ system results in polyethylene that displays relatively narrow and unimodal molecular weight distributions.¹¹⁰ Interestingly, by mixing AlMe₃/Al(*i*-Bu)₃ the catalytic activity was found to be higher than that obtained by taking each activator individually.¹¹¹ Use of the tetraethylaluminum Et₂AlOAlEt₂ has proved a potent activator for **16a** with activities reported to be higher than using AlEt₃ or Al(*i*-Bu)₃.¹¹² The bis(imino)pyridine–cobalt precatalyst/cocatalyst systems have also been examined with regard to cocatalyst variation. Semikolenova et al. showed that the [2,6-((2,6-Me₂C₆H₃)N=CMe)₂C₅H₃N]CoCl₂ (**17b**)/AlMe₃ system possesses similar activities to MAO-based systems, while **17b**/Al(*i*-Bu)₃ was almost inactive at a molar ratio Al/Co = 500.¹¹³ The activities of these cobalt systems are less than their iron counterparts.

Fink et al. showed that the low activities for propylene polymerization using a bis(imino)pyridine–iron/MAO (and MMAO)³¹ catalyst can be considerably increased by using CPh₃B(C₆F₅)₄/AlR₃ (R = *i*-Bu, Et) as the cocatalyst, the combination of [2,6-((2-*i*-Pr-6-MeC₆H₃)N=CMe)₂C₅H₃N]-FeCl₂ (**16w**)/CPh₃B(C₆F₅)₄/Al(*i*-Bu)₃ proving the most active system.¹¹⁵

The effect of adding metal alkyls to an MAO-activated bis(imino)pyridine–iron catalyst has also been studied. Addition of AlR₃ (Me, Et) to **16a**/MAO catalysts results in a polyethylene displaying a bimodal distribution similar to that observed using **16a**/MAO_{large excess}.¹¹⁶ In contrast, use of excess Al(*i*-Bu)₃ gives a monomodal distribution in a manner similar to that seen using Al(*i*-Bu)₃ alone (vide supra). As observed when using AlEt₂Cl as the sole cocatalyst,¹¹⁰ addition of AlEt₂Cl to **16a**/MAO deactivates the catalyst system. Analysis of the polymer end groups reveals that chain transfer to aluminum is the operative mechanism for termination. To probe whether this chain transfer can occur with other metals, addition of a range of metals [e.g., *n*-BuLi, Mg(*n*-Bu)₂, BEt₃, GaR₃ (R = Me, Et, *n*-Bu), SnMe₄, PbEt₄, ZnEt₂] to **16a**/MAO was also reported. In the case of ZnEt₂, **16a**/MAO is shown to catalyze polyethylene chain growth to zinc with a Poisson distribution of linear alkanes.^{116–118}

2.6. Iron and Cobalt Alkyl Complexes

A key objective since the initial discovery of highly active bis(imino)pyridine–cobalt and –iron catalysts has been to prepare well-defined alkyl complexes. It was thought that these could serve as precursors for single-component olefin polymerization catalysts and also provide insight into the nature of the propagating species (see sections 2.3 and 2.4).

Treatment of **16** or **17** with LiMe, however, results in reduction to give the alkylated M(I) species [2,6-(ArN=CMe)₂C₅H₃N]MCH₃ [**35**, M = Fe; **36**, M = Co; Ar = 2,6-*i*-Pr₂C₆H₃]. Alternatively, **35** or **36** can be prepared from the corresponding monovalent metal halide species [2,6-(ArN=CMe)₂C₅H₃N]MCl (**37**, M = Fe; **38**, M = Co) on reaction with LiMe.^{56,101,102,119–121}

The cobalt(II) complex containing ligand **3**, [2,6-((2,6-*i*-Pr₂C₆H₃)N=CPh)₂C₅H₃N]CoCl₂ (**39**), has been reduced

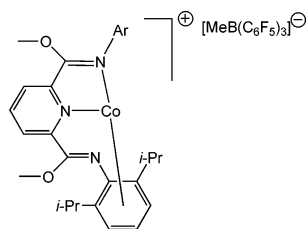
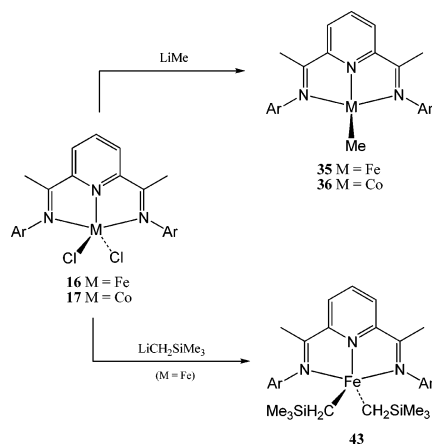


Figure 7. η^6 -Arene cationic complex **42**.

Scheme 12



using either methyllithium or butadiene/magnesium to afford the cobalt(I) chloride [2,6-((2,6-*i*-Pr₂C₆H₃)N=CPh)₂C₅H₃N]-CoCl (**40**). Reaction of **39** with methyllithium (3 equiv) affords the corresponding cobalt(I) methyl complex, which upon activation with Li[B(C₆F₅)₄] gave low-activity ethylene polymerization catalysts.⁵⁶ For [2,6-((2,6-*i*-Pr₂C₆H₃)N=C(OMe)₂C₅H₃N)]CoMe (**41**), treatment with an excess of B(C₆F₅)₃ led to cleavage of a Co–N bond and formation of a η^6 -arene cation **42** (Figure 7).⁵⁶

Unlike the reaction of **16** with LiMe, treatment of **16** with the more bulky LiCH₂SiMe₃ gave the crystallographically characterized dialkyl ferrous species [2,6-(ArN=CMe)₂-C₅H₃N]M(CH₂SiMe₃)₂ (**43**, Ar = 2,6-*i*-Pr₂C₆H₃) (Scheme 12).¹²¹

While the nature of the active species for MAO-activated iron species remains speculative (see section 2.3), it has recently been shown by Chirik et al. that iron(II) alkyl cations can act as propagating species. For example, treatment of **43** with [PhMe₂NH][BPh₄] in the presence of diethylether or THF gives [{2,6-(ArN=CMe)₂C₅H₃N}M(CH₂SiMe₃)(L)]-[BPh₄] (**44**, L = Et₂O or THF, Ar = 2,6-*i*-Pr₂C₆H₃), respectively (Scheme 13); the somewhat unusual base-free species [{2,6-(ArN=CMe)₂C₅H₃N}M(CH₂SiMe₂CH₂SiMe₃)]-[MeB(C₆F₅)₃] (**45**, Ar = 2,6-*i*-Pr₂C₆H₃) is accessible on reaction of **43** with B(C₆F₅)₃. Although **44** gives very low activity for ethylene polymerization, the base-free species **45**, with the lesser coordinating anion, shows productivities approaching the MAO-activated catalyst.¹²²

Grignard reagents have also been used to generate reduced alkylated species of the form [2,6-(ArN=CMe)₂C₅H₃N]-CoMe (**36**).¹²³ Dialkyl iron(II) species (**43**) can be more conveniently prepared from the reaction of **1** with the precursor complex [FeR₂(py)₂] (R = CH₂Ph, CH₂CMe₂Ph, and CH₂SiMe₃). Cations are also available via use of AgSbF₆ or Ag(acac).¹²⁵

While alkylolithiums may lead smoothly to alkylated products, use of trialkylaluminums can lead to quite different products resulting from extrusion of the iron center, the

Scheme 13

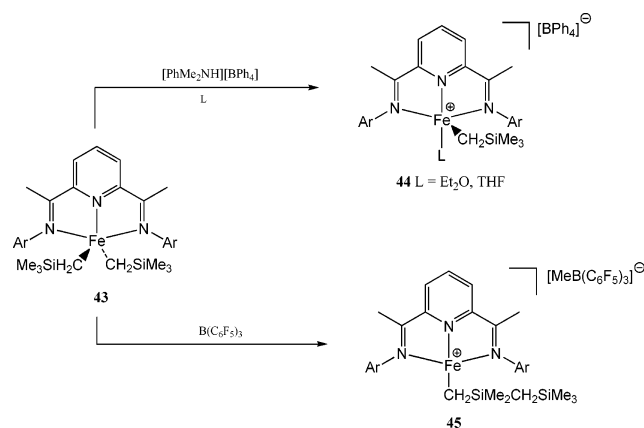
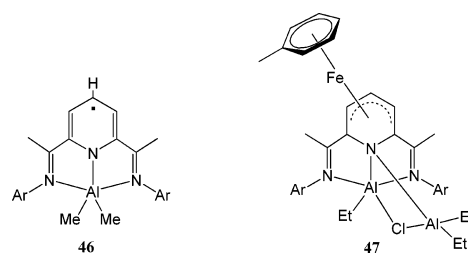


Chart 6



precise nature of the product being dependent on the aluminum alkyl employed (Chart 6). For example, treatment of **16a** with AlMe₃ (10 equiv) afforded the orange paramagnetic [2,6-((2,6-*i*-Pr₂C₆H₃)N=CMe)₂C₅H₃N]AlMe₂ complex (**46**) in ca. 40% yield.¹²⁶ The complex is also available from **43**. Complex **46** is best viewed as [(L⁻¹)Al^{III}(Me)₂] with the unpaired electron associated with the reduced bis(imino)pyridine radical anion. In contrast, reaction with AlEt₃ afforded the dark orange complex **47** in 41% yield. The pyridine-derived ligand of the folded N₃ ligand in **47** adopts an η^4 -bonding mode with an Fe atom; the latter is also bound (η^6) to a toluene molecule. The N₃ ligand is considered dianionic with the two Al centers present being trivalent. Given this, the Fe center in **47** can be regarded as being in its formal zerovalent state, unless the N₃ ligand is the recipient of three electrons, in which case the iron center is formally monovalent. The difference in product formation here (i.e., **46** vs **47**) is thought to be due to the lower stability of Fe–Me bonds versus Fe–Et bonds.¹²⁶ These products may be the result of longer reaction times, since it has been shown that under conditions approaching those used for polymerizations, **16a**/AlR₃ are known to form neutral species of the type [2,6-((2,6-Me₂C₆H₃)N=CMe)₂C₅H₃N]Fe^{II}(Cl)(μ -R)₂-AlR₂ or [2,6-((2,6-Me₂C₆H₃)N=CMe)₂C₅H₃N]Fe^{II}(R)(μ -R)₂-AlR₂ (see section 2.3).

2.7. Other Metals

As outlined in section 2.2, early work on the bis(imino)pyridine system focused mostly on the late transition metals, in particular, copper, rhodium, and iridium,^{81,82,85–87} as well as studies on molybdenum carbonyls.^{88,89} Work has continued with these metals, and a number of interesting complexes have been synthesized and identified. For copper, the reaction between CuBr and bis(imino)pyridines leads to unusual Cu(I)–Cu(II) complexes of the form [{2,6-(RN=CMe)₂C₅H₃N}CuBr]₂[Cu₂Br₄] (**48**) (Figure 8), while reaction with [Cu(MeCN)₄](PF₆) affords the copper(I) complex [{2,6-(RN=CMe)₂C₅H₃N}Cu(THF)(CH₃CN)](PF₆) (**49**).¹²⁷

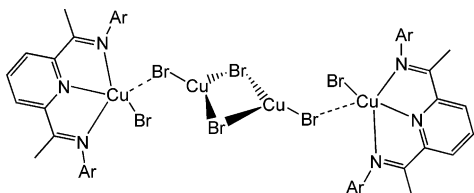


Figure 8. Cu(I)–Cu(II) complex **48**.

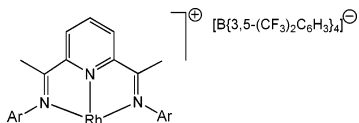


Figure 9. Three-coordinate rhodium complex **56** (Ar = 2,6-*i*-Pr₂C₆H₃).

Conan et al. prepared copper(II) complexes containing both **1** and tetracyanoquinodimethane (TCNQ) viz. [2,6-{(2,6-Me₂-C₆H₃)N=CMe}₂C₅H₃N]CuX(TCNQ) (**50**, X = Cl; **51**, X = Br). Crystallographic studies suggest intermolecular dimerization resulting from π - π overlap of two adjacent TCNQ⁻ radical anions.¹²⁸ For molybdenum, further investigations using Mo(CO)₆ have recently been reported, with the bis(imino)pyridine ligand binding in a bidentate fashion.^{129,130}

A number of rhodium(I) phenoxide complexes [(2,6-(R'N=CH)₂C₅H₃N)]Rh(OPh) (**52**, R' = *i*-Pr; **53**, R' = *t*-Bu) have been reported,^{131,132} which on further reaction with acetyl chloride and benzoyl chloride afford the rhodium(III) acetyl (or benzoyl) complexes [(2,6-(R'N=CH)₂C₅H₃N)]RhCl₂(COR'') (**54**, R'' = Me; **55**, R'' = Ph). Vrieze et al. observed that the oxidative addition is facile for square-planar bis(imino)pyridine–rhodium(I) complexes, and use of dichloromethane as solvent (chloroform, benzoyl chloride, and α , α -dichlorotoluene behave similarly) led to isolation of chloromethyl rhodium(III) complexes.¹³³ Further reaction of such chloromethyl complexes with both water and oxygen afforded bis(imino)pyridine–rhodium(III) trichlorides.¹³⁴ For the α -chlorotolyl derivative, both benzaldehyde and H₂O₂ were also identified as products. It is noteworthy that the cationic three-coordinate 14-electron complex **56** (Figure 9) can be used in chlorinated solvents, i.e., no oxidative addition occurs, and has been shown to catalyze hydrosilylation, Mukaiyama aldol, and cyclopropanation reactions.¹³⁵ Both rhodium(III) and rhodium(I) alkyl complexes bound by bis(imino)pyridines are found to be inactive for alkene polymerization.^{136,137}

The rhodium(III) and iridium(III) triflate complexes [2,6-(ArN=CMe)₂C₅H₃N]Rh(R')(O₂SCF₃)₂ (**57**, R' = Me, Et or Cl, Ar = 2,6-*i*-Pr₂C₆H₃, 2,6-Me₂C₆H₃) and [2,6-(ArN=CMe)₂C₅H₃N]IrCl(Me)(O₂SCF₃) (**58**) are both accessible from the oxidative addition reaction of the corresponding monovalent bis(imino)pyridine group 9 chloride complex, [2,6-(ArN=CMe)₂C₅H₃N]MCl (**59**, M = Rh; **60**, M = Ir), with alkyltriflate.⁵⁸ None of the complexes **57**–**60** have shown any activity for ethylene polymerization.

Bis(imino)pyridine complexes of cobalt and rhodium have been utilized for the hydrogenation of mono- and disubstituted olefins; sterically hindered trisubstituted olefins do not react. For the cobalt system, a diamagnetic hydride intermediate was observed.¹³⁸ Cobalt complexes containing tridentate ligands derived from 4-methoxyaniline have also been reported.¹³⁹

A stable cationic ruthenium(II) ethylene–methyl complex **61** has been isolated (Figure 10) but does not polymerize ethylene under the conditions employed.¹³⁶ Ruthenium

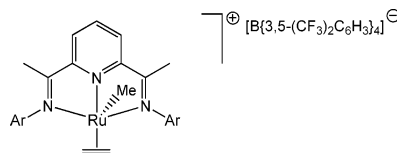
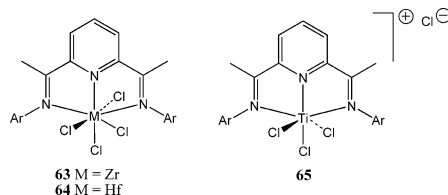


Figure 10. Stable cationic ruthenium(II) methyl complex **61** (Ar = 2,6-Me₂C₆H₃).

Chart 7



complexes supported by bis(imino)pyridines have been used to catalyze both the epoxidation of cyclohexene (in the presence of iodosylbenzene)²⁵ and the cyclopropanation of styrene with ethyl acetate,¹⁴⁰ while iridium(I) complexes have found use in hydrogen transfer reactions.¹⁴¹

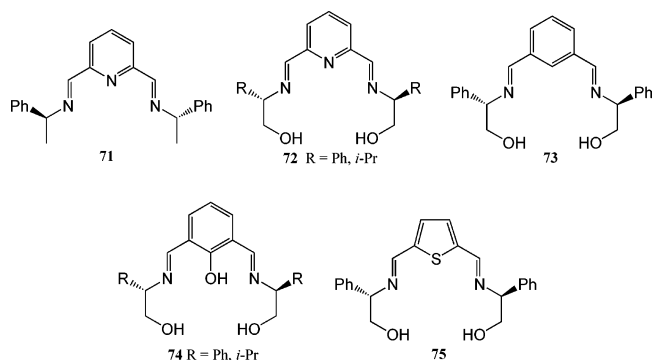
A series of high-spin divalent monometallic manganese complexes [2,6-(R'N=CMe)₂C₅H₃N]MnX₂ (**62**, R' = Ar, NR₂) has been prepared in which the metal centers adopt either a trigonal-bipyramidal or square-pyramidal geometry. These manganese complexes, upon activation with MAO, exhibit low activity for ethylene polymerization.^{142,143} The synthetic methodology has also been extended to include polymeric manganese complexes, and these are discussed in section 2.12. Other manganese (and zinc) complexes of the form [2,6-(ArN=CMe)₂C₅H₃N]MX₂ (X = Cl, Br) have been reported by Edwards et al.¹⁴⁴

The early transition metals have also recently received attention.^{43,145–151} Tetravalent group IV halide complexes bound by bis(imino)pyridine ligands including [2,6-(ArN=CMe)₂C₅H₃N]MCl₄ [**63**, M = Zr; **64**, M = Hf; Ar = C₆H₅, 2,6-*i*-Pr₂C₆H₃] and [{2,6-(ArN=CMe)₂C₅H₃N}]TiCl₃(Cl) (**65**, Ar = C₆H₅, 2,6-*i*-Pr₂C₆H₃) have been reported (Chart 7).¹⁴⁶ On treatment with MAO, **63**–**65** are all active for the polymerization of ethylene. Notably, the titanium system containing the unsubstituted bis(phenylimino)pyridine is the most productive system, giving branched polymers (this contrasts with the iron system where for Ar = phenyl, ML₂ complexes result leading to inactivity).

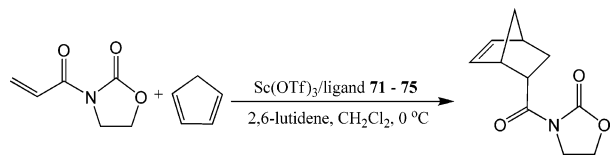
The groups of Gambarotta,¹⁴⁷ Schmidt,^{24,100,148} and Grassi¹⁴⁹ have all examined the use of vanadium(III) complexes in olefin oligomerization and polymerization. Indeed, treatment of [2,6-(ArN=CMe)₂C₅H₃N]VCl₃ (**66**) with MAO leads to some highly active catalysts for ethylene polymerization. Activation of **66** (Ar = 2,6-*i*-Pr₂C₆H₃) with a variety of alkylaluminum cocatalysts has also shown promise in chemoselective 1,4-polymerization of butadiene. With MAO, the system will also copolymerize ethylene and butadiene, affording polymers with up to 45 mol % *trans*-1,4-butadiene.¹⁵⁰ Further intriguing reactivity of related bis(imino)pyridine–vanadium(III) systems is discussed in sections 2.8 and 2.11.

The chromium chloride complexes, [2,6-(ArN=CMe)₂C₅H₃N]CrCl₃ (**67**), can be readily prepared from the reaction of [CrCl₃(THF)₃] with **1** in tetrahydrofuran or dichloromethane. The X-ray structure of the Ar = 2,6-*i*-Pr₂C₆H₃ example is isostructural with its vanadium analogue **66**, with the geometry around the metal centers being described as octahedral with the chloride ligands held in a mer disposi-

Chart 8



Scheme 14



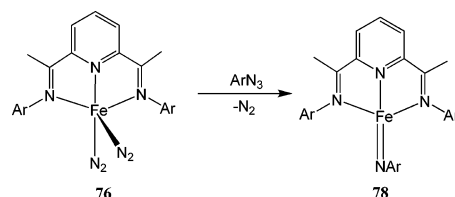
tion.⁴³ Upon aging with MAO at 70 °C, the chromium systems become highly active for ethylene polymerization and, as with the iron(II) systems, the nature of the aryl group dictates the oligomerization/polymerization behavior. Recently the molybdenum trichloride complex [2,6-(2,6-*i*-Pr₂C₆H₃)N=CMe₂]₂C₅H₃N]MoCl₃ (**68**), on activation with MMAO, has shown some activity for ethylene polymerization.¹⁵¹ Notably, use of MAO as cocatalyst has proved ineffective. The catalyst **68**/MMAO also proved effective for ROMP of norbornene, affording high molecular weight polymers with high *cis* content. The group of Yasuda has utilized nickel bis(imino)pyridines in random and block copolymerizations of norbornene with 1,3-butadiene, copolymerizations of norbornene with styrene, and homopolymerizations of both styrene and 1,3-butadiene.^{152,153}

Wieghardt reported a number of 2:1 complexes of the form [L₂M]PF₆ [**69**, M = Mn(II) to Zn(II), L = bis(imino)pyridine]. Mono-, di-, and tricationic as well as neutral species were identified by a variety of techniques including cyclic voltammetry and EPR spectroscopy.¹⁵⁴ Using *p*-hydroxy (or *p*-methoxy) phenylimine arms, Busch et al. also synthesized both 1:1 (M = Zn) and 2:1 (M = Ni, Zn) complexes.⁷³ The metal-to-ligand electron transfer in ML₂ⁿ⁺ complexes (M = Mn to Zn) have been investigated by theoretical methods; a biradical description in which ligand radical anions are antiferromagnetically coupled to the metal center is prevalent.¹⁵⁵

Oxidizing metallic neodymium with iodine in THF in the presence of **1** affords dark-brown [2,6-(2,6-Me₂C₆H₃)N=CMe₂]₂C₅H₃N]NdI₂(THF) (**70**), the magnetic behavior of which indicates that **70** is best regarded as trivalent Nd antiferromagnetically coupled to a radical anion.¹⁵⁶ Scandium(III) triflate complexes with the chiral ligands **71**–**75** (Chart 8) have been screened as catalysts in asymmetric Diels–Alder reaction of cyclopentadiene with 3-acyloyloxazolidine-2-one in the presence of 2,6-lutidine (Scheme 14).¹⁵⁷

Bis(imino)pyridine complexes have also shown promising luminescent properties. A series of cadmium(II) complexes possesses fluorescent emission both in the solid state and in dichloromethane solution.¹⁵⁸

Scheme 15



Scheme 16

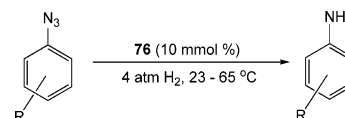
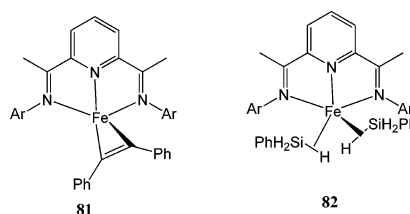


Chart 9



2.8. Dinitrogen Ligation

The potential for nitrogen activation by complexes bound by the bis(imino)pyridine ligands has further fuelled research in the area. For example, Chirik et al. has shown that reducing the original bis(arylimino)pyridine–iron(II) precatalysts **16** with sodium amalgam under nitrogen affords square-pyramidal, high-spin iron(0) bis(nitrogen) complexes of the form **76**.¹⁵⁹ The bis(dinitrogen) complex **76** readily loses one of the N₂ ligands in solution to afford [2,6-(ArN=CMe₂)₂C₅H₃N]Fe(N₂) (**77**), and when treated with arylazides, three equivalents of N₂ are lost, resulting in formation of deep blue/purple iron imides of the form **78** (Scheme 15).¹⁶⁰ Crystal structure analyses for Ar = 2,6-*i*-Pr₂C₆H₃ and 2,4,6-Me₃C₆H₂ reveal considerable distortion away from planarity, thought to be the result of a number of orbital factors.

Further reaction of **76** with CO (1 atm) afforded the iron dicarbonyl complex [2,6-(ArN=CMe₂)₂C₅H₃N]Fe(CO)₂ (**79**) and aryl isocyanate, whereas under H₂, the iron dihydrogen complex [2,6-(ArN=CMe₂)₂C₅H₃N]Fe(H)₂ (**80**) was formed along with free aniline; **80** rapidly converts to **76** under N₂. Indeed, **76** can be used as a catalyst for the hydrogenation of aryl azides to the corresponding anilines (Scheme 16). The hydrogenation rates appeared to increase with increasing size of aryl azide substituent closest to the iron, i.e., 2,6-*i*-Pr₂C₆H₃ (16 h, 23 °C) > 2,5-*t*-Bu₂C₆H₃ (16 h, 65 °C) > 2,6-Et₂C₆H₃ (96 h, 65 °C) ≫ 2,4,6-Me₃C₆H₂ (ineffective). The mechanism is thought to involve a 1,2-addition of H₂ across the Fe–N bond with subsequent reductive elimination of aniline.¹⁶⁰

The complexes **76** and **77** also serve as effective precatalysts for hydrosilylation of olefins and alkynes. The putative catalytic intermediates **81** and **82** (Chart 9) have been structurally characterized.

The iron analogue of cobalt **39**, namely, [2,6-(2,6-*i*-Pr₂C₆H₃)N=CPh]₂C₅H₃N]FeCl₂ (**83**), can be reduced by sodium amalgam under nitrogen to afford the bis(nitrogen) complex **84** (Chart 10). Similar reduction under CO affords the dicarbonyl complex **85**. As for **76**, complex **84** gradually loses one molecule of N₂ in solution. Indeed, prolonged stirring (23 h) of **84** in C₆D₆ led to the identification of two

Chart 10

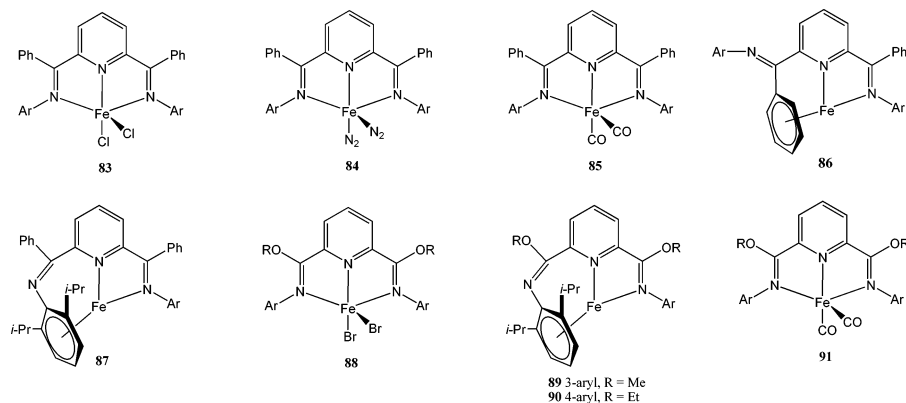
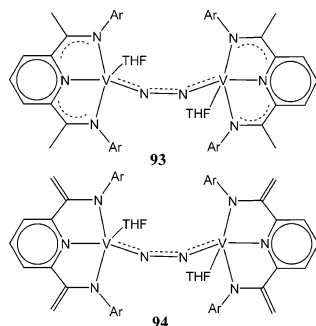


Chart 11



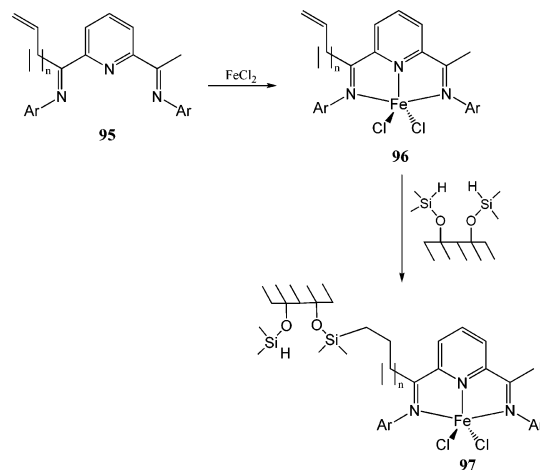
H₆-arene complexes—the 2-phenyl compound **86** and the 2-aryl complex **87** in 85% and 15% yield, respectively. Interestingly, reduction of complex **88**, featuring alkoxide groups on the imine backbone, results in either a 3-aryl **89** or a 4-aryl complex **90**, depending on the alkoxide substituent present. Complexes **89** and **90** on treatment with CO afford complexes of the type **91**.¹⁶¹

The vanadium complexes [2,6-((2,6-*i*-Pr₂C₆H₃)N=CMe)₂C₅H₃N]VCl₃ (**66**) and [2,6-((2,6-*i*-Pr₂C₆H₃)N=CMe)₂C₅H₃N]VCl(THF) (**92**) are reduced with excess NaH to afford the end-on dinitrogen-bridged complexes **93** and **94** (Chart 11). Paramagnetic **93** exhibits substantial metal-to-ligand electron transfer and is best viewed as being generated via a two-electron attack of two zerovalent vanadium centers, each bound to the same N₂. Complex **94** is viewed in terms of formally divalent vanadium centers reducing the N₂ unit.^{147,162}

2.9. Supported Catalysts

The supporting of bis(imino)pyridine ligands or complexes on various media through covalent and noncovalent interactions has been the subject of a number of reports.^{163–186} Some examples have also been included in a review article.¹⁸⁷ Herrmann and co-workers reported the immobilization of bis(imino)pyridine–iron-type precatalysts on silica. Introduction of an alkenyl group onto the alkyl substituent of the imino carbon of the ligand to give [2-((2,6-*i*-Pr₂C₆H₃)N=CMe)-6-((2,6-*i*-Pr₂C₆H₃)N=C(CH₂)_{*n*}CH=CH₂)C₅H₃N] (**95**, *n* = 1–3)¹⁶³ followed by treatment with iron dichloride gave [2-((2,6-*i*-Pr₂C₆H₃)N=CMe)-6-((2,6-*i*-Pr₂C₆H₃)N=C(CH₂)_{*n*}CH=CH₂)C₅H₃N]FeCl₂ (**96**). Hydrosilylation of **96** with the surface-containing SiMe₂H groups of the silica gave the covalently tethered complex **97** (Scheme 17). This heterogeneous system shows good activity (with MAO) for ethylene polymerization, the activity increasing with tether

Scheme 17



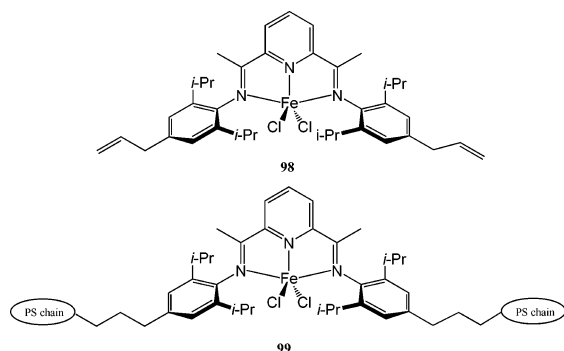
chain length. These supported catalysts are short-lived compared with the homogeneous systems. It is noteworthy that the polymers produced are substantially different than those of the homogeneous systems. High molecular weight fractions dominate with the highest molecular weight produced by the system with the shortest tethering chain. In general, the activities of these supported catalysts are an order of magnitude lower than their homogeneous counterparts. Complex **96** can also act as a self-immobilized catalyst by treating it with MAO and ethylene for a short period of time.

An alternative approach developed by Liu and Jin utilizes a 4-allyl-2,6-diisopropylphenyl-substituted ligand version of **1**, [2,6-((4-(CH₂CHCH₂)-2,6-*i*-Pr₂C₆H₂)N=CMe)₂C₅H₃N], to react with iron dichloride to give [2,6-((4-(CH₂CHCH₂)-2,6-*i*-Pr₂C₆H₂)N=CMe)₂C₅H₃N]FeCl₂ (**98**).¹⁶⁴ The *para*-allyl groups in **98** are active and can be copolymerized (at 79–81 °C) with styrene in the presence of a radical initiator to afford polymer-incorporated iron catalysts **99** (Chart 12).

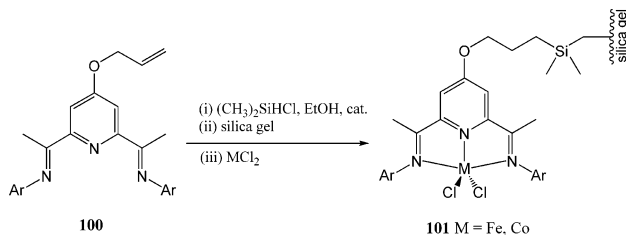
Use of the 4 position on the central pyridyl ring has also been employed as the site for supporting the catalysts. Kim et al. used the 4-substituted vinyl groups in **100** (Ar = 2,6-Me₂C₆H₃) as a means of generating silica-supported iron and cobalt systems (**101**) (Scheme 18).¹⁶⁵ On activation with MAO these systems showed about 100-fold lower activity when compared to the analogous homogeneous catalysts. The authors ascribe this to either diffusion limitation of monomer into the interior pores of the supported catalyst or the result of reduced active sites present in the heterogeneous variant.

In addition, Guo, Dong et al. supported the iron precatalyst **16** on a calcosilicate and studied its catalytic performance with either MAO or TEA as cocatalyst. Higher molecular

Chart 12



Scheme 18



weight polymers are obtained cf. the homogeneous systems.¹⁶⁶ The iron complex **16** can also be supported on the oxide supports silica and alumina and activated with $\text{Al}(i\text{-Bu})_3$ to afford highly active, thermally robust catalysts. IR spectroscopy in DRIFT mode indicates that only a few of the silica hydroxyl groups are used, leading to supported catalysts with low iron content. Higher iron content is achievable using alumina for which IR studies using CO as a probe indicate that there are two types of iron species present.¹⁶⁷

The use of dendrimers as supports for iron catalysts has also been reported. Li et al. reacted the *para*-allyl unsymmetrical bis(imino)pyridine ligand **102** with tetra- and octasilanes, in the presence of $\text{H}_2[\text{PtCl}_6]$, to afford the ligands **103** and **104**, respectively (Chart 13). Complexation with iron(II) chloride tetrahydrate yields carbosilane dendrimers with FeCl_2 moieties bound at the periphery.¹⁸⁸ On activation with MMAO the metallodendrimers are active catalysts for ethylene polymerization and, notably in the case of low Al/Fe molar ratios, display much higher catalytic activities and produce much higher molecular weight polyethylenes than the corresponding single-nuclear complex.

Moss et al. showed that the 2-methyl-4-hydroxy version of **1**, $[2,6\text{-}\{(2\text{-Me},4\text{-}(\text{OH})\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}]$, could be used to attach dendritic wedges of the carbosilane type as well as the benzylphenyl ether type.⁴⁹ After attachment, complexation with iron(II) chloride afforded dendritically functionalized bis(imino)pyridyl-iron complexes **105** (Scheme 19). Using MAO as a cocatalyst, it was shown that **105** are active in the oligomerization of ethylene. The activity of these new catalysts is not related to the type of dendritic wedge employed.

2.10. Tandem Catalysis

Tandem catalysis, using two or more different single-site catalysts in the same reactor, have recently been carried out using bis(imino)pyridine-iron systems as one component of the process.^{189–197} For example, use of $[2,6\text{-}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ (**16a**)/MAO in combination with a nickel-based late transition metal affords blended

polymers consisting of linear and branched polyethylenes, while use of **16a**/MAO with a metallocene gives blends of polyethylenes with different molecular weights.¹⁸⁹ When an iron catalyst capable of forming α -olefins is paired up with a metallocene copolymerization catalyst, low-density polyethylene from a single ethylene feedstock has been shown in a number of reports.^{192–196} Bazan et al. showed that application of $[2,6\text{-}\{(\text{Ar})\text{N}=\text{CMe}\}_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ (**16**, Ar = 2-EtC₆H₄)/MAO in conjunction with $[\text{Me}_2\text{Si}(\text{Ind})_2]\text{ZrCl}_2/\text{MAO}$ or $[\text{Et}(\text{Ind})_2]\text{ZrCl}_2/\text{MAO}$ gave branched polyethylenes with ethyl, butyl, along with longer chain branches (Scheme 20).¹⁹³

2.11. Reactivity of the Ligand: Deprotonation, Reduction, and Alkylation

The capacity of bis(arylimino)pyridine (**1**) to undergo deprotonation reactions, alkylation, and participate in reduction chemistry has been the subject of a number of reports. In many cases the newly formed species can undergo further reactions. In a similar way, bis(imino)pyridine complexes are susceptible to related reaction chemistry.

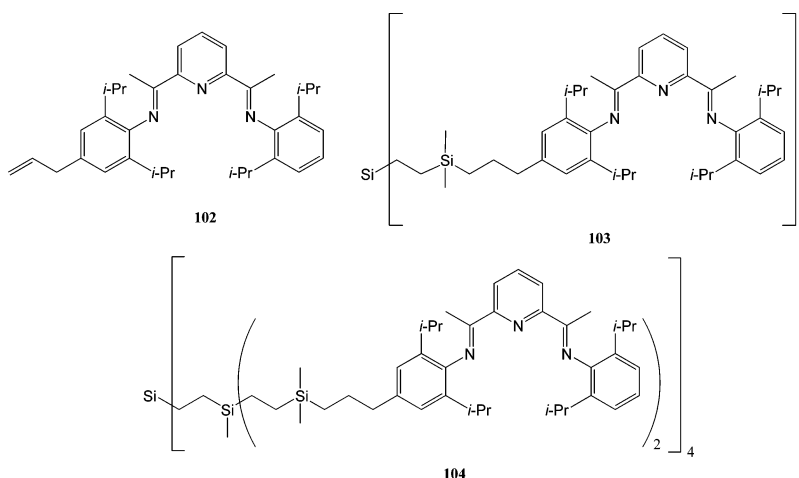
Deprotonation of ligand **1** in THF using $\text{LiCH}_2\text{SiMe}_3$ affords smoothly the dilithium salt **106**,^{156,198} while use of LiMe results in methylation at the pyridine nitrogen to afford the dinuclear complex **107** (Scheme 21).¹⁹⁹ Thermolysis of **107** results in the elimination of methane with deprotonation of one of the imino methyl groups to give **108**. In contrast, treatment of deuterated **1** (Ar = 2,6-*i*-Pr₂C₆H₃) with LiMe results in an *N*-methylated monolithium species **109** and the dedeuterated analogue of **108**, ²H₅-**108**.^{200,201} Conversion of **109**, by liberation of deuterated methane, to the thermodynamically favored ²H₅-**108** is achieved on warming. Both one-electron and three-electron reductions of **1** are possible with addition of KC_8 in Et_2O , leading to a potassium salt containing **110**,⁹⁸ while treatment with Li metal (or with lithium naphthalenide) in THF gave both paramagnetic **111** and diamagnetic **112**.²⁰²

Alkylation of the pyridine nitrogen atom in per-protio **1** can also be achieved using MgR_2 (R = Et, *i*-Pr) or ZnEt_2 , affording the *N*-alkylated products (**113**) with no evidence for deprotonated products. Interestingly, in these magnesium and zinc systems when bulky aryl substituents are present, further migration of the *N*-alkyl group in **113** to the 2 position on the pyridine ring can occur to give **114** (Scheme 22). Dealkylation of the zinc ethyl group in **113** with $\text{B}(\text{C}_6\text{F}_5)_3$ results in migration of the *N*-ethyl group back to the metal center to give **115**.²⁰¹

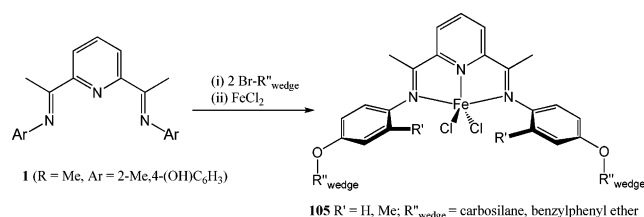
With alkyl aluminum reagents, nucleophilic attack on the bis(imino)pyridine ligand can also occur. In the original reports, the reaction conditions employed allowed the isolation of pure products resulting from alkylation of the imino-carbon (see **116** in Chart 14).^{149,203} Budzelaar et al. reacted a variety of alkylaluminum reagents with bis(imino)pyridine **1** (R = Me, Ar = 2,6-*i*-Pr₂C₆H₃) and observed that, depending on the choice of alkyl and reaction conditions, alkyl addition occurs at a number of different positions, viz. the imine carbon and the pyridine C2 and C4 positions, can occur. The reactions result in multiple products, which in some cases can be isolated through fractional crystallization. Use of AlR_3 (R = Me, Et) or Et_2AlCl led to the identification of complexes of the form **116**, **117**, **118**, and **119** (Chart 14).^{204,205}

With $\text{Al}(i\text{-Bu})_3$ and **1**, the low yields of **118a** (R = R₁ = R₂ = *i*-Bu) and **118b** (R = R₁ = *i*-Bu, R₂ = H) were

Chart 13



Scheme 19



identified by NMR spectroscopy. Heating of this reaction mixture afforded uniquely the dimer **119** (R = R₁ = *i*-Bu, R₂ = H). Complex **119** could be more conveniently prepared from reaction of **1** with (*i*-Bu)₂AlH. DFT calculations suggest a nonsynchronous biradical path for this dimerization process. Reaction with AlCl₃ gave the ionic complex [(2,6-((2,6-*i*-Pr₂C₆H₃)N=CMe)₂C₅H₃N}AlCl₂][AlCl₄] (**120**).²⁰⁵

The reactivity of the various anions that are derived from bis(imino)pyridine **1** (see Scheme 21) can also be used as reactants in combination with metal halides. For example, treatment of **109** with [FeCl₃] gives, on activation with MAO, an active catalyst for ethylene polymerization.²⁰⁰ Use of the dianion **106** with [LnCl₃(THF)₃] (Ln = Nd, La) affords the isostructural complexes **121** and **122**. Reduction of **121** and **122** with K(naphthalenide) afforded low yields of the complexes **123** and **124** (Scheme 23), which result from ligand dimerization via C–C bond formation through one of the two ene–amido functions of each molecule.¹⁵⁶ Alkylated neodymium species are best obtained by reacting [NdCl₃(THF)₃] with alkyl lithium reagents at low temperature, followed by subsequent addition of bis(imino)pyridine **1**. Such procedures lead to potent catalysts for the *cis*-polymerization of butadiene.¹⁹⁸ Treatment of **106** with [CoCl₂(THF)_{1.5}] also affords C–C-coupled products, **125** and **126**, in this case their precise nature depending on the atmosphere under which the reaction is carried out (Scheme 23).²⁰⁶

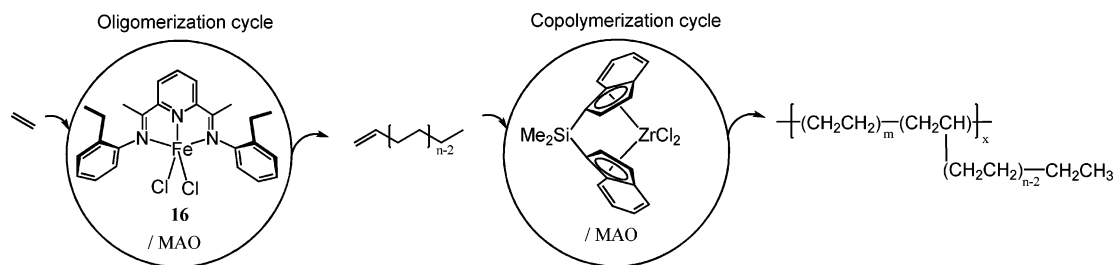
With bis(imino)pyridine-containing complexes deprotonation of the ligand can also occur. Thus, treatment of manganese chloride complex **62** (Ar = 2,6-*i*-Pr₂C₆H₃) with Me₃SiCH₂Li in toluene at ambient temperature proceeds via deprotonation of a methyl group, followed by C–C bond formation (reductive coupling) and a formal reduction in the oxidation state of the manganese center to afford the dimeric [2-((2,6-*i*-Pr₂C₆H₃)NCMe)]₂{(2,6-*i*-Pr₂C₆H₃)NC(CH₂)(C₅H₃N)}₂-Mn₂(CH₂SiMe₃)₂ (**127**).²⁰⁷ On the basis of these observations, the complex [(2,6-*i*-Pr₂C₆H₃)N=CMe]₂(C₅H₃N)Mn-

(CH₂SiMe₃)[Li(OEt₂)₄] (**128**), previously thought to contain zerovalent manganese, has been reformulated as the Mn(II) “ate” complex [(2,6-*i*-Pr₂C₆H₃)N=C(CH₂)₂(C₅H₃N)Mn-(CH₂SiMe₃)[Li(OEt₂)₄] (**129**) (Scheme 24).¹⁴²

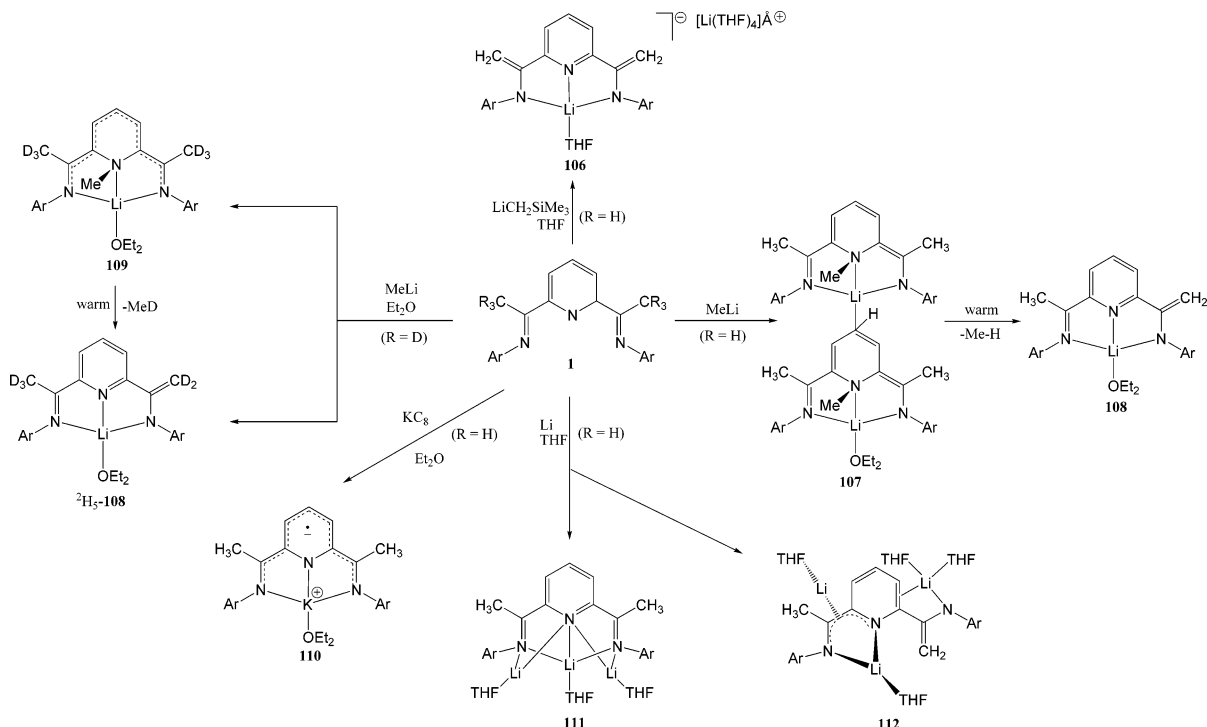
Addition of LiNMe₂ (2 equiv) to **16a** (Ar = 2,6-*i*-Pr₂C₆H₃) also results in deprotonation of the imino methyl groups, forming in this case the bis(enamide)pyridine complex **130** (Scheme 25) as its dimethylamine adduct. Similar use of KN-(SiMe₃)₂ afforded the bis(THF) adduct **131**, which loses one THF in vacuo. The THF or amine ligands in **130** and **131** are readily replaced by the likes of pyridine and *tert*-butylisocyanide. Treatment of **130** with additional KN-(SiMe₃)₂ or LiNMe₂ yielded ferrous amide–ate complexes of the type **132**. Treatment of **132** (M = K) with water resulted in formation of a dimeric bis(hydroxyl), potassium-bridged complex.²⁰⁸

Reaction of **16a** with LiCH₂SiMe₃ to give the dialkylated product has been reported by Chirik to give the dialkyl species **43** (see Scheme 12).¹²¹ Gambarotta and Budzelaar re-examined this reaction under a number of different conditions. Reaction of in-situ-generated **16a** with two equivalents of LiCH₂SiMe₃ gave as the major product the expected dialkyl complex **43** together with the minor products [(2,6-((2,6-*i*-Pr₂C₆H₃)N=CMe)₂-2-CH₂SiMe₃]-C₅H₃N]Fe(CH₂SiMe₃) (**133**) and {2-((2,6-*i*-Pr₂C₆H₃)N=CMe)-6-[(2,6-*i*-Pr₂C₆H₃)NCMe(CH₂SiMe₃)]C₅H₃N]Fe(CH₂SiMe₃) (**134**), for which alkylation had occurred at either the pyridine ring 2 position or the imine C atom, respectively. Interestingly, use of analytically pure **16a** yielded **43** together with a new alkylated product, namely, [2,6-((2,6-*i*-Pr₂C₆H₃)NC=(CH₂)₂C₅H₃N]Fe(μ-Cl)Li(THF)₃ (**135**). Complex **135** can be prepared more conveniently via direct reaction with the dianionic form of the ligand **106** with iron dichloride. Reductive coupling of the two ligand frameworks through the methyl carbon wings can also occur during these alkylation reactions, and indeed, the dinuclear iron(I) complex **136** has been structurally characterized (Figure 11). Attempts to reproducibly form this dinuclear species by reacting the monodeprotonated form of the ligand **109**, as its lithium salt, with [FeCl₂(THF)₂] and LiCH₂SiMe₃ failed to reveal any sign of reductive coupling and instead led to [(2,6-((2,6-*i*-Pr₂C₆H₃)NC=(CH₂)₂C₅H₃N)]Fe(CH₂Si(CH₃)₃)-[Li(THF)₄] (**137**). All the species (**43**, **133**–**137**) display, on activation with MAO, high activity for olefin polymerization, forming two types of polymer, the nature of which is related to the formal oxidation state of the metal center.²⁰⁹

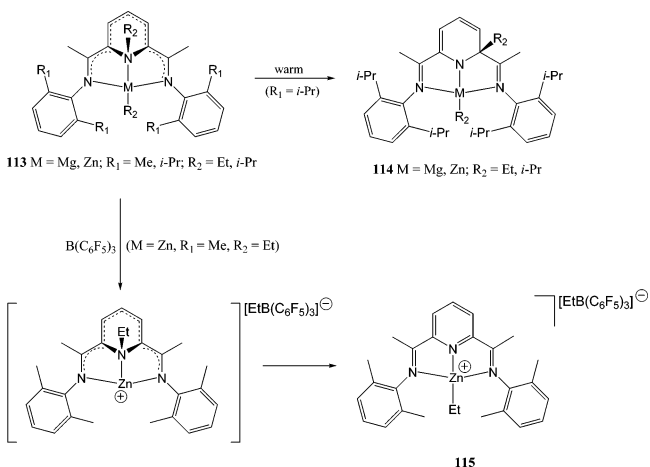
Scheme 20



Scheme 21



Scheme 22



Interaction of **66** (Ar = 2,6-*i*-Pr₂C₆H₃) with either two equivalents of MAO or an equimolar amount of MeLi affords the complex [2,6-{(2,6-*i*-Pr₂C₆H₃)₂N=CMe}₂-2-MeC₅H₃N}]-VCl₂ (**138**) in which the pyridine ring has been methylated at the 2 position (Scheme 26).¹⁴⁷ Calculations revealed that the two pyridine 2 positions were indeed the most likely to undergo nucleophilic attack. The tridentate ligand is now best described as an anionic diimine–amide. Loss of the extended conjugation is thought to be offset by increased π bonding

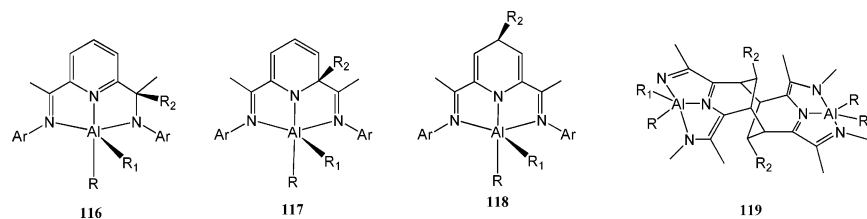
between the vanadium and former pyridine nitrogen. Interestingly, further reaction of **138** with MeLi leads to species (isolated in the presence of TMEDA) in which either the 2-methyl group has been removed (**139**) or in which there is now a second methyl group at the meta position of the pyridine ring (**140**, Chart 15).¹⁴⁷

Alkylation of the trivalent chromium analogue [{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂C₅H₃N]CrCl₃ (**67**) proved to be equally interesting. Interaction of **67** with two equivalents of PhCH₂MgCl gave the bimetallic complex [2,6-((2,6-*i*-Pr₂C₆H₃)N=CMe)₂-4-PhCH₂C₅H₃N}Cr(CH₂Ph)₂ (**143**) in 21% yield. It seems likely that reaction of **67** proceeds initially via reduction of the chromium center to give the chromium(II) complex [2,6-((2,6-*i*-Pr₂C₆H₃)N=CMe)₂C₅H₃N]CrCl₂ (**142**), which then undergoes alkylation at both the metal atom and the pyridine 4 position (Scheme 27). It is uncertain whether direct alkylation of the 4 position of the pyridine ring occurs or whether this is the result of an alkyl transfer from the chromium center to afford a square-planar chromium(II) intermediate. Dimerization of this chromium(II) complex results in the tricyclic structure **143**.²⁰⁷

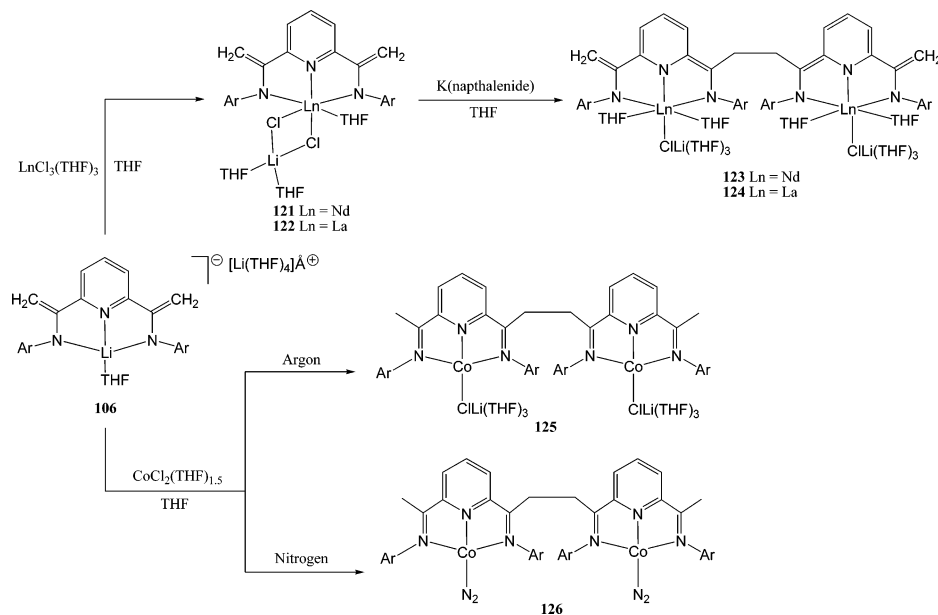
2.12. Macrocyclic and Polymeric Derivatives

As indicated in section 2.2, the development of macrocycles incorporating the bis(imino)pyridine unit have been known since the beginning of bis(imino)pyridine chemis-

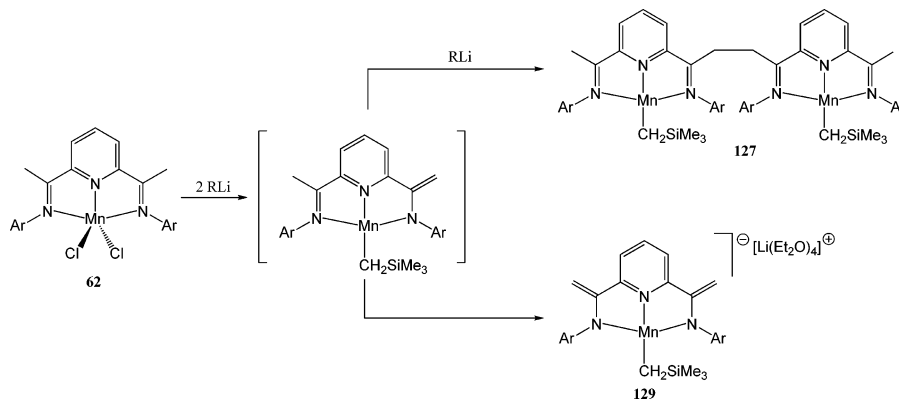
Chart 14



Scheme 23



Scheme 24



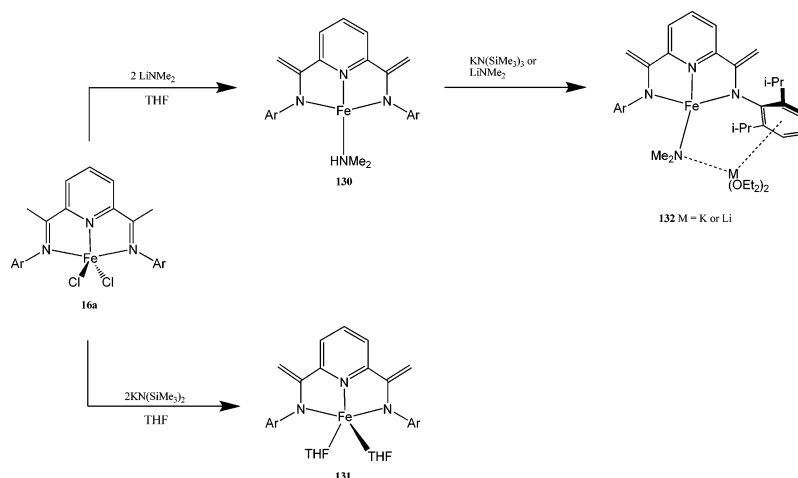
try.^{83,84} Recent years have seen some new examples in this area, some of which have been employed as polymerization precatalysts. In addition, introduction of the bis(imino)pyridine unit into polymeric chains in which polymerization-active metal centers are bound has been reported.

Gibson et al. found that incomplete condensation results on treatment of 2,6-diacetylpyridine with the diamine 2,2'- $\{(NH_2)-C_6H_4\}_2(CH_2CH_2)$ to give the unsymmetrical 2-imino-6-carbonyl-pyridine compound [2- $\{(2'-H_2NC_6H_4-C_2H_4-2''-C_6H_4)N=CMe\}-6-(O=CMe)C_5H_3N]$ (**144**). Complete condensation can be achieved (Scheme 28) on reaction with manganese dichloride in refluxing acetonitrile to afford the orange air-stable antiferromagnetically coupled polymetallic salt $\{[2,6-\{2',2''-C_6H_4-CH_2\}_2(N=CMe)_2\}_2(C_5H_3N)_2\}Mn_2Cl_3-(NCMe)_2\} [2,6-\{2',2''-C_6H_4-CH_2\}_2(N=CMe)_2\}_2(C_5H_3N)_2\}Mn_2Cl_3(MnCl_4)_n$ (**145**).¹⁴³ An X-ray crystal structure determination reveals that cocrystallization of two distinct species

has occurred. A polymeric manganese anion of alternating LMn_2Cl_3 and $MnCl_4$ moieties together with discrete dimanganese cations $[LMn_2Cl_3(NCMe)_2]$ forms; each ionic unit is supported by a 26-membered macrocyclic hexadentate ligand L.

Treatment of 2,6-diacetylpyridine with the diamine [(3,5-*i*-Pr₂C₆H₂-4-NH₂)₂CH₂] using *p*-toluenesulfonic acid as a catalyst under high dilution conditions gives the macrocyclic ligand (**146**).²¹⁰ Complexation of **146** with iron(II) chloride tetrahydrate in THF (Scheme 29) gives the trinuclear macrocyclic complex **147** in high yield. However, the structure of **147** has yet to be unequivocally determined by single-crystal X-ray diffraction studies. Complex **147** has shown high activity for the polymerization of ethylene on activation with MMAO, and notably the lifetime of the catalyst is reported to be enhanced when compared with its mononuclear analogue **16**/MAO.

Scheme 25



Scheme 26

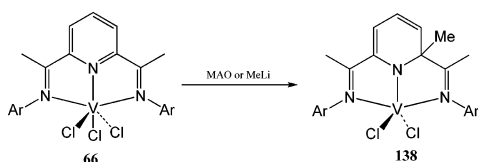
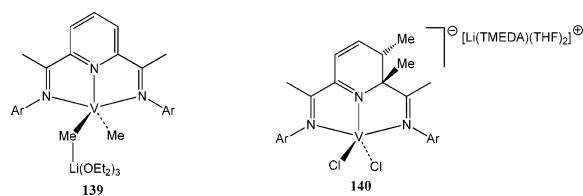
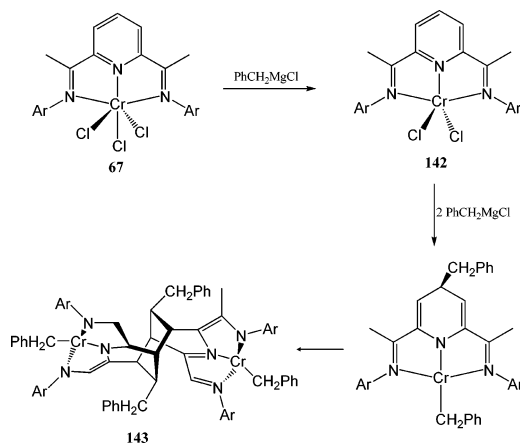


Chart 15



Scheme 27



Use of the related diamines **148** and **149** led, on treatment with 2,6-diacetylpyridine, to the oligomeric polyimines **150** and **151**, respectively (Chart 16). Further treatment with iron dichloride afforded **152** and **153**, which upon activation with MAO produced catalytic systems more efficient at elevated temperatures than those of the original bis(imino)pyridine–iron precatalyst **16**.²¹¹

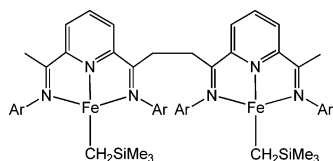


Figure 11. Dinuclear iron complex **136** (Ar = 2,6-*i*-Pr₂C₆H₃).

Use of phenylenediamines also leads to polymeric structures, e.g., **154** to **155** (Scheme 30). *Ortho*-, *meta*-, or *para*-phenylenediamine-derived backbones lead to polymeric species containing different amounts of iron(II) chloride—see **156**, **157**, and **158** in Chart 17. Calculations reveal a more open structure for the “meta” ligand, thereby allowing for increased accessibility of coordination sites and hence the observed highest iron coordination for the “meta” system. Following activation with MAO, observed activities and polymer properties are found to be highly dependent upon the ligand backbone.²¹²

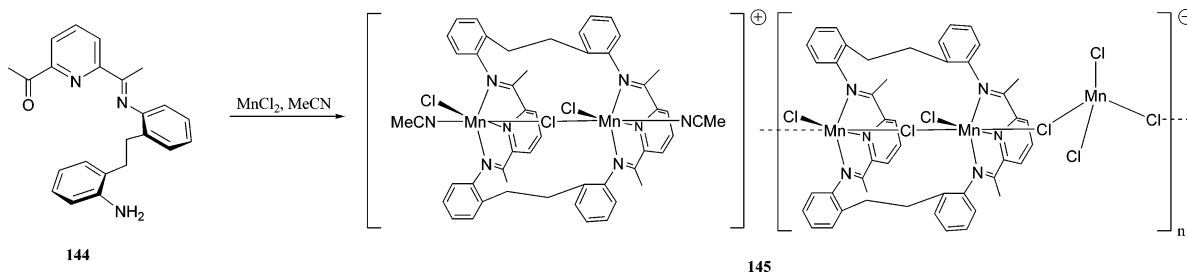
2,6-Bis(imino)pyridine-capped α - and β -cyclodextrin ligands, prepared from the diamines **159** ($n = 1$) and **160** ($n = 2$), are readily complexed with iron dichloride (Scheme 31). Polymerization studies using a large excess of MAO indicate near inactivity for precatalyst **161** ($n = 1$), while **162** ($n = 2$) does show some activity albeit it around 5000 times less active than the corresponding aldimine precatalysts incorporating the ligand series **1**. The decreased activity here is thought to be due to an overprotective cyclodextrin, which tightly wraps around the metal center, thereby inhibiting any potential chain growth.²¹³

3. Variation of the 2,6-Substituted-Pyridine Donor Arms

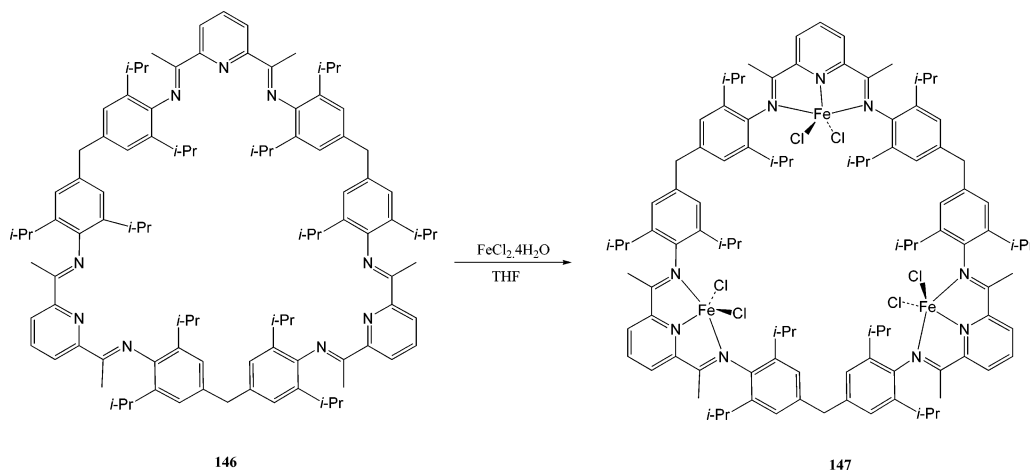
3.1. 2-Imino-6-(methylamido)- and 2-Imino-6-(methylamino)pyridines

In section 2.11 we saw that alkylation of one of the carbons of the imino groups in a bis(imino)pyridine has been observed as one outcome of the reaction with a trialkylaluminum.^{203–205} Indeed, attack at an imino carbon has been previously seen with α -diimines and pyridylimines on reaction with AlMe₃.^{214–216} With bis(arylimino)pyridines and excess AlMe₃, the reaction proceeds to give the imino–amido–pyridine complexes [2- $\{ArNCR(Me)\}$ -6-(ArNCR)-C₅H₃N]AlMe₂ (**116**, R = H, Ar = 2,6-*i*-Pr₂C₆H₃ or 2,4,6-Me₃C₆H₂; R = Me, Ar = 2,6-*i*-Pr₂C₆H₃) in good yield (Chart 16).²⁰³ Further treatment of **116** with B(C₆F₅)₃ yields the cationic methyl species [$\{2-\{ArNCR(Me)\}$ -6-(ArNCR)-C₅H₃N}AlMe][MeB(C₆F₅)₃] (**163**) (Scheme 32); such cationic species are active for the polymerization of ethylene with activities best described as low. Higher molecular weight polymers are obtained for the aldimine-derived ligand system (R = H).

Scheme 28



Scheme 29



Hydrolysis of the dimethylaluminum species **116** ($R = H, Me, Ar = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3, 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) gives, in near quantitative yields, the pale yellow imino–amino–pyridine ligand [2- $\{\text{ArNCR}(\text{Me})\}$ -6-($\text{ArNCR})\text{C}_5\text{H}_3\text{N}$] (**164**). A single-crystal X-ray structure shows that **164** ($R = H, Ar = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) possesses a transoid relationship between the imine and amine groups. Complexation of **164** with iron dichloride in *n*-butanol affords the pale blue complexes [2- $\{\text{ArNCR}(\text{Me})\}$ -6-($\text{ArNCR})\text{C}_5\text{H}_3\text{N}$] FeCl_2 (**165**).²¹⁷ The structure of **165** ($R = H, Ar = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) reveals the weak nature of the iron–amino ligation [2.310(8) Å]; the iron center is distorted square pyramidal. The catalytic activity of **165**/MAO displays only moderate activity (ca. 100 g/mmol·h·bar) when compared with bis(imino)pyridine **16**/MAO systems, perhaps as a consequence of the weakness of the iron–amino interaction, resulting in potential dissociation of the amine arm in the active catalyst. As observed for the bis(imino)pyridine–iron (**16**) and –cobalt (**17**) complexes, the aldimines and cobalt derivatives are the poorest performers.

3.2. 2,6-Bis(methylamino)- and 2,6-Bis(methylamido)pyridines

Reaction of 2,6-bis(bromomethyl)pyridine with two equivalents of LiNHAr ($Ar = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) readily affords the bis(amino)pyridine ligands [2,6- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NHCH}_2\}$] $_2\text{-C}_5\text{H}_3\text{N}$ (**167**).²¹⁸ Such ligands are also available from the condensation reaction between 2,6-bis(carbaldehyde)pyridine and the respective aniline.²¹⁹ For complexation with iron it is necessary to use $[\text{FeCl}_2(\text{THF})]$ in toluene, affording blue/green, air-stable [2,6- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NHCH}_2\}$] $_2\text{C}_5\text{H}_3\text{N}$] FeCl_2 (**168**) in high yield (Scheme 34).²¹⁷ Both monoclinic (distorted square-pyramidal iron) and orthorhombic (trigonal bipyramidal iron) forms of **168** have been obtained, depend-

ing on the method of crystallization. Only low activities are observed for these systems on activation with MAO.

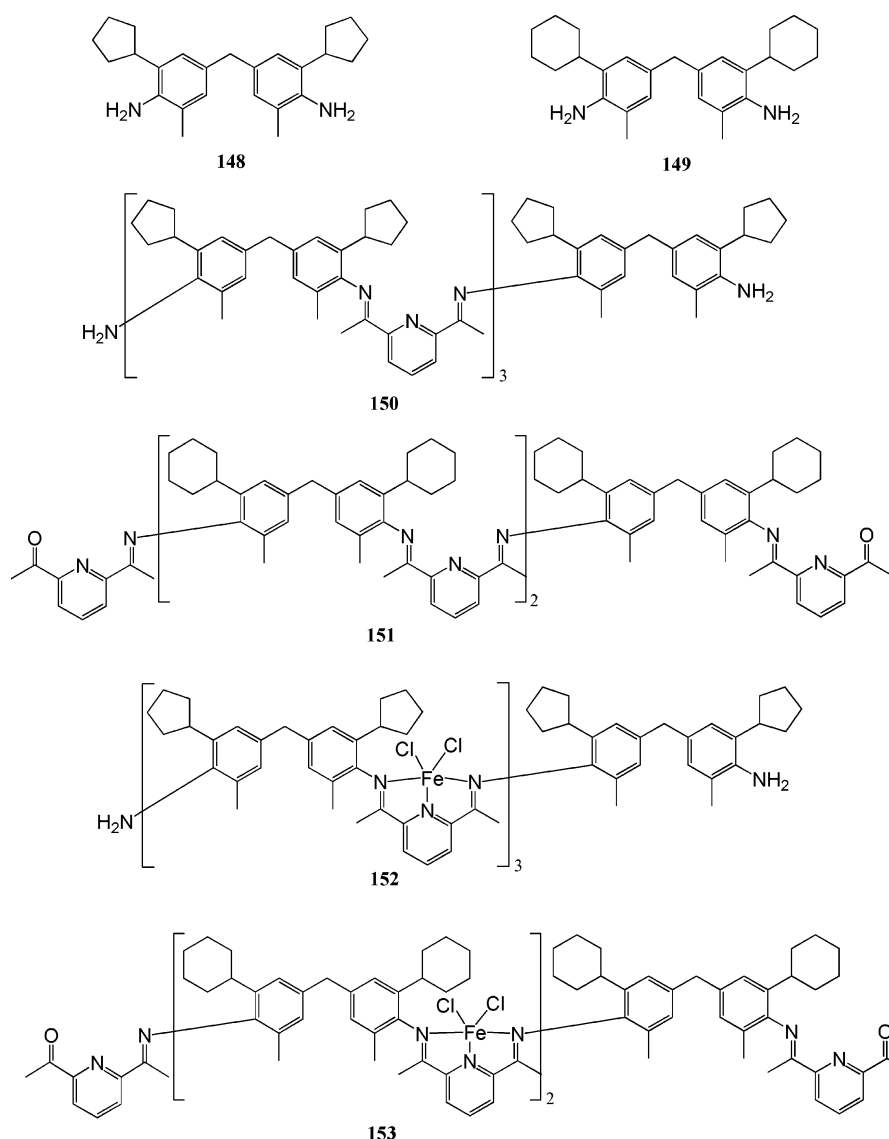
Treatment of **167** with $[\text{Zr}(\text{NMe}_2)_4]$ generates [2,6- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NCH}_2\}$] $_2\text{C}_5\text{H}_3\text{N}$] $\text{Zr}(\text{NMe}_2)_2$ (**169**), which can be readily converted to dihalide or dialkyl derivatives.²¹⁸ Complex **169** and its derivatives have shown high activities for ethylene polymerization on activation with MAO; the titanium analogues show only low activities.²²⁰ Such ligands also readily form organo-rare-earth complexes (Figure 12). For example, ligand **167** ($Ar = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) reacts with $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$ ($\text{Ln} = \text{Sc, Lu, Y}$) to afford **170** and **171** in good yields (76–99%) and **172** in 21% yield.²²¹

3.3. 2-Imino-6-carboxypyridines

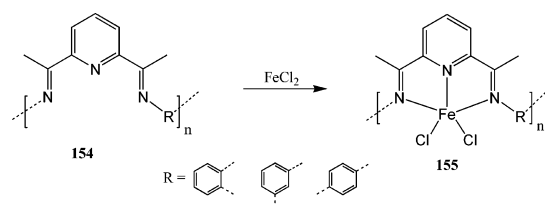
The 2-imino-6-carboxypyridine ligands, [2-($\text{ArN}=\text{CMe}$)-6-($\text{O}=\text{CMe}$) $\text{C}_5\text{H}_3\text{N}$] (**173**, $Ar = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3, 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$), are readily accessible by the condensation reaction of equimolar quantities of the corresponding aniline with 2,6-diacetylpyridine in methanol.^{31,60} Complexation of **173** with iron dichloride affords [2-($\text{ArN}=\text{CMe}$)-6-($\text{O}=\text{CMe}$) $\text{C}_5\text{H}_3\text{N}$] FeCl_2 (**174**) in high yield (Scheme 35). Complex **174**, on activation with MAO, is highly active for the polymerization of ethylene forming, it is claimed,²²² branched polyethylene (6–8 branches per 100 carbons). We have, however, found no evidence for branched polyethylene and instead observed a mixture of high molecular weight linear α -olefins and linear paraffins.^{223a}

Both chromium dichloride and $[\text{CrCl}_3(\text{THF})_3]$ have been reacted with ligands of type **173**, and upon activation with MAO, highly active catalysts are formed which produce waxes/polyethylene.⁶⁰ Conan et al. recently prepared molybdenum carbonyl complexes containing **174** along with complexes based on bis(imino)pyridine and 2-amino-6-iminopyridine ligands; a preference for *N,N*-chelation is

Chart 16



Scheme 30



observed.¹³⁰ An interesting variation of this class of ligand and its application in macrocycle formation is discussed in section 2.12 (see Scheme 28).¹⁴³

Variation in the nature of the carbonyl R substituent within the 2-imino-6-carbonylpyridine ligand frame has also been reported. For example, the ethylcarboxylato-substituted ligands [2-(ArN=CMe)-6-(OCOEt) $\text{C}_5\text{H}_3\text{N}$] (**175**) have been prepared and their iron and cobalt halide complexes [2-(ArN=CMe)-6-(OCOEt) $\text{C}_5\text{H}_3\text{N}$]MCl₂ (**176**, M = Fe, Ar = 2,6-*i*-Pr₂C₆H₃, 2,6-Me₂C₆H₃; **177**, Co, Ar = 2,6-*i*-Pr₂C₆H₃, 2,6-Me₂C₆H₃) synthesized (Chart 18).²²⁴ X-ray studies of **176** have shown that the ketone moiety can be, depending on the substitution on the aryl group, weakly bound or pendant.

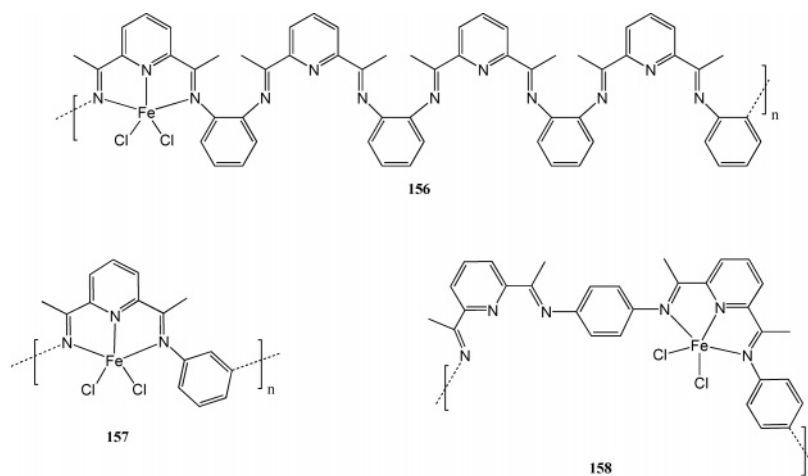
It was found that, on activation with MAO, the ferrous complexes exhibit higher activities for ethylene polymerization than for oligomerization, while the cobaltous complexes show higher activities for ethylene oligomerization. Related ligands have also been complexed with nickel²²⁵ and palladium,²²⁶ while 1:1 and 2:1 (**178**) 2-carbomethoxy-6-iminopyridine complexes have been prepared by Su and Zhao for the metals Mn to Ni.²²⁷

3.4. 2-Imino-6-(methylalcohol)- and 2-Imino-6-(methylalkoxide)pyridines

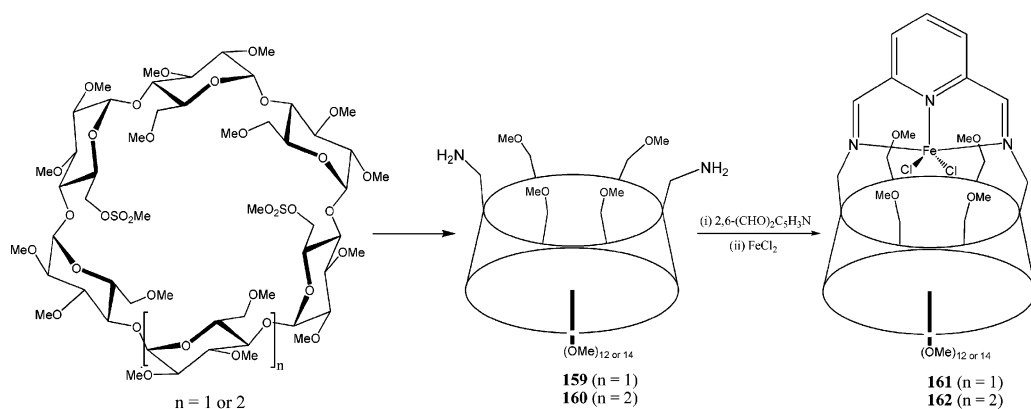
2-Imino-6-(methylalcohol)pyridines **180** can be readily obtained by treating **173** with excess trimethylaluminum and treating the aluminum intermediate with water. The intermediate aluminum species can be isolated as the imino-pyridine-alkoxide complex [2-{ArNC(Me)}-6-{(Me₂Al)-OC(Me)₂} $\text{C}_5\text{H}_3\text{N}$]AlMe₂ (**179**, Ar = 2,6-*i*-Pr₂C₆H₃, 2,4,6-Me₃C₆H₂) in which a molecule of trimethylaluminum is additionally bound to alkoxide oxygen atom (Scheme 36).^{223b}

Complexation of **180** with iron dichloride gives the imino-pyridine-alcohol species [2-(ArN=CMe)-6-{(H)-OCMe₂} $\text{C}_5\text{H}_3\text{N}$]FeCl₂ (**181**). Upon activation with MAO,

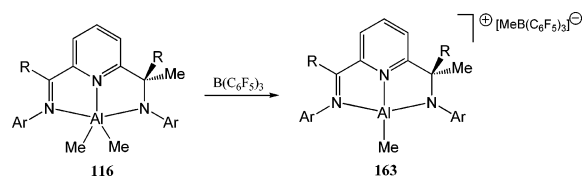
Chart 17



Scheme 31



Scheme 32



181 displays moderate activity for ethylene oligomerization/polymerization.

3.5. 2-Imino-6-(organyl)pyridines

A series of 6-(organyl)-2-(imino)pyridyl-containing cobalt(II) complexes (**184**) (Figure 13) has been shown to act as oligomerization catalysts upon activation with MAO, with the thiophen-2-yl derivatives producing short-chain α -olefins with very high turnover rates (up to 10^6 mol). Phenyl and furanyl derivatives were five times less productive for selective ethylene dimerization. The ligands were prepared via either Stille coupling between 6-bromo-2-[(2,6-diiso-

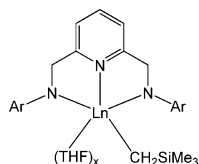


Figure 12. Lanthanide complexes: **170** ($\text{Ln} = \text{Sc}$, $x = 1$), **171** ($\text{Ln} = \text{Lu}$, $x = 2$), and **172** ($\text{Ln} = \text{Y}$, $x = 2$); $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$.

Chart 18

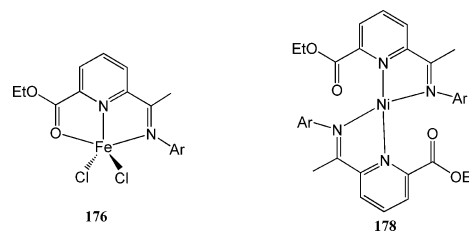


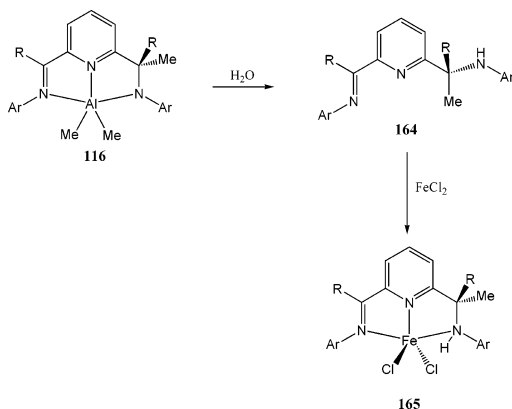
Figure 13. Complex **184** ($\text{X} = \text{S}$, $\text{R} = \text{H}$; $\text{X} = \text{S}$, $\text{R} = \text{C}_2\text{H}_5$; $\text{X} = \text{O}$, $\text{R} = \text{H}$; $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$).

propylphenyl)imino}pyridine and the respective stannane (for **182**) or a Suzuki reaction (for **183**) between 6-bromo-2-acetylketone and $\text{PhB}(\text{OH})_2$ followed by a condensation with the requisite aniline (Scheme 37).²²⁸ The related benzo[b]-thiophen-2-yl and naphthyl derivatives have also been prepared.²²⁹

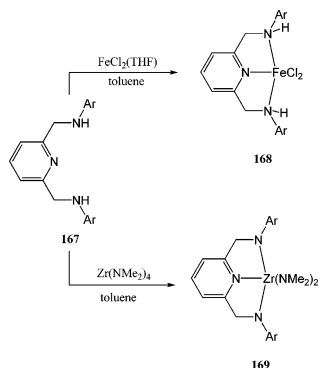
3.6. 2-Imino-6-pyridylpyridines (iminobipyridines) and 2-Imino-1,10-phenanthrolines

Condensation of 6-acetyl-2,2'-bipyridine with 2,6-diisopropylaniline affords the 2-imino-6-pyridylpyridine, [2-($\text{ArN}=\text{CMe}$)-6-(2'- $\text{C}_5\text{H}_4\text{N}$) $\text{C}_5\text{H}_3\text{N}$] (**185**, $\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$), which

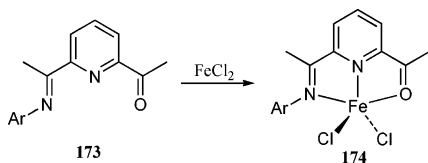
Scheme 33



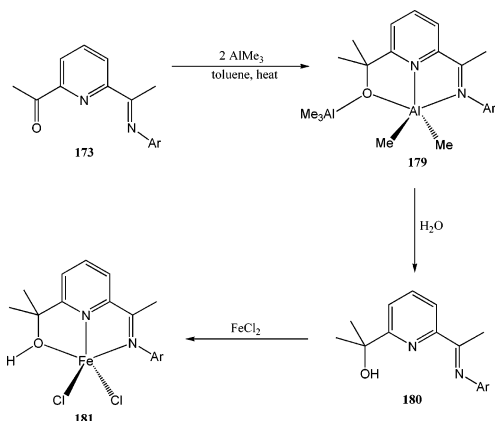
Scheme 34



Scheme 35



Scheme 36



on reaction with ferrous chloride in *n*-butanol affords the corresponding iron complex [2-(ArN=CMe)-6-(2'-C₅H₄N)-C₅H₃N]FeCl₂ (**186**) (Scheme 38). The latter in the presence of MAO behaves as a highly active oligomerization catalyst (activity ≈ 500 g/mmol \cdot h \cdot bar), producing mainly 1-butene and 1-hexene.²³⁰

As a variation on the 2-imino-6-pyridylpyridine, the corresponding 2-imino-1,10-phenanthrolyl ligands, [2-(ArN=CR)-1,10-C₁₂H₇N₂] (**187**, R = H or Me, Ar = 2,6-*i*-Pr₂C₆H₃, 2,6-Me₂C₆H₃, 2,4,6-Me₃C₆H₂), have also been prepared

(Chart 19)^{231,232} and can be complexed with iron dichloride to give complexes of the form [2-(ArN=CR)-1,10-C₁₂H₇N₂]-FeCl₂ (**188**). The iron complexes (**188**) when activated with MAO or MMAO are highly active oligomerization catalysts, giving a much broader range of molecular weights than **186**/MAO.²³¹ Both steric and electronic effects of the ligand frame affect the catalytic activity and the properties of the oligomer formed. Complexes featuring cobalt²³² and nickel²³³ have also been reported recently.

3.7. 2,6-Bis(pyridyl)pyridines (terpyridines)

Interaction of the substituted terpyridines [2,6-(2'-C₅H₄N-6-R)₂C₅H₃N] (**189**, R = 3,5-Me₂C₆H₃, 2,4,6-Me₃C₆H₂) with iron dichloride in THF affords the corresponding iron complexes [2,6-(2'-C₅H₃N-6-R)C₅H₃N]FeCl₂ (**190**, R = 3,5-Me₂C₆H₃, 2,4,6-Me₃C₆H₂) (Figure 14).²³⁴ However, only low activities for the polymerization of ethylene are reported on their treatment with MMAO. Notably, the unsubstituted terpyridine iron(III) halide complex [2,6-(2'-C₅H₄N)C₅H₃N]FeCl₃ (**191**) on activation with MMAO (although inactive for ethylene polymerization) displays good activities for the polymerization of isoprene, affording polymers composed of 1,2-, 3,4-, and *cis*-1,4-poly(isoprene).

3.8. 2,6-Bis(iminophosphoranyl)pyridines

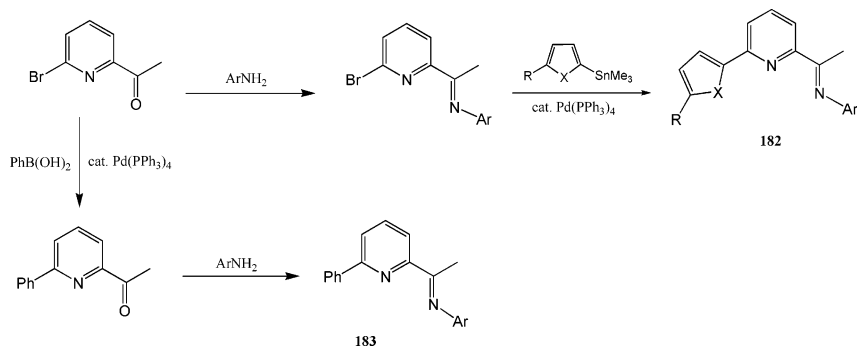
The bis(aryliminophosphoranyl)pyridine ligands [2,6-(ArN=PPh₂)₂C₅H₃N] (**192**) can be synthesized by reacting NaPPh₂ with 2,6-difluoropyridine in liquid ammonia followed by oxidation with the corresponding aryl azide.²³⁵ Treatment of **192** with [VCl₃(THF)₃] or [MX₂] (M = Fe, Co; X = Cl or Br) gives the six-coordinate vanadium complex [2,6-(ArN=PPh₂)₂C₅H₃N]VCl₃ (**193**, 2,6-*i*-Pr₂C₆H₃, 2,4,6-Me₃C₆H₂) and the five-coordinate iron and cobalt complexes [2,6-(ArN=PPh₂)₂C₅H₃N]MX₂ (**194**, M = Fe, Co; X = Cl or Br; 2,6-*i*-Pr₂C₆H₃, 2,4,6-Me₃C₆H₂), respectively (Scheme 39).²³⁶ On activation with MAO the iron systems display low activity for ethylene polymerization (at 10 bar/50 °C), the cobalt systems are moderately active (at 10 bar/50 °C), while the vanadium system shows higher activities even at ambient temperature and 1 bar ethylene pressure.

The bis(iminophosphoranyl)pyridine ligand, **192**, featuring *N*-alkyl or *N*-silyl groups, can also be prepared by the Staudinger reaction of bis-2,6-diphenylphosphanylphosphine with the respective alkyl- and silylazide (Scheme 40). Treatment of **192** with the THF adducts [CoCl₂(THF)₂] or [FeCl₂(THF)_{1.5}] in THF affords the tri- and tetrametallic complexes **195** and **196**, respectively. Substitution of acetonitrile for THF in the reaction of **192** with [CoCl₂(THF)₂] leads to the cationic complex **197** (Chart 20). Complex **196**/MAO polymerizes ethylene with an activity of 62 g/mmol \cdot h.²³⁷

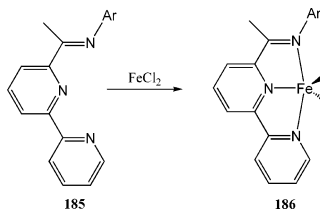
3.9. 2,6-Bis(methylphosphine)pyridines

Treatment of diarylphosphines with 2,6-bis(chloromethyl)pyridine in the presence of base afforded the bis(methylphosphine)pyridine ligands [2,6-(Ar₂PCH₂)₂C₅H₃N] (**198**, Ar = Ph, 2-MeC₆H₄, 2,4,6-Me₂C₆H₂) in good yield. Complexation of **198** with iron(II) and cobalt(II) chloride in ethanol furnishes the PNP-coordinated species [2,6-(Ar₂PCH₂)₂C₅H₃N]-MCl₂ (**199**, M = Fe, Co) (Scheme 41).²³⁸ While the cobalt species show some activity for ethylene polymerization on treatment with MAO, attempted formation of the iron complexes results in decomposition.

Scheme 37



Scheme 38



Scheme 40

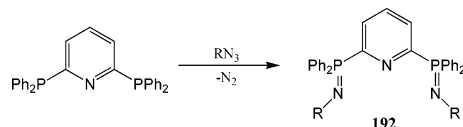


Chart 19

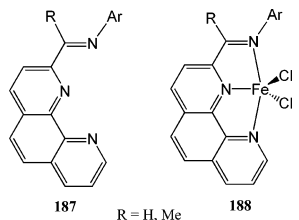
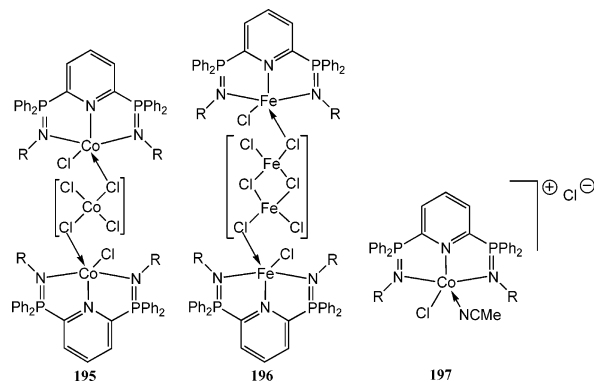
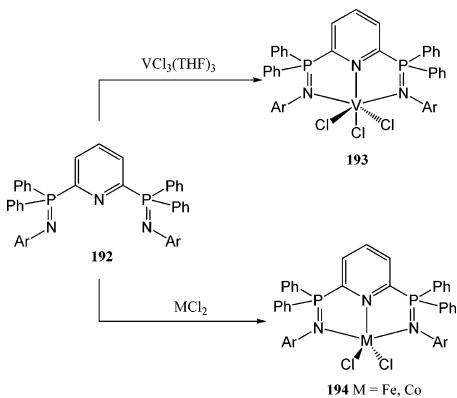


Chart 20



Scheme 39



Scheme 41

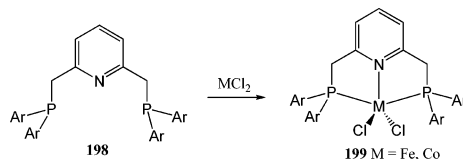
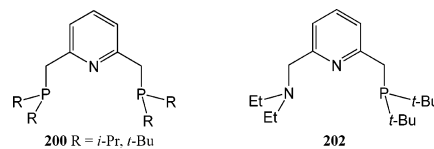


Chart 21



Complexation of the alkyl-substituted bis(methylphosphine)pyridine ligands **200** (Chart 21) with iron(II) chloride in THF at 65°C similarly affords the dichloride complexes $[2,6\text{-}(\text{R}_2\text{PCH}_2)_2\text{C}_5\text{H}_3\text{N}]\text{FeCl}_2$ (**201**). A related five-coordinate complex **203** can be obtained on treating the PNN ligand, $[2\text{-}(t\text{-Bu}_2\text{PCH}_2)\text{-6-(Et}_2\text{NCH}_2)\text{C}_5\text{H}_3\text{N}]$ (**202**) with iron dichloride, which on further reaction with TIPF_6 yields the cationic complex $[\{2\text{-}(t\text{-Bu}_2\text{PCH}_2)\text{-6-(Et}_2\text{NCH}_2)\text{C}_5\text{H}_3\text{N}\}\text{Fe}(\text{THF})\text{Cl}](\text{PF}_6)$ (**203**).²³⁹

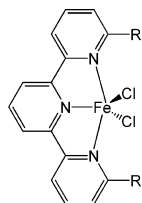


Figure 14. Complex **190** ($\text{R} = 3,5\text{-Me}_2\text{C}_6\text{H}_3, 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$).

The iron complex **201** ($\text{R} = i\text{-Pr}$) has been reduced with excess 0.5% sodium amalgam in the presence of CO (4 atm) to afford the red dicarbonyl complex **204** (Chart 22). Treatment of **201** with NaBEt_3H (2 equiv) under nitrogen gave the orange/red dinitrogen/dihydride complex **205**, which is prone to decomposition. Further treatment of **205** with one equivalent of PhSiH_3 yields the distorted octahedral silyl complex **206**, which has been characterized by single-crystal X-ray diffraction; the hydride trans to the pyridine has been replaced by the silyl group. Both **205** and **206** have been reacted with 1 atm of CO to form complexes **204** and **207**, respectively. Treatment of **206** with PMe_3 gave **208** in which the N_2 has been substituted by phosphine. Under 4 atm of

Chart 22

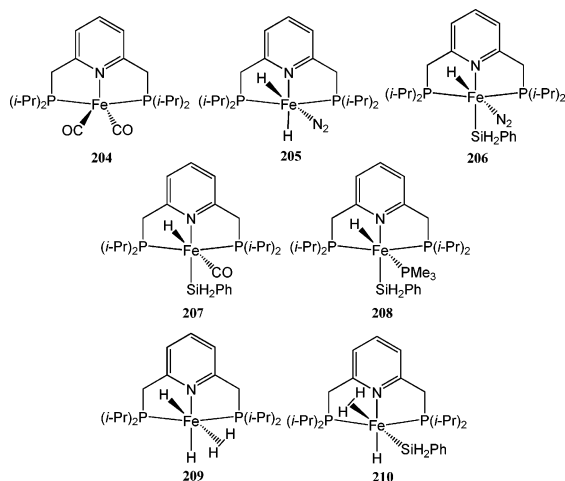
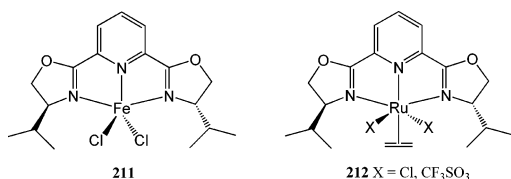


Chart 23



H₂, **205** and **206** afford the η^2 -dihydrogen complexes **209** and **210**, which are in rapid exchange with the respective iron hydride.²⁴⁰

Ruthenium complexes containing the ligand **198** have recently been used to catalyze the conversion of alcohols into esters and dihydrogen²⁴¹ and the dehydrogenation of secondary alcohols to ketones.²⁴² Related iridium complexes exhibit novel C–H activation properties.^{243,244}

3.10. 2,6-Bis(oxazoline)pyridines and 2,6-Bis-(2-benzimidazolyl)pyridines

Divalent iron (**211**) and ruthenium (**212**) complexes have been prepared featuring the [2,6-bis{(4*S*)-4-isopropyl-2-oxazolin-2-yl}C₅H₃N] ligand (Chart 23). Both **211** and **212** show some activity for ethylene polymerization on activation with MAO with that for **211** being considerably lower than the bis(arylimino)pyridine–iron catalysts. Notably, the ruthenium complex has showed some catalytic activity for ethylene/1-hexene copolymerization.^{245,246}

Treatment of 2,6-bis(2-benzimidazolyl)pyridine with [CrCl₃(THF)₃] in CH₂Cl₂ affords a series of distorted octahedral chromium(III) trichloride complexes of the form **213** (Figure 15).²⁴⁷ With MAO as cocatalyst, these chromium species showed high activity for ethylene oligomerization/polymerization, the products formed being dependent upon the substituents present on the tridentate ligand system. With DEAC as cocatalyst, activities were lower and the products formed were higher molecular weight linear polyethylenes.

3.11. 2,6-Bis(carbene)pyridines

Both iron²⁴⁸ and chromium²⁴⁹ complexes bound by bis(carbene)pyridine ligands have been reported. For example,

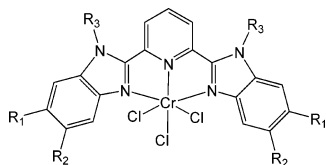


Figure 15. Bis(2-benzimidazolyl)pyridine complex **213**.

Scheme 42

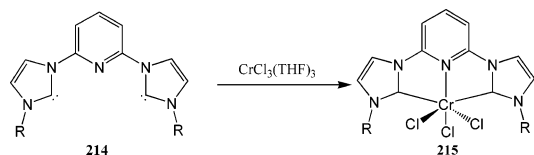
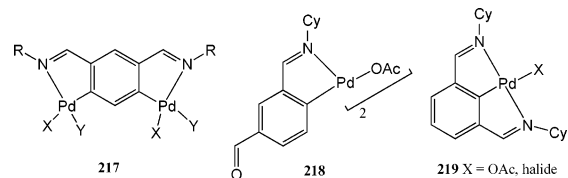


Chart 24



Scheme 43

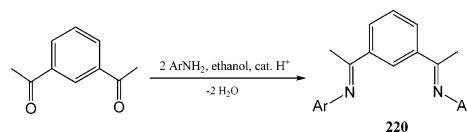


Chart 25

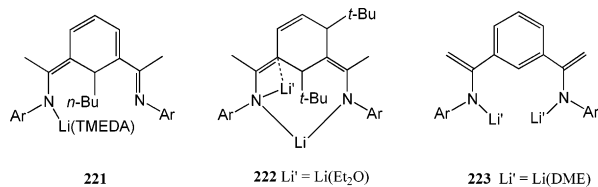
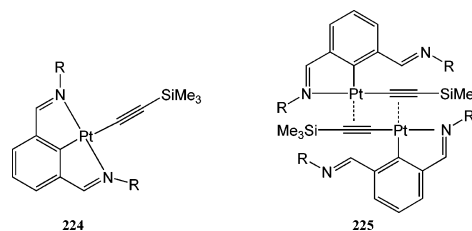


Chart 26



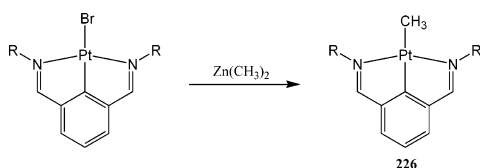
the six-coordinate bis(carbene) pyridine chromium trichloride complexes (**215**, R = *i*-Pr, 2,6-*i*-Pr₂C₆H₃, 1-adamantyl) can be prepared in high yield from reaction of the corresponding bis(carbene)pyridine ligand (**214**) with [CrCl₃(THF)₃] (Scheme 42). In combination with MAO, complexes **215** are exceptionally active catalysts for oligomerization of ethylene, forming α -olefins.²⁴⁹

4. Variations on the Central Donor

4.1. 1,3-Bis(imino)benzenes

The earliest reports on the coordination chemistry of bis(imino)benzene [1,3-(RN=CH)₂C₆H₄] (**216**) concerned the palladium(II) complex **217** (Chart 24) in which the ligand acts as a bridge between the two metal centers following a double orthometalation reaction; the crystal structure of the derivative resulting from reaction of *N,N'*-diethylbenzene-1,3-dicarbaldimine and benzoyltrifluoroacetone has been determined.²⁵⁰ Later work by Vila et al. centered on the use of *N,N*-isophthalylidenebis(cyclohexylamine) **216** (R = Cy). Reaction with palladium(II) acetate afforded a monocyclometalated dimer **218** together with complex **219** (X = OAc). Further reaction of this mixture with NaX (X = Cl, Br, or I) afforded the halide analogues of **219** in varying degrees of

Scheme 44



purity. A number of manganese carbonyl complexes were also reported.²⁵¹

Nüchel and Burger reported the synthesis of the ligand [1,3- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CMe}\}_2\text{C}_6\text{H}_4$] (**220**) by a route similar to that used for the bis(arylimino)pyridines **1** (Scheme 43).²⁵² However, unlike **1**, ligands of the form **220** are difficult to complex to late transition metals. This inactivity is thought to be due to the need to overcome a C–H activation to allow the carbon of the central ring to participate in binding to the metal. Using the deprotonation strategy developed by van Koten et al. for the amine ligand [1,3-(CH_2NMe_2) $_2\text{C}_6\text{H}_4$],²⁵³ **220** was treated with *n*-BuLi in the presence of TMEDA to afford the highly sensitive red complex **221** in 50% yield. This complex, in which an *n*-butyl group has been added to the central ring, is known as the Meisenheimer butyllithium adduct. The use of *tert*-butyllithium in diethylether, again in the presence of TMEDA, led to a yellow-orange double-addition product **222** in which *tert*-butyl groups have been added to the central ring at the 2 and 4 positions (Chart 25). Overall the structure is best described as being of the bis(enamide) type, with Li–N distances typical of lithium amides. Reaction of **220** with the hard base lithium dimethylamide in diethylether/DME (50:1) led to deprotonation at the diimine methyl group to afford the diketiminate **223**.

Platinum(II) bromide complexes incorporating bis(imino)benzene have been synthesized via an oxidative addition reaction, which on further reaction with LiCCSiMe_3 affords either monomeric *trans*-diorganoplatinum(II) (**224**) or dimeric *cis*-diorganoplatinum(II) (**225**) complexes (Chart 26), depending on the imine substituent present, viz. 2,6-*i*-Pr $_2$ C $_6$ H $_3$ versus 4-MeOC $_6$ H $_4$.²⁵⁴

Platinum(II) chlorides, synthesized from $\text{K}_2[\text{PtCl}_4]$, have been prepared by Fossey and Richards for a range of 1,3-bis(imino)benzenes.²⁵⁵ Further reaction with silver salts yields cationic complexes in which water is bound to the metal, and such complexes have been found to accelerate the rate of certain Michael and Diels–Alder reactions. A stable *trans*-arylplatinum methyl complex **226** has been prepared by a transmetalation reaction involving ZnMe_2 (Scheme 44).²⁵⁶

4.2. Bis(imino)pyrrolides

The colorless bis(arylimino)pyrrole, [2,5- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}_2\text{C}_4\text{H}_2\text{NH}$] (**227**), prepared from the condensation reaction of pyrrole-2,5-dicarboxaldehyde with two equivalents of 2,6-diisopropylaniline in methanol, adopts a structure with *cis*-oriented imino arms.²⁵⁷ Complexation of **227** with $[\text{Zr}(\text{NMe}_2)_4]$ leads only to the monosubstituted fluxional product [2,5- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}_2\text{C}_4\text{H}_2\text{N}$]Zr(NMe $_2$) $_3$ (**228**) (Chart 27) in which the metal binds only to two of the three potential nitrogen donors at any one time. Lithiated **227** reacts with zirconium(IV) chloride to afford [2,5- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}_2\text{C}_4\text{H}_2\text{N}$]ZrCl $_4$ Li(OEt) $_2$ (**229**), whereas with iron(II) chloride a bis(ligand) complex [2,5- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}_2\text{C}_4\text{H}_2\text{N}$] $_2$ Fe (**230**) is isolated. For $[\text{CoCl}_2(\text{THF})]$ the green salt [$\{2,5\text{-}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}_2\text{C}_4\text{H}_2\text{N}\}\text{CoCl}_2$][Li-

(THF) $_4$] (**231**) is obtained, which loses two molecules of THF on warming to give [$\{2,5\text{-}\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}_2\text{C}_4\text{H}_2\text{N}\}\text{CoCl}_2$][Li(THF) $_2$] (**232**). The zirconium complexes **228** and **229**, in the presence of MAO, catalyze the polymerization of ethylene, while the iron complex **230** is inactive. Interestingly, the cobalt complexes **231/232** exhibit moderate activity (with MAO) for the oligomerization of ethylene, giving linear and branched products. **231/232** have also shown some activity for propylene polymerization.

Reaction of **227** with either tetrabenzyl zirconium or hafnium, $[\text{M}(\text{CH}_2\text{Ph})_4]$, results in the benzylation of one of the imino moieties to afford the amino–pyrrolyl complexes [2- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}_2\text{C}_4\text{H}_2\text{N}\}$ -5- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NCH}(\text{CH}_2\text{Ph})\}\text{C}_4\text{H}_2\text{N}$]Zr(CH $_2$ Ph) $_2$ (**233**) (cf. AlMe_3 behavior with **1**) (Figure 16). One of the benzyl groups in **233** exhibits η^2 coordination, and the complexes can be activated with MMAO to polymerize ethylene. Cationic monobenzyl complexes are readily formed on treatment of **233** with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$.²⁵⁸

4.3. Bis(imino)furans and Bis(imino)thiophenes

The bis(imino)furan [2,5- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}_2\text{C}_4\text{H}_2\text{O}$] (**234**) and the bis(imino)thiophene compounds [2,5- $\{(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}_2\text{C}_4\text{H}_2\text{S}$] (**235**) are readily available in good yields from the condensation reactions of furan-2,5-dicarboxaldehyde or thiophene-2,5-dicarboxaldehyde and the 2,6-diisopropylaniline (Chart 28). Attempts to complex **234** and **235** with either iron(II) or cobalt(II) chloride in tetrahydrofuran or *n*-butanol have been unsuccessful.²⁵⁹

4.4. Bis(imino)pyrimidines and Bis(imino)triazenes

The bis(imino)pyrimidine ligands [2,4-(ArN=CPh) $_2$ -6-MeC $_4$ HN $_2$] (**236**) are readily accessible from 2,4-dibenzoyl-6-methylpyrimidine and the required aniline in the presence of $\text{Si}(\text{OEt})_4$ and a catalytic amount of H_2SO_4 .²⁵⁹ A crystal structure for the Ar = 2,6-*i*-Pr $_2$ C $_6$ H $_3$ example shows it to exist in the solid state as the *Z,Z* isomer, a configuration quite different from the bis(imino)pyridines **1** which adopt *E,E* configurations in both the solid and solution state (see section 2.1). Complexation of **236** with iron(II) or cobalt(II) chloride is readily achieved in hot *n*-butanol to give [2,4- $\{\text{ArN}=\text{CPh}\}_2$ -6-MeC $_4$ HN $_2$]MCl $_2$ (**237**, M = Fe, Co) (Scheme 45). However for cobalt, formation of the 2,6-*i*-Pr $_2$ C $_6$ H $_3$ derivative is unfavorable on steric grounds. Catalytic studies on these systems show them to possess only one-third (Fe) or one-half (Co) of the activity of the analogous bis(imino)pyridine systems **16** and **17**; polymer data of the pyrimidine- and pyridine-based systems follow similar trends. The bis(imino)triazine ligands [2,4- $\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}=\text{CR}^1\}_2$ -6-R $^2\text{C}_4\text{HN}_3$] (**238**, R 1 = H or Ph; R 2 = CH $_2$ Ph or CHNAr – Figure 17) were recovered unreacted, however, on treatment with the iron(II) or cobalt(II) chloride.

4.5. Bis(imino)carbazoles and Bis(imino)-dibenzofurans

The bis(imino)carbazole [1,6- $\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}=\text{CH}\}_2$ -3,6-Me $_2\text{C}_{12}\text{H}_4\text{NH}$] (**239**) and the bis(imino)dibenzofuran [1,6- $\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}=\text{CH}\}_2$ -3,6-Me $_2\text{C}_{12}\text{H}_6\text{O}$] (**240**) have recently been reported.^{259,260} Only **239** reacts with iron(II) or cobalt(II) chloride to give [1,6- $\{(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}=\text{CH}\}_2$ -3,6-Me $_2\text{C}_{12}\text{H}_4\text{N}$]MCl (**241**, M = Fe, Co) (Scheme 46); however, the resulting “pre-catalysts” are, in the presence of MAO, inactive toward the polymerization of ethylene.

Chart 27

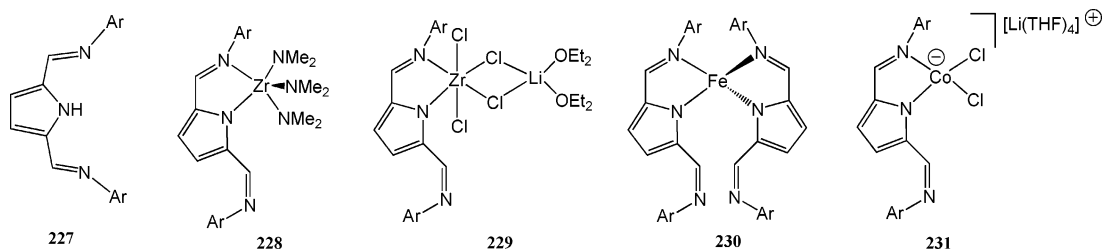
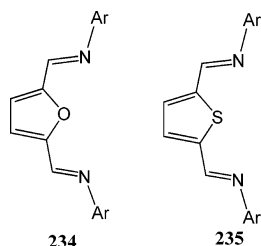
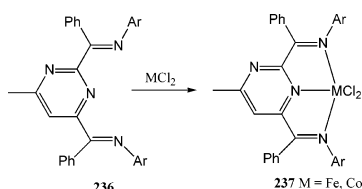


Chart 28



Scheme 45



Scheme 46

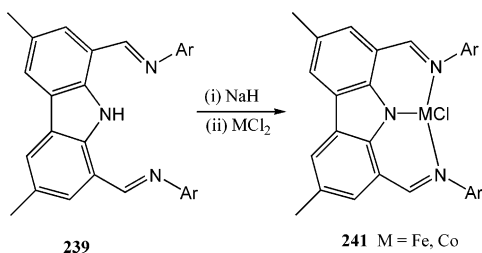
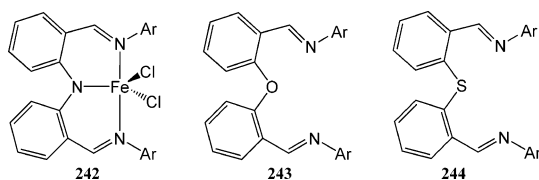
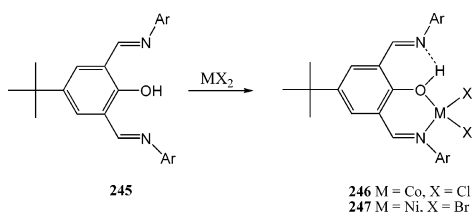


Chart 29



Scheme 47



4.6. Bis(imino)diphenylamines, Bis(imino)diphenylethers, and Bis(imino)diphenylthioethers

The bis(imino)diphenylamide iron complex $[\{2-(\text{ArN}=\text{CH})\text{C}_6\text{H}_4\}_2\text{N}]\text{FeCl}_2$ (**242**, Chart 29) has been prepared from the corresponding bis(imino)diphenylamine and shown to display low ethylene polymerization activities.²⁶¹ The bis(imino)diphenylether, $[\{2-(\text{ArN}=\text{CH})\text{C}_6\text{H}_4\}_2\text{O}]$ (**243**), and

bis(imino)diphenylthioether, $[\{2-(\text{ArN}=\text{CH})\text{C}_6\text{H}_4\}_2\text{S}]$ (**244**), compounds have, however, not been amenable to complexation with iron(II) or cobalt(II) chloride.²⁵⁹

4.7. Bis(imino)phenols

The bis(imino)phenoxy-cobalt and -nickel complexes $[2,6-(\text{ArN}=\text{CH})_2-4-t\text{-BuC}_6\text{H}_3\text{OH}]\text{MX}_2$ (**246**, $\text{M} = \text{Co}$, $\text{X} = \text{Cl}$, $\text{Ar} = 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$; **247**, $\text{M} = \text{Ni}$, $\text{X} = \text{Br}$, $\text{Ar} = 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$) can be readily prepared from the corresponding bis(imino)phenol ligand $[2,6-(\text{ArN}=\text{CH})_2-4\text{-MeC}_6\text{H}_3\text{OH}]$ (**245**) in high yield (Scheme 47). Both the nickel and cobalt complexes are active for ethylene oligomerization on treatment with MAO, with the nickel catalysts displaying the higher activity, giving a mixture of 1-hexene, 1-octene, and some 1-butene.²⁶²

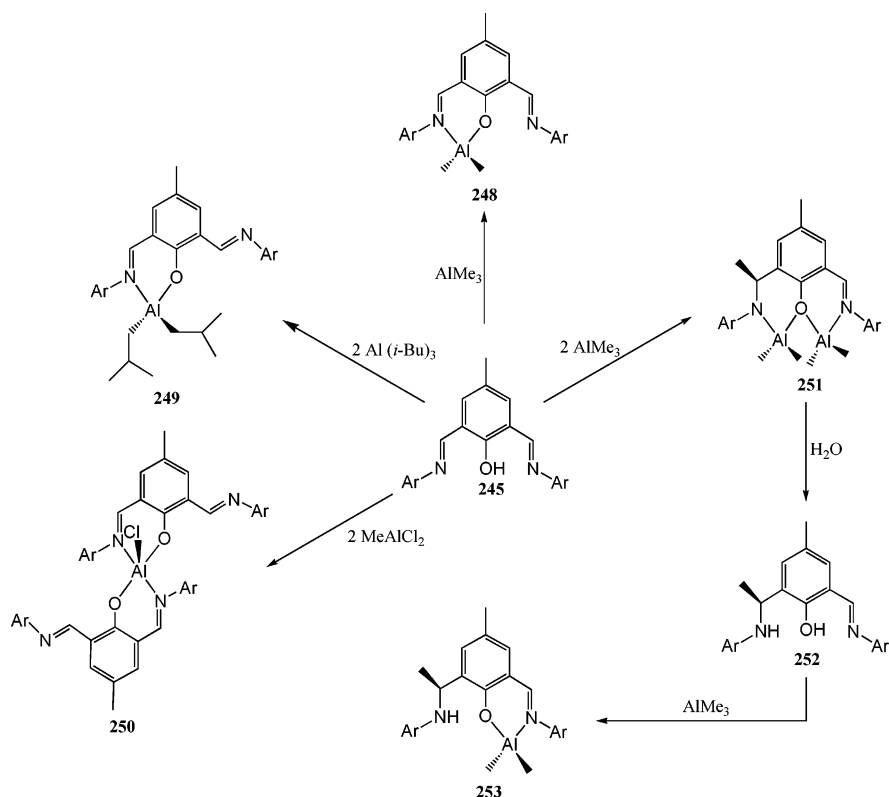
Redshaw et al. reacted **245** ($\text{Ar} = 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3$) with a number of alkylaluminum reagents.²⁶³ With one equivalent of AlMe_3 or two equivalents of $\text{Al}(i\text{-Bu})_3$, dialkyl complexes of the form $[2,6-(\text{ArN}=\text{CH})_2-4\text{-MeC}_6\text{H}_3\text{O}]\text{AlR}_2$ (**248**, $\text{R} = \text{Me}$; **249**, $\text{R} = i\text{-Bu}$) are formed, with imino-alkoxide ligation at aluminum. Use of MeAlCl_2 leads to the bis(*N,O*-chelate) complex $[2,6-(\text{ArN}=\text{CH})_2-4\text{-MeC}_6\text{H}_3\text{O}]_2\text{AlCl}$ (**250**), whereas with two equivalents of AlMe_3 the red complex $[2\text{-ArNCH}(\text{Me})-6-(\text{ArN}=\text{CH})-4\text{-MeC}_6\text{H}_3\text{O}](\text{AlMe}_2)_2$ (**251**) containing two aluminum centers, one with imino-alkoxide and the other amido-alkoxide ligation, is obtained. Hydrolysis of **251** readily affords the imino-amino-phenol ligand **252**, which can be further reacted with AlMe_3 to afford **253** (Scheme 48).

Reaction of ferric chloride with **245** ($\text{Ar} = 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3$, $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) in acetonitrile leads to the formation of ion pairs of the type $[\text{FeCl}_4][2,6-(\text{ArHN}=\text{CH})_2-4\text{-MeC}_6\text{H}_3\text{O}]$ (**254**: the phenoxy group is deprotonated, while the $\text{C}=\text{N}$ groups are protonated), which adopt a columnar helix structure through H bonding of anion/cation molecules and intermolecular $\pi-\pi$ interactions. When the ortho aryl groups are H, the complex $[2,6-(\text{ArN}=\text{CH})_2-4\text{-MeC}_6\text{H}_3\text{OH}]\text{FeCl}_3$ (**255**) is formed.²⁶⁴

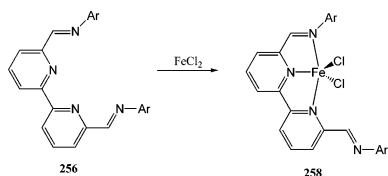
4.8. Bis(imino)bipyridines and Bis(imino)phenanthrolines

The ligands $[6,6'-(\text{ArN}=\text{CH})_2-2,2'\text{-C}_{10}\text{H}_2\text{N}_2]$ (**256**, $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, $2,6-i\text{-Pr}_2\text{C}_6\text{H}_3$) and $[2,9-(\text{ArN}=\text{CH})_2-1,10\text{-C}_{12}\text{H}_6\text{N}_2]$ (**257**, $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, $2,6-i\text{-Pr}_2\text{C}_6\text{H}_3$) were prepared by selective oxidation of the methyl precursors to give 6,6'-diformyl-2,2'-bipyridine and 2,9-diformyl phenanthroline, respectively, and subsequent condensation with the corresponding aniline.^{230,265} Treatment of **256** and **257** with iron dichloride gives the monometallic complexes $[6,6'-(\text{ArN}=\text{CH})_2-2,2'\text{-C}_{10}\text{H}_2\text{N}_2]\text{FeCl}_2$ (**258**) and $[2,9-(\text{ArN}=\text{CH})_2-1,10\text{-C}_{12}\text{H}_6\text{N}_2]\text{FeCl}_2$ (**259**), respectively (Schemes 49 and 50). An X-ray study of **259** ($\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) reveals a severely distorted trigonal-bipyramidal iron center to which

Scheme 48



Scheme 49



only one imine arm is coordinated. Similarly, **259** is thought to contain a tridentate imino-phenanthroline ligand with a pendant imino substituent. Neither **258** nor **259** is catalytically active in the presence of MAO.

4.9. Bis(imino)terpyridines

The bis(imino)terpyridine frameworks [6,6''-(2,6-*i*-Pr₂C₆H₃)N=CR₂-2,2':6',2''-C₁₅H₉N₃] (**260**, R = H, Me) have been recently studied by Solan et al. The nature of the imino-carbon substituent has been found to be influential on the bonding capacity of **260**.²⁶⁶ While treatment of the

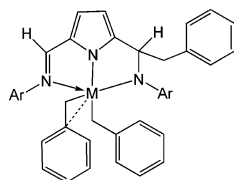


Figure 16. Dibenzyl complex **233** (M = Zr, Hf).

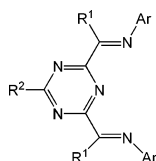
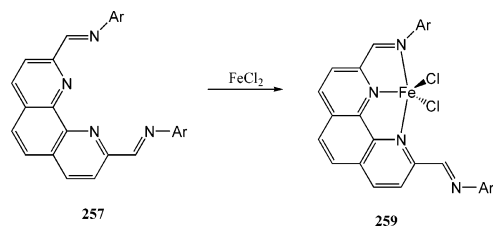


Figure 17. Bis(imino)triazine **238**.

Scheme 50

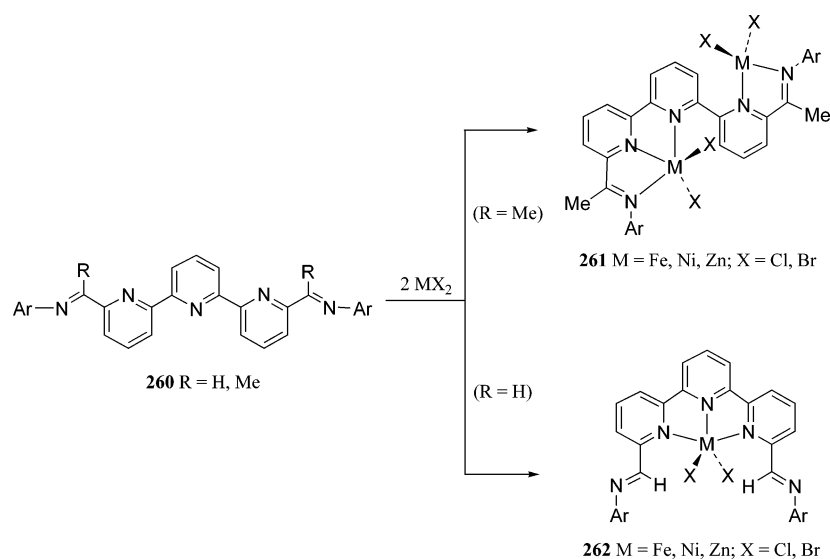


ketimine derivative with two equivalents of MX₂ (M = Fe, X = Cl; M = Ni, X = Br; M = Zn, X = Cl) affords smoothly the bimetallic complexes [6,6''-(2,6-*i*-Pr₂C₆H₃)N=CMe₂-2,2':6',2''-C₁₅H₉N₃]M₂X₄ (**261**) (Scheme 51), two equivalents of MX₂ (M = Fe, X = Cl; M = Ni, X = Br; M = Zn, X = Cl) with the aldimine version only gives the mononuclear five-coordinate complexes [6,6''-(2,6-*i*-Pr₂C₆H₃)N=CH₂-2,2':6',2''-C₁₅H₉N₃]MX₂ (**262**). Notably, on treatment with MAO the nickel derivative of **261** displays high activity for ethylene oligomerization.²⁶⁷

5. Conclusions and Outlook

Research activities based around the bis(imino)pyridine framework have resulted in a wealth of new chemistry over the past 8 years. Following the initial discovery of highly active iron and cobalt catalysts for olefin polymerization, both vanadium and chromium supported by the same ligand frame have also been identified as compatible metals for catalytic polymerization applications. These discoveries have, in turn, highlighted the susceptibility of the framework to attack by the cocatalyst. Alkylation has now been identified at all sites on the pyridine moiety (including the N atom) and also at the imino-carbon atom, while reduction and deprotonation of one or both methylamine substituents can additionally result.

Scheme 51



The ability of the ligand to support metals in different oxidation states has been observed and is thought to be crucial to its role in supporting the function of the polymerization catalyst. Indeed, there is evidence that the bis(imino)pyridine cobalt(II) precatalyst is reduced to a Co(I) species upon addition of MAO,^{101,102} while the corresponding iron(II) precatalyst under similar conditions has been reported to either maintain its oxidation state⁹⁷ or be oxidized to an Fe(III) species.⁹⁸ Moreover, it is possible that metal to ligand electron transfer (paired vs biradical) may be a feature in the catalytic species.^{154,155}

Directed modification of the ligand frame has led to a range of new tridentate ligand families. These efforts have been targeted at the central donor group, the side arms, and the imino substituents with the intent of making structure–activity correlations. However, it is worth noting that none of these systems have reproduced the activities or the lifetimes shown by the first-generation bis(arylimino)pyridine systems. Through an understanding of the chemistry of the ligand, sites for immobilization on a polymer support have been identified and implemented.

While use of bis(imino)pyridines as supporting ligands for an olefin polymerization catalyst has been the focus of this review, recent efforts have seen its potential exploited as an anchoring ligand for other catalytic processes (e.g., asymmetric Diels–Alder,¹⁵⁷ hydrosilylation,¹³⁵ Mukaiyama aldol,¹³⁵ cyclopropanation, hydrogenation,¹³⁸ and cross-coupling reactions⁹²) and for metal-based activation of small molecules.^{159–161} It seems likely that this ligand set will emerge as a highly compatible support for a range of catalytic processes in the future.

6. Glossary

acac	acetylacetonate
Ad	adamantyl
Ar	aryl
ATRP	atom transfer radical polymerization
<i>i</i> -Bu	isobutyl
<i>t</i> -Bu	<i>tert</i> -butyl
Bn	benzyl
dba	dibenzoylacetate
Cy	cyclohexyl
DFT	density functional theory
DEAC	diethylaluminum chloride

DME	1,2-dimethoxyethane
DRIFT	diffuse reflectance infrared Fourier transform
Et	ethyl
Et ₂ O	diethyl ether
EPR	electron paramagnetic resonance
ESI-MS	electrospray ionization tandem mass spectrometry
Fc	ferrocenyl
g/mmol·h·bar	grams per millimole (of precatalyst) per hour per bar
Ind	indenyl
IR	infrared
<i>i</i> -Pr	isopropyl
MAO	methylaluminoxane
Ln	lanthanide
Mesityl or Mes	2,4,6-trimethylphenyl
MMAO	modified methylaluminoxane, AlMeO:Al- <i>i</i> -BuO = 3:1
Me	methyl
MeCN	acetonitrile
NMR	nuclear magnetic resonance
Ph	phenyl
PS	polystyrene
py	pyridine
ROMP	ring-opening metathesis polymerization
TCNQ	tetracyanoquinodimethane
TEA	triethylaluminum
Tf	triflate anion, CF ₃ SO ₃ [−]
THF	tetrahydrofuran
TM	transition metal
TMEDA	tetramethylethylenediamine

7. Acknowledgment

We thank Dr. S. J. Lancaster (UEA, Norwich) for useful discussion.

8. Note Added in Proof

Since this review was prepared, a number of relevant publications have appeared in the literature. Neese, Wieghardt, and Chirik established via a combined structural, spectroscopic, and computational study that the iron precatalyst [2,6-{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂C₅H₃N]FeCl₂ (**16a**) has a high-spin ferrous center bound by a neutral bis(imino)pyridine ligand, while the single-electron reduction product [2,6-{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂C₅H₃N]FeCl (**37**) was also found to be

high-spin ferrous but with $S_{\text{Fe}} = 2$ antiferromagnetically coupled to a ligand-centered radical ($S_{\text{L}} = 1/2$).²⁶⁸ Further reduction to [2,6-{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂C₅H₃N]Fe(L_{*n*}) [L = N₂, *n* = 1 (**77**), 2 (**76**); CO, *n* = 2 (**79**); 4-(*N,N*-dimethylamino)pyridine, *n* = 1] resulted in a doubly reduced bis(imino)pyridine diradical, preserving the ferrous ion. A series of ligands of the form [2,6-(ArN=CR)₂C₅H₃N] [R = Et, *i*-Pr, CH₂CH₂Ph, or CH(CH₂Ph)₂; Ar = 2,4,6-Me₃C₆H₂, 2,6-*i*-Pr₂C₆H₃] have been prepared by Gibson et al. by deprotonation of the methyl substituent of the α -imino carbon in **1** (R = Me) using LDA followed by primary alkyl-halide.²⁶⁹ Further treatment with iron(II) chloride readily affords high-spin bis(imino)pyridine-iron(II) complexes. For the ligands with bulky backbone substituents, restricted rotation is evident on the NMR time scale. In terms of ethylene polymerization, increasing the size of the ligand backbone in the precatalyst increases the molecular weight of the resultant polyethylene without lowering the catalyst productivity. Wesolek et al. modified the parent ligand **1** by incorporating a *para*-chloro group on the central pyridine ligand.²⁷⁰ The same group also reported cyclohexylimino derivatives which in the case of iron were found to be completely inactive for oligomerization/polymerization of ethylene. Vanadium-, chromium-, and iron-based bis(imino)pyridine complexes have been immobilized on MgCl₂/AlR_{*n*}-(OEt)_{3-*n*} and screened for polymerization of ethylene.²⁷¹ In the case of iron, a broad molecular weight distribution was observed with somewhat higher polyethylene molecular weights than were found in the homogeneous systems. For vanadium, a narrow molecular weight distribution was observed, while data for chromium suggested incomplete catalyst immobilization; both V and Cr gave polyethylene with molecular weights far greater than those for homogeneous polymerizations. Two papers have appeared from Noels group describing the synthesis, characterization, and catalytic behavior (homo- and heterogeneous) of a series of iron precatalysts containing 2,6-bis(arylimino)pyrazine ligands (aryl = 1-naphthyl, 2,6-Me₂C₆H₃, 2,6-*i*-Pr₂C₆H₃).^{272,273} Catalyst activities were found to be lower than those of the pyridine-based ligand family. Chen et al. reported iron, cobalt, chromium, copper, and zinc complexes bearing bis(imino)pyridines with either two 2,6-diisopropylphenyl or 2,5-*tert*-butylphenyl *N*-aryl groups.²⁷⁴ The Fe, Co, and Cr complexes, upon activation with MAO, can polymerize both ethylene (highly active for Fe and Co, while Cr is moderate) and norbornene (good activities); Cu and Zn complexes were inactive. Alt et al. prepared coordination compounds of iron(II) chloride with bis(arylimino)pyridine ligands bearing ω -alkenyl substituents on the central pyridine starting from chelidamic acid (six steps prior to complexation).²⁷⁵ When activated with MAO, they can be used as self-immobilizing catalysts for ethylene polymerization, albeit with low activities. Cowley observed C-H activation of the imino methyl group upon treatment of the parent ligand **1** (Ar = 2,6-*i*-Pr₂C₆H₃) with TeCl₄; the ¹²⁵Te{¹H} NMR chemical shift (δ 1317.3) was consistent with a Cl₃TeN₂ moiety.²⁷⁶ Knijnenburg, Gambarotta, and Budzelaar recently reviewed their work in this area, with particular emphasis on electron transfer, alkylation, dimerization, and deprotonation of the bis(imino)pyridine ligand.²⁷⁷ The potential of this ligand set in organic synthesis has been shown by Chirik et al., who utilized the iron catalyst [2,6-{(2,6-*i*-Pr₂C₆H₃)N=CMe}₂-C₅H₃N]Fe(N₂)₂ (**76**) for the synthesis of cycloaddition of α,ω -dienes; the oxidation state of the iron is maintained as

ferrous throughout the process by the redox activity of the bis(imino)pyridine ligand.²⁷⁸

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