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Progression of Diiminopyridines: From Single Application to Catalytic Versatility

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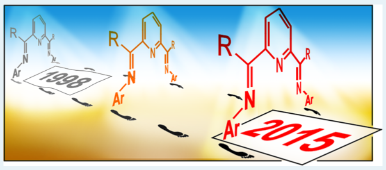
ABSTRACT: Diiminopyridyl metal complexes, first characterized several decades ago, found practical application in 1998 when they were used as precatalysts in coordinative ethylene polymerization. This discovery contributed to the so-called *postmetallocene revolution* and triggered the large-scale experimental and theoretical research aimed at understanding diversified diiminopyridine chemistry. The results of this quest, some of which were intriguing and difficult to anticipate, are discussed and summarized in the current Review.



KEYWORDS: *diiminopyridine, transition metal complex, catalysis, olefin polymerization, aluminum alkyl, redox reaction, cooperative effects*

1. INTRODUCTION

Development of diiminopyridines, along with the α-diimines, salans, and phenoxyimines, was instrumental in initiating the postmetallocene revolution in the polymer science and polyolefin industry at the turn of the century. The empirical finding[1−5] that ethylene polymerization can be catalyzed by the complexes belonging to the class of compounds synthesized several decades ago[6,7] revived widespread interest in diiminopyridines and prompted detailed investigations into their properties. Meticulous research triggered by this discovery and carried out in the following years revealed surprising facts about the reactivity of diiminopyridines and their potential application in various fields. These organic compounds have been the topic of active research in numerous groups, and almost 20 years after their popularization within the chemical community, we are still taken aback by the unexpected findings.

The current review focuses on the synthesis, structure, and reactivity of the diiminopyridines and their complexes with transition metals, lanthanides, and main group elements. Although emphasis is placed on the coordinative olefin polymerization catalyzed by the late-transition metal complexes with the diiminopyridines, rich reactivity patterns of the ligands and their complexes revealed by different methodology are also discussed. The subject has already been surveyed several times, but the previous comprehensive reviews were either published relatively long time ago and therefore did not cover recent findings[8,9] or were devoted exclusively to the olefin polymerization process.[10−13]

2. DIIMINOPYRIDINES AND THEIR COMPLEXES

2.1. Structural Features. Diiminopyridine, also called bis(imino)pyridine, contains a system of conjugated double bonds, which is thought to be responsible for many properties of the molecule. X-ray diffraction studies on the single crystals of the organic compound indicate that in the solid state, both imine groups are coplanar with the pyridine ring: they exhibit the *E* substitution at the imine double bonds, and unlike in the complexes with the transition metals, the two imine N atoms adopt the trans−trans relationship[14−18] (see Figure 1a).

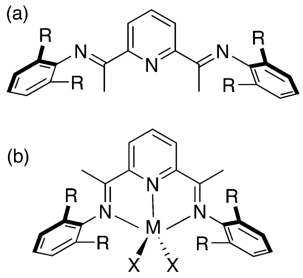


Figure 1. Diiminopyridine conformations: (a) isolated molecule and (b) the ligand in a metal complex. M denotes a metal, R is an alkyl substituent, and X represents a halide.

However, NMR spectra in solution indicate the existence of several forms, probably due to the *E*,*Z* isomerization process taking place either via the C═N bond rotation or nitrogen inversion.[19,20] Sterically demanding substituents, such as *tert*-butyl or phenyl placed at the imino carbon atoms enforce certain amount of rotation along the bond linking pyridine moiety with the imine group, thus suppressing such a coplanar arrangement.[21,22] In the transition metal complexes, however, the amount of this rotation reaches 180° with respect to the isolated diiminopyridine (see Figure 1b).

The highest possible symmetry for the diiminopyridine occurring in the complex is C_{2v}; this applies, for example, to the

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case in which both imine nitrogen atoms are substituted with the phenyl rings bearing identical substituents at the 2,6 positions (see Figure 2a). Variations in the substitution pattern within these rings may further reduce the symmetry to C_2, C_s, or even C_1 (see Figure 2). The C_1-symmetric molecules usually feature two phenyl rings with different substituents, as shown in Figure 2d; one of the phenyl rings attached to the imine nitrogen atom can also be replaced either by an aliphatic chain[16,23] or an aliphatic ring,[24] as shown in Figure 2e.

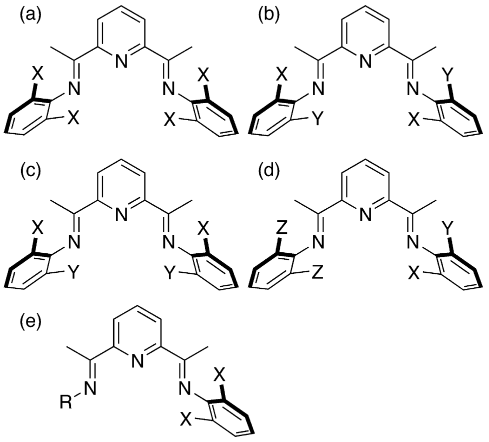

Figure 2. Diiminopyridine ligands occurring in the complexes show different symmetry according to the substitution pattern: (a) C_{2v}; (b) C_2; (c) C_s; (d, e) C_1. X, Y, and Z denote different substituents.

One of the inherent properties of the diiminopyridyl metal complexes that makes the C_2 and C_s diastereomers distinguishable is the limited rotation around the C−N bond between the imino group and the aromatic substituent with the bulky groups at the ortho positions. Cámpora and co-workers showed that the equilibration between the two isomers, proceeding with the dissociation of the Fe−N bond, takes place slowly in solution.[25] The isolated enantiomers display marked differences in activity when treated with a cocatalyst, and there is sufficient experimental evidence to support the enantiomorphic site control in propene polymerization, on top of the chain-end control demonstrated indirectly much earlier,[26] as in the case of metallocenes.[27] Atropisomerism in the diiminopyridyl iron(II) complexes was reported relatively early and recognized as the phenomenon responsible for the selectivity of the catalysts based on these complexes;[3] later, it was also observed for free diiminopyridine.[25]

The diiminopyridine molecule may exist as two tautomeric forms: imine and enamine. The presence of both forms in certain diiminopyridine species can be detected by NMR spectroscopy.[18,28] The diiminopyridine also acts as an ambidentate ligand; the usual *N-N′-N″* (or *N*−*N′*)[19] mode of binding is encountered exclusively in the transition metal complexes; however, the molecule binds tellurium in either a regular fashion[29] or the alternative *N-N′-C* mode.[30,31] There is substantiated speculation that tautomerism contributes to the reactivity of the diiminopyridine molecules with certain chalcogen and pnictogen compounds because it is believed that either the C−H bond of the diiminopyridine undergoes activation[30] or the enamine intermediate is involved;[31,32] however, the existence of such an intermediate has not yet been proven.

2.2. Distinct Synthetic Methods. The diiminopyridines are usually obtained by Schiff-base condensation of substituted anilines with 2,6-diacetylpyridine (for ketimine derivatives) or 2,6-diformylpyridine (for aldimines). The original method applied by Alyea and Merrel more than 40 years ago[7] and applied independently by Brookhart[1] and by Gibson[2] uses 2 equiv of the amine and results in the symmetrically substituted diiminopyridine molecules, which is shown in Figure 3a. This synthetic procedure was adopted by many authors to prepare a range of diiminopyridine compounds, and it is now widely used because of its simplicity. However, sequential condensation of diacetylpyridine, first with 1 equiv of aniline to yield the monoiminopyridine, followed by another condensation employing a different amine, leads to the unsymmetrical products, as depicted in Figure 3b.[33,34] It must be stressed that the formation of the Schiff base is reversible, which imposes certain constraints on the synthesis.[35]

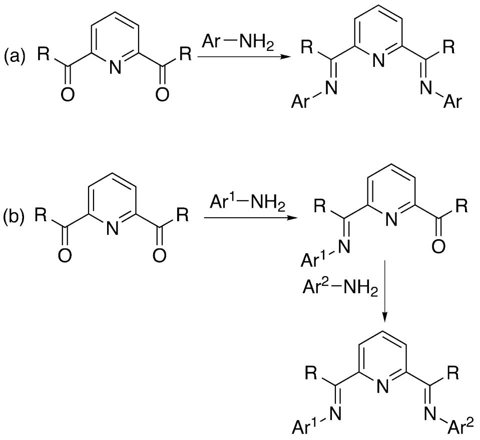

Figure 3. Typical synthetic procedure leading to the diiminopyridines bearing (a) identical and (b) different substituents at the imine nitrogen atom.

2,6-Dimethylpyridine was also used as a starting material to synthesize dibenzoylpyridine, which was subsequently condensed with the aniline derivative to yield the diiminopyridine incorporating the phenyl rings attached to the imine carbon atoms (see Figure 4a).[21] Alternatively, dibenzoylpyridine was also obtained in a Friedel−Crafts acylation of benzene with 2,6-dicarbonylpyridine dichloride.[36]

The condensation reactions described above fail for the diiminopyridines incorporating the *tert*-butyl groups at the imine carbon atom; instead, the respective products can be accessed via the multistep synthetic procedure illustrated in Figure 4b, utilizing pivaloyl chloride, 2,6-dimethylaniline, and 2,6-dibromopyridine as the starting materials.[22]

The trihydroquinoline derivatives may also be used to obtain the diiminopyridines containing cycloalkyl rings fused with the pyridine moiety, which is shown in Figure 5.[37] By analogy, the products with five- and seven-membered cycloalkyl rings fused with the pyridine moiety were synthesized in a similar way.[18,38]

There are also other synthetic paths leading to certain special diiminopyridines. Diiminopyridines with the alkoxy or thioalkyl substituents at the imine carbon can be obtained from the corresponding imidoyl chlorides and sodium alkoxides or sodium thioalkoxides.[39] Ligands containing alkyl substituents attached to the pyridine ring can be synthesized from metal alkyls and unsubstituted diiminopyridines (see section 2.4).

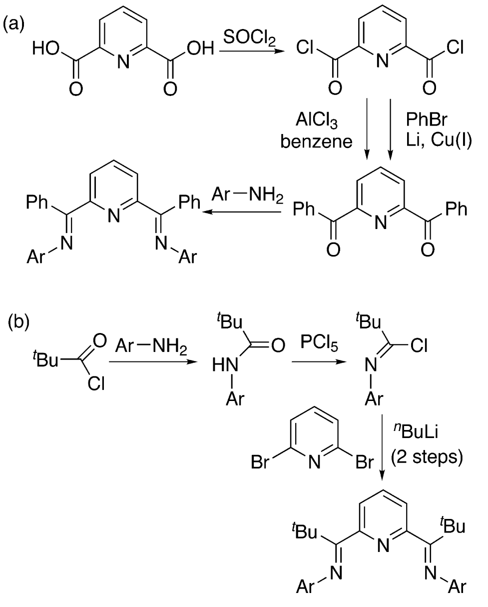

Figure 4. Synthesis of the diiminopyridines with the (a) *tert*-butyl and (b) phenyl substituents attached to the imine carbon atom.

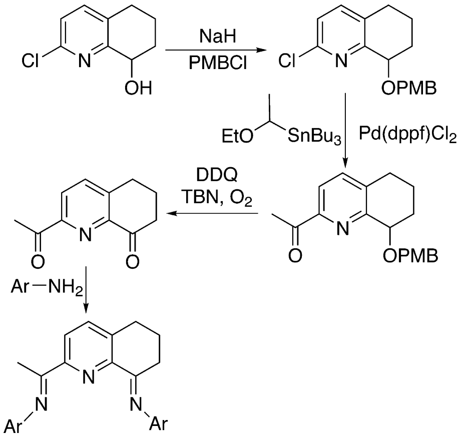

Figure 5. Synthesis of the diiminopyridines with the cycloalkyl ring fused with the pyridine moiety.

Finally, the substituents attached to the imine carbon atom can be modified by deprotonation of the ketimine methyl group (vide infra), followed by its alkylation.[40]

It must be mentioned that the attempts to modify the diiminopyridine backbone deteriorate the activity of the resulting catalyst;[41] therefore, modifications of the original diiminopyridine system focus merely at the derivatization of the pyridine ring and the substituents attached to the imine group, or changing of the transition metal atom. Examples of such an approach include, but are not limited to, those described in refs 4, 14, 18, 28, 33, 34, 36, 39, 42, and 43.

2.3. Diiminopyridine Complexes across the Periodic Table.

Initially, the studies of diiminopyridyl complexes were driven by their interesting structural, electronic, and magnetic properties; thus, the early works on the subject can be placed in the domain of basic research. Representative examples of such complexes were obtained and characterized several decades before the discovery by Brookhart and by Gibson. These are almost exclusively *d*-block metal complexes, in which the metal coordination number is 5; for example, zinc, cobalt, and nickel species.[7,44] Apart from this, iron, cobalt, and copper complexes bearing two molecules of the ligand with a metal coordination number of 6 are also known.[45] Interestingly, no gold diiminopyridine complex had been reported by 2011,[46] and to the best of our knowledge, there is still no progress in this area.

In the *d*-block complexes, the diiminopyridine molecule usually binds all three nitrogen atoms to the central metal atom; however, there are certain exceptions in which the ligand is bidentate.[19,47,48] In many such cases, NMR experiments indicate fluxionality and metallotropic shift in solution.[19,47]

As opposed to the transition metals, the diiminopyridine main-group metal complexes have been discovered relatively recently. There exist gallium, germanium, tin, and lead complexes (see Table 1), but the most intriguing nonmetal dicationic complexes with chalcogens[29] and cationic species containing pnictogens[32] were synthesized and isolated only in recent years by Ragogna and co-workers. This fact lends even more mystery to the diiminopyridine ligand that has been omnipresent in organometallic chemistry for more than a half century and confirms its versatility in the formation of unusual compounds.

2.4. Reduction and Electronic Flexibility.

Classical redox reactions defined in terms of inorganic transition metal chemistry typically involve changes in the formal oxidation states of the metal atom. The same definition translated into the field of organometallic chemistry has much wider connotation. Although it holds true for the metal complexes with ancillary ligands, certain other ligands may exhibit a propensity to accept or donate electrons, that is, participate in the redox reactions. The term *noninnocent ligand* coined to describe such properties is now widely recognized. Although it was proven that almost any ligand can be considered as being noninnocent in certain special settings,[82] there exist only a limited number of ligands whose innocent behavior is widely and universally perceived as such.

In this respect, diiminopyridine ligands are truly noninnocent, serving as an electron reservoir being able to either source or sink the electrons.[81] This reversible phenomenon results from the presence of two highly delocalized and low-lying π^* orbitals that can accept up to three electrons from the metal d orbitals.[49,83] Thus, the diiminopyridine ligand in the complexes of metals occurring at otherwise inaccessible low oxidation states, such as 1+ for cobalt,[84] iron, and manganese; 2+ for neodymium and aluminum, should in certain situations be treated as the radical anion coordinating to the metal at its usual, higher oxidation state.[83,85,86] The electronic configuration in such complexes is determined by the properties of ancillary ligands (other than diiminopyridines) that govern the spin configuration of the metal ion. Thus, by careful selection of these ligands, the potential redox process can be diverted either to the diiminopyridine or to the metal center.[87,88]

Although the aluminum complex containing the diiminopyridine radical anion is the product of the action of the alkylaluminum on the diiminopyridyl iron complex,[89] in the stepwise reaction of the free diiminopyridine with trimethylaluminum, both imine carbon atoms can be reduced.[90] The first step of this reaction is a process consisting of the intramolecular methyl group transfer described earlier for the monoiminopyridine molecule.[91] However, the intermediate aminoiminopyridine obtained in the hydrolysis reaction and treated with another AlMe$_3$ equivalent does not form the expected cyclic aluminum complex; instead, the remaining imine group is reduced. The origin of such behavior is not known, but the

Table 1. Elements Whose Atoms Can Be Bound by Diiminopyridines[c]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H[a]																	
2	Li 49																	
3		Mg 50											Al 51		P 32	S 29, 31		
4		Ca 50		Ti 48	V 52	Cr 36, 53	Mn 54, 55	Fe[b] 1, 2, 34	Co[b] 1, 56	Ni 57	Cu 58, 59	Zn 7, 54, 60	Ga 61	Ge 62, 63	As 64	Se 29, 31		
5		Sr 50		Zr 48	Nb 65	Mo 66		Ru 23, 67, 68	Rh 69	Pd 70, 71	Ag 46	Cd 60, 72	In 73	Sn 62, 74		Te 29–31		
6		Ba 50	La 75	Hf 48	Ta 65	W 76	Re 47	Os 77	Ir 69	Pt 19, 47		Hg 78		Pb 79				
7																		
						Nd 75											Lu 80	
						U 81												

[a] Diiminopyridine can be protonated. [b] The number of reported diiminopyridyl Fe and Co complexes exceeds that for any other element. [c] Numbers placed under the symbol of the element indicate selected literature references. Complexes incorporating the deprotonated form of the ligand are included, but those with additional donor side arms are not shown.

noninnocence of the ligand cannot be ruled out.[90] On the contrary, the formation of the cyclic complexes is clearly preferred over the imine group reduction in the phenoxyimines.[92,93]

Diiminopyridines show even more diverse and puzzling reactivity. Because the cocatalysts applied in the coordinative polymerization process are customarily strong alkylating and reducing agents, the alkylation of the diiminopyridine ligand is invariably impossible to avoid, even though it might be considered as being an unwanted side reaction. There are two possible targets for the reducing agent: the imine group and the pyridine ring (see Figure 6).

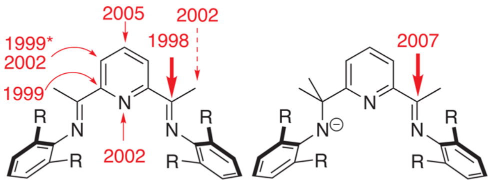

Figure 6. Timeline of diiminopyridine reactivity extends for almost a decade. Regular arrows show the attacks on all possible positions in the pyridine ring. Thick ones indicate the attack on the imine group, and the dashed one points at the deprotonation site. The year of the first report is given. Marked with the asterisk is the year of the report on the double-alkylated derivative, in both the ortho and the meta positions. Monoalkylated derivative was obtained three years later.

It is expected that the pyridine ring itself should be susceptible to reduction, albeit with the loss of aromaticity. This thermodynamically unfavorable process may in some cases be relieved by the stabilizing interaction of the resulting conjugated systems with the central atom.[94] Gambarotta and co-workers demonstrated in 1999 that the action of the methyl alumoxane (MAO) on the diiminopyridyl vanadium complex results in the methylation of the pyridine ring in the ortho position;[94] later, it was determined that the titanium complex behaves in a similar manner.[48] Another work from the Gambarotta group announced the formation of the unusual tricyclic compound with the pyridine moiety substituted in the meta position, resulting from the action of a Grignard reagent on the diiminopyridyl chromium complex. The authors maintain that the reaction proceeds through the intermediate, in which the pyridine ring is initially substituted at the para position.[95] However, they did not isolate such an intermediate, and the first glaring evidence for the attack at the pyridine para position in the diiminopyridyl iron complex appeared in 2005.[89] In addition to that, unexpected alkylation of the pyridine nitrogen atom in the diiminopyridine molecule was discovered simultaneously by Gibson and Gambarotta in 2002.[96,97]

Despite the fact that, depending on the reactants used, alkylation may take place at any position within the pyridine ring, the most obvious site prone to the alkylating agent attack seems to be the imino functionality. Indeed, monoiminopyridines show this kind of reactivity,[91] leading to the pyridinoamine derivatives, which was reported as early as in 1998, the year when the application of diiminopyridyl complexes in coordinative olefin polymerization was described. Several months later, the analogous transformation of the diiminopyridine molecule was carried out to produce the pyridyliminoamide aluminum complex, which after hydrolysis yielded the corresponding aminoiminopyridine.[98]

Intuitively, the monoanionic ligand resulting from the alkylation of diiminopyridine described above should resist further nucleophilic attacks, but such a hypothesis is not true because successful alkylation of the remaining imine groups assisted by the lanthanide species and leading to aluminum and lanthanide diamidopyridyl complexes was reported.[99] The corresponding diaminopyridine can be retrieved from such complexes by hydrolysis.

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Following these initial reports, recent years have witnessed further refinement of the synthetic methods, taking advantage of the unusual properties of the diiminopyridine compounds, and offering easy routes to the products that are otherwise inaccessible or difficult to obtain. For example, clean and selective synthesis of the para-substituted diiminopyridine molecules was achieved in the Cámpora group by employing the manganese alkyls acting on the free unsubstituted organic compound and causing the alkyl migration.[100,101] Substituents introduced in this way can serve as potential linkers for immobilization and usually have little or no impact on the properties of the catalytic systems derived from them.[102] Similar alkyl migration was also observed for the diiminopyridine zinc alkyls; however, a diiminodihydropyridine derivative was the outcome of this reaction.[103] Furthermore, as already mentioned, it was also demonstrated that the stepwise process consisting of monoalkylation of the free diiminopyridine, followed by the hydrolysis of the resulting aluminum complex, another alkylation of the remaining imino group by the alkylaluminum, and final hydrolysis, yields the diaminopyridine, but such a product cannot be obtained by treating the diiminopyridine compound incorporating bulky substituents at the nitrogen atom with sodium borohydride.[90]

Deprotonation of one methyl group attached to the imine carbon in the ketimine diiminopyridine may take place under the action of methyllithium.[97] This process can be followed by dimerization.[95] By careful selection of the lithium compound, deprotonation of both the methyl group attached to the imine group carbon can also be attained.[76] Single or double deprotonation of the diiminopyridine ligand is not uncommon in complexes of metals, such as chromium[104] and manganese.[95]

In some cases, the action of an organoaluminum compound on the diiminopyridyl metal complex may lead to the extrusion of the metal atom from the original complex. For example, iron diiminopyridyl complex exposed to trimethylaluminum[89] or triethylaluminum[105] loses the central atom; however, no evidence of vanadium abstraction was found for the diiminopyridyl vanadium complex treated with methylalumoxane.[94]

From the examples given in this section, it can be inferred that the rich reactivity patterns of diiminopyridines, although reasonably well explored, still lack systematic rationalization. Cooperative effects of the transition metal and ligand may play a limited role in determining the reaction products; however, unexpected reactivity pathways are also demonstrated by the free diiminopyridines and the complexes containing merely main group elements unable to participate in the potential redox reactions.[51,96,97,106] For this reason, diiminopyridyl complexes with closed-shell zinc(II) may serve as reference models for theoretical studies.[107]

It has been clearly demonstrated that the kind of reducing (or alkylating) agent dictates the nature of the final product, but the underlying mechanism that governs such selection still remains unclear.[51]

3. APPLICATIONS

3.1. Olefin Polymerization and Oligomerization. The seminal works by Brookhart and by Gibson accentuated the role of bulky substituents attached to the arylimine moiety in the catalyst, which retard the termination reactions and thus ensure a high molecular weight of the resultant polymers. The first catalytic systems based on diiminopyridyl complexes of late transition metals exhibited a clear increase in activity when the temperature was raised from 0 to 25 °C;[1] however, such a temperature range is impractical from an industrial point of view. Later, it was reported that the activity of the catalysts based on diiminopyridyl complexes of the late transition metals dropped by a factor of 2−6 when the temperature was increased from 35 to 70 °C; simultaneously the molecular weight of the product also clearly diminished.[4] The catalyst deactivation at elevated temperatures may be attributed to the rotation of the aryl substituents attached to the imine groups along the C−N bond, as was found in the α-diimine-based systems.[108] This rotation gives rise to the plethora of various side reactions, such as C−H activation involving the ligand and the formation of metal hydrides.[109] Further factors that may contribute to the degradation of the catalytic performance at an elevated temperature are the higher rates of termination reactions and also decreased solubility of ethylene in the polymerization medium. Thermally robust catalysts are usually prepared by careful selection of the substituents that restrict these rotations; the active site may also be protected against possible termination reactions by its encapsulation into the macrocycle at the stage of the precatalyst preparation;[110] improvement in thermal stability as a result of catalyst immobilization was also reported.[111,112]

It is important that the catalyst with prospective industrial application be thermally stable. The exergonic olefin polymerization process produces a significant amount of heat inside the reactor, where the heat transfer is limited as a result of low heat conductivity of the polymerization medium. Apart from that, the potential ability of conducting the exergonic reaction at elevated temperatures ensures better control over the process, contributes to energy saving,[113] and eliminates the need for an expensive cooling system. Unfortunately, the original diiminopyridyl complexes developed by Brookhart and by Gibson, featuring the symmetrically substituted diiminopyridine ligands with substituents of moderate bulkiness at the imine nitrogen atoms, turned out to be thermally unstable.

To overcome these limitations, which render the majority of the diiminopyridine-based catalysts unsuitable in the industrial praxis, unsymmetrical diiminopyridine ligands with substituents of marked bulkiness attached to one of the imine nitrogen atoms were designed. Iron, cobalt, and nickel complexes with diiminopyridine ligands incorporating benzhydryl substituents are especially worth mentioning (see Figure 7). First reported in 2011,[34,114] they form the catalysts that are inactive at room temperature but perform extremely well in the temperature range of 60−80 °C, exhibiting significant activity and producing linear polyethylene of high molecular weight and no oligomeric byproducts[115] or polyethylenes of relatively low molecular weight, suitable for application as lubricants.[116−119] In some cases, control of molecular weight within a wide range of

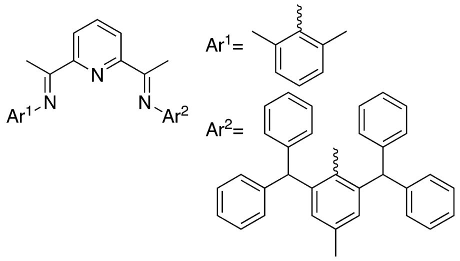

Figure 7. Example of a diiminopyridine compound reported in ref 34.

several thousand to several hundred thousand was possible by adjusting the polymerization temperature.[120] It was also found that introducing the halogen substituent, either within the benzhydryl substituent[118] or at the phenyl ring directly attached to the imine nitrogen,[120] usually leads to more active catalysts. The activity is rather insensitive on the position of the bulky substituents at the phenyl ring (2,6-dibenzhydryl in ref 34 vs 2,4-dibenzhydryl in ref 120), and the number of such substituents (2 in refs 34 and 120 vs 1 in ref 56); in most cases it exceeds 10^6 g mol^{-1} (Fe) h^{-1}.

In further quest for industrially acceptable catalytic systems, binuclear diiminopyridine catalysts have recently been developed by our group[121,122] (see Figure 8). The new precatalysts incorporate two diiminopyridine moieties linked with a biphenyl bridge. Both iron and cobalt systems are very active and relatively stable, with productivities exceeding 10^7 g mol^{-1} (Fe) h^{-1} and 10^6 g mol^{-1} (Co) h^{-1}, respectively. Linear polyethylene of a wide molecular weight distribution is produced with the iron catalysts.

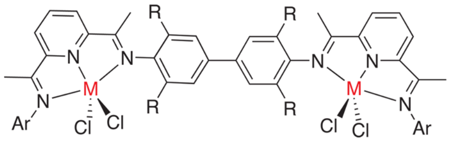

Figure 8. Binuclear precatalysts; M = Fe or Co.

Regarding the industrial application of iron diiminopyridine catalysts, there were also successful attempts aiming at the heterogenization of the diiminopyridine-based catalyst, on the classical $MgCl_2$ support[112] or calcosilicates[111] or even on the surface of carbon nanotubes by means of the pyrene moiety incorporated into the ligand.[123] In most of the cases, the catalytic activity was enhanced compared with the homogeneous system.

The catalytic activity and the kind of products (polymers vs oligomers) depends not only on the nature of the ligands, but also on the kind of the transition metal atom. Iron catalysts are usually significantly more active than their cobalt counterparts,[9,11,13,124] but the resulting products exhibit a wider molecular weight distribution because of the multiple kinds of catalytic active sites,[124] whereas nickel-based precatalysts are even less active and produce mainly oligomers.[125] It is also worth mentioning that early transition metals can form complexes with diiminopyridine ligands; therefore, titanium- and vanadium-based diiminopyridine catalysts were also tested in polymerization. It was demonstrated that the bulky substituents at the imine nitrogen atoms may prevent the usual *N*−*N*′−*N*′′ coordination mode of certain diiminopyridines with titanium and favor bidentate complexes[48] as a result of two factors: low metal−nitrogen bond energy for the early transition metals and the neutral charge of the ligand itself.[99] This phenomenon has a negative impact on the catalytic activity. Furthermore, vanadium(III)-based diiminopyridine catalysts turned out to be very productive, but their active sites were susceptible to transformations, especially at an elevated temperature; chromium(III) precatalysts were also promising because they displayed single-site character and favorable thermal stability.[124] In contrast, the catalysts obtained by using diiminopyridyl manganese complexes were inactive.[39,55] Therefore, overall it is assumed that the activities attained by the precatalysts based on early transition metal complexes do not match those of their iron counterparts; however, variations within the ligand may result in the active systems for many metals.[39]

The molecular weight of the product can be finely tuned by careful selection of the substituents at the imine nitrogen atom within the ligand (see Figure 9). Reduction of steric hindrance at the phenyl rings attached to the imine nitrogen groups favors termination reactions; thus, diiminopyridyl iron(II) complexes bearing such rings substituted with only one alkyl groups at the ortho position turned out to be useful in ethylene oligomerization,[1,2,8] similar to the iron diiminopyridyl complexes with the ligands incorporating fluoro-substituted phenyl rings, developed several years later.[126] Not surprisingly, projection of this idea onto alkyne conversion chemistry resulted in observation of acetylene cyclotrimerization to benzene by using the less sterically crowded precatalyst shown in Figure 9a and acetylene polymerization when a regular precatalyst depicted in Figure 9c was applied.[127] Nevertheless, on the basis of the number of papers published, it can be stated that diiminopyridyl metal complex precatalysts seem to be promising in ethylene polymerization, but still challenging in oligomerization.

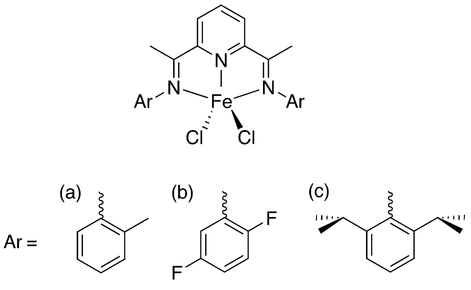

Figure 9. Substituents at the phenyl ring in the precatalyst determine the catalyzed process: (a) ethylene oligomerization and acetylene cyclotrimerization, (b) ethylene oligomerization, and (c) ethylene and acetylene polymerization.

Correspondingly, there is little success in the application of diiminopyridine precatalysts in higher α-olefin activation. Polymerization[3,26] and oligomerization of propylene[128] was successfully carried out, but the activities were moderate; in some cases, the experiment was aiming at understanding the mechanistic features of the process.[129] Vinyl polymerization of norbornene was also conducted on nickel diiminopyridine catalysts.[57,130]

3.1.1. Mechanism of Olefin Polymerization Catalyzed by the Late-Transition Metal Diiminopyridine Complexes. The initial discovery by Brookhart and by Gibson initiated extensive search for modified catalysts of olefin polymerization with improved properties. Screening of prospective new catalytic systems is often based on the empirical basis, since our knowledge regarding the mechanism of polymerization still seems to be incomplete. It is generally believed that in the olefin polymerization catalyzed by the diiminopyridyl late-transition metal complexes, the insertion event proceeds according to the widely accepted Cossee−Arlman mechanism, but the nature of the active sites is still under debate. Although it was shown that the cationic alkyl species derived from the diiminopyridyl iron complexes polymerize ethylene,[131,132] the reality turned out to be much more complicated.

Ample experimental findings related to the ligand reduction and alkylation add complexity to the description of the active sites. The outcome of these processes depends not only on the nature of the alkylating agent but also on the kind of transition metal (vide supra). Current understanding of the active site structure in diiminopyridine-based catalysts is constantly revised as more and more knowledge on this subject is gained. For example, it was initially thought that the activation process performed with MAO acting on the iron diiminopyridyl complex leads to the catalytic ion pair, whereas the application of aluminum alkyls as cocatalysts generates the neutral active sites.[133] Accumulation of experimental and theoretical data demonstrating the noninnocence of the diiminopyridine ligand from different research groups together with the series of sophisticated NMR experiments carried out later by Bryliakov and Talsi[134] changed our perception of aluminum−alkyl-generated active sites. Nowadays, it is believed that the diiminopyridine ligand reduced in the one-electron process by the cocatalyst plays the role of the counteranion interacting with the cationic Fe(II) catalytic center; thus, it must be stressed that ion pairs are formed independently of the cocatalyst applied (see Figure 10).

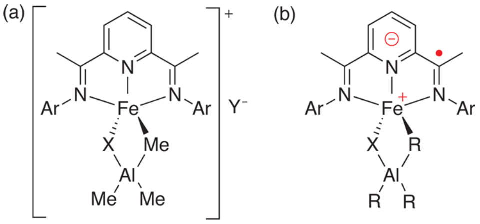

Figure 10. Structure of heterobimetallic active sites formed under the action of (a) MAO; (b) and aluminum alkyls, such as $AlMe_3$ or Al(*i*-Bu)$_3$, on an iron diiminopyridyl complex. X = alkyl group or Cl; Y^- = $[MeMAO]^-$.

It is sensible to expect that the precatalyst undergoes reduction during the activation process. As was discussed above, in the most widely used precatalysts containing iron(II), the oxidation state of the metal is preserved throughout the activation, and the reduction process involves the ligand rather than the metal.[86,105,134] Surprisingly, the presence of iron(III)-based active sites in the catalytic systems derived from iron(II) precatalysts was once suspected on the basis of EPR and Mössbauer measurements,[135] and the density functional theory (DFT) studies performed independently in the Adamo and de Bruin as well as Toro-Labbé groups suggest higher productivity of iron(III)-based active species compared with those incorporating iron(II),[136,137] yet the process of iron(II) oxidation is considered unlikely to occur in the strongly reductive conditions found in the polymerization medium containing aluminum alkyls.[11] Interestingly, the performance of iron(III)-based precatalysts was also investigated in the polymerization process,[43,138] and there is strong evidence that the metal atom undergoes reduction in the polymerization medium.[139] Reduction processes were also observed for the cobalt(II)-based precatalysts activated with both MAO and aluminum alkyls.[140] It was found that the presence of the monomer assists the reduction process when MAO is applied as a cocatalyst (see Figure 11). In contrast, it has also been demonstrated that vanadium(III) in its diiminopyridyl complexes is resistant against the reduction with cocatalysts.[141]

Diiminopyridyl iron(II) dialkyl complexes that form the active catalyst under the action of the cocatalyst[142] were transformed in many ways to understand the mechanistic details of olefin polymerization. After reduction with AlR_3, alkyl exchange takes place; excess organoaluminum compounds leads to the iron displacement,[105] and the formation of the respective aluminum complex containing diiminopyridine radical anion.[89] It must be stressed that many intermediates, precursors of active sites, and active sites themselves are unstable and undergo spontaneous transformations, which are reflected by changes in the NMR and EPR spectra.[105,133,134,140] Alternatively, protonolysis of the Fe−C bond was also carried out to understand the spectral properties of the diiminopyridyl complexes.[143]

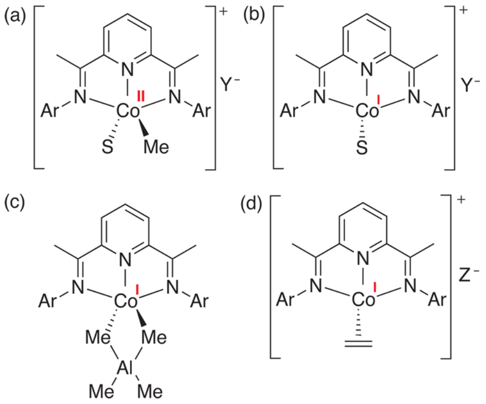

Figure 11. Structure of cobalt-derived active sites: (a) Co(II) ion pair generated with MAO; (b) Co(I) ion pair generated with MAO in the presence of ethylene; (c) Co(I) heterobinuclear species generated with $AlMe_3$; and (d) Co (I) ion pair generated with $AlMe_3$ in the presence of ethylene. S = solvent, Y^- = $[MeMAO]^-$, Z^- = $AlMe_3Cl^-$.

The spin state for many precatalysts can be determined experimentally on the basis of magnetic susceptibility measurements, Mössbauer spectroscopy, and EPR spectroscopy. The bond lengths obtained from the X-ray diffraction experiment also provide certain information pertaining to the ligand's engagement in redox reactions. It was established a long time ago that the diiminopyridyl iron complexes are paramagnetic with the high-spin quintet ground state.[1] DFT together with computationally demanding multiconfigurational calculations, such as complete active space multiconfiguration self consistent field, were employed to determine the spin state of the reduced species derived from this precatalyst,[107] and the analysis of spin densities on the particular components of the complex indicates the presence of commonly observed antiferromagnetic coupling between the high-spin iron(II) and the radical-anion form of the ligand, noticed earlier for many other metals in the Budzelaar group.[85,95,144] DFT calculations were also helpful in tracing the origin of structural differences between the ketimine- and aldimine-based ligands as well as the distribution of the spin density within the transition metal complex molecules containing such ligands.[145]

Although theoretical methods are of inestimable worth in assessing certain unusual properties of diiminopyridyl complexes, there is no agreement as to the spin state of the reactants, intermediates, and the products of the polymerization process,[146−150] and the results depend on the density functional chosen. It has been proven that the hybrid functionals tend to favor high-spin states;[149,151] occasionally, because of small energetic separation between several spin states, there might be more than one candidate for the ground state. What is even more important is that individual processes (initiation, propagation, termination) may take place on the potential energy surfaces belonging to different spin states.[146−148]

Extensive computational investigation performed by Ziegler and co-workers served to rationalize the profound role of bulky substituents in the diiminopyridine catalytic systems; it was clearly demonstrated that the steric bulk destabilizes the ethylene complex with the active site, thus reducing the insertion barrier; simultaneously the formation of the termination precursor is also suppressed.[146,147] Both phenomena make the catalyst more efficient in the polymerization process. For the iron-based catalyst, it was observed that the resting state in the polymerization process is the iron−alkyl complex rather than its olefin π-complex. This theoretical result was echoed by the more recent experimental report confirming the formation of the intramolecular π-complex for the diiminopyridyl ruthenium(II) complex with the pendant alkenyl group,[23] whereas the analogous iron(II) and cobalt(II) complexes were not found.[16]

Our group demonstrated how the strength of the metal−nitrogen bond in the diiminopyridyl complex influences the activity of the resulting catalyst. A series of three precatalysts containing the diiminopyridine ligand was synthesized. In these precatalysts, one of the imine nitrogen atoms is attached to the 5-, 6-, or 7-membered cycloalkyl ring fused with the pyridine moiety,[18,28,37,38] and the strength of one of the metal−nitrogen bonds depends on the spatial constraints determined by the geometry of the cycloalkyl ring (see Figure 12). For the smallest ring, the imine nitrogen atom cannot efficiently coordinate to the central atom, and the catalyst does not reach significant activity.[38]

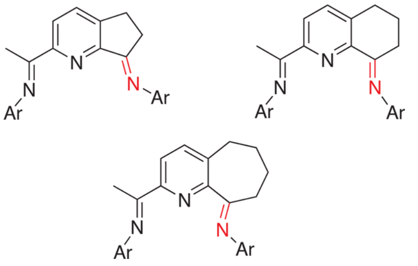

Figure 12. Diiminopyridine molecules containing cycloalkyl rings fused with the pyridine moiety. The size of the ring determines the position of the donor nitrogen atom.

3.2. Other Applications.

In the field of polymer chemistry, olefin polymerization is not the only area in which diiminopyridine transition metal complexes turned out to be useful. Copper[152,153] and vanadium[52,154] complexes were successfully applied as mediators that control the growth of polymer chains in the atom transfer radical polymerization and organometallic mediated radical polymerization processes.

The reactions catalyzed by the diiminopyridyl complexes rely on the ability of the ligand to accept and donate electrons (vide supra). In this respect, diiminopyridine metal dinitrogen complexes synthesized in the Chirik group are worth noting because of their diversified chemistry; the redox reactions leading to such complexes involve mainly the ligand.[86] Likewise, the reactivity of these complexes manifests itself mainly in the ligand reduction and oxidation; only deep, multielectron reduction processes affect the metal atom,[155] as shown in Figure 13.

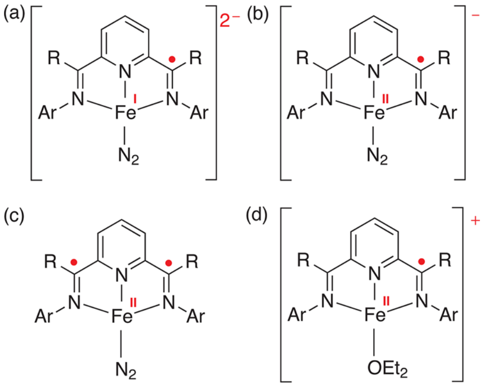

Figure 13. Redox chemistry of the diiminopyridyl iron dinitrogen complexes: (a) deeply reduced form with iron(I) and the three-electron-reduced ligand; (b) intermediate species with iron(II) and the three-electron-reduced ligand; (c) starting material with the two-electron reduced ligand and iron(II); (d) oxidation of part c leads to the product with iron(II) and the ligand in its monoanionic form.

This behavior of the ligand is reflected in the numerous catalytic processes. For example, reductive transformation of the diiminopyridine ligand was observed in the reaction of ammonia with the molybdenum dinitrogen complex;[156] this N−H activation reaction was associated with the release of gaseous nitrogen. Another example of such process involving the reaction between the aluminum complex containing the two-electron-reduced diiminopyridine ligand and anilines proceeds through the intermediate, in which the amido nitrogen within the reduced diiminopyridine ligand gets protonated, and the resulting anilide anion coordinates to the aluminum; one of the final products is hydrogen.[157] Cooperative effects between the ligand and the central atom are often clearly visible in such processes. These effects are not restricted to the transition metal complexes; very often, main group elements are also involved, as shown in Figure 14.

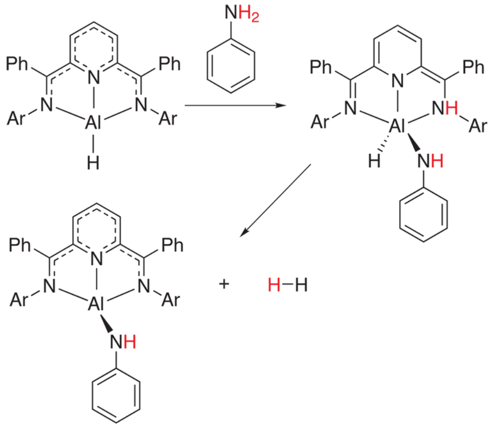

Figure 14. Metal−ligand cooperative mechanism of the N−H bond activation catalyzed by the diiminopyridyl aluminum complex.

Extensive study of the diiminopyridyl aluminum complexes resulted in not only the preparation of new catalysts, but also the discovery of surprising structural motifs, such as square-planar tetracoordinate aluminum (see Figure 15).[157,158]

Diiminopyridyl complexes with Earth-abundant metals have been applied in commercial manufacture of certain consumer products other than polyolefins, thus replacing expensive

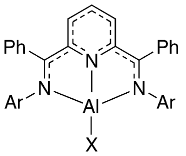

Figure 15. Square-planar aluminum complexes with the two-electron-reduced diiminopyridine ligand incorporating phenyl substituents at the imine carbon atoms, where X = Cl or H. Please note that these species are diamagnetic; therefore the two-electron-reduced ligand is in its closed-shell singlet state, as opposed to the complex shown in Figure 13c, where the ligand forms the biradical dianion.

catalysts based on precious metals. Initially, diiminopyridine iron dinitrogen complexes were used to catalyze hydrogenation[159] and hydrosilylation reactions;[159,160] recently, the potential of the diiminopyridyl cobalt methyl complexes in dehydrogenative silylation has also been demonstrated.[161] The latter process, retaining the unsaturated character of the product, was once considered the unwanted side-reaction; now, it is the source of valuable products. Consistent with the diiminopyridyl late-transition metal complexes used as precatalysts for olefin polymerization (see section 3.1), fine-tuning of the ligand framework may dramatically change the properties of the resulting catalysts in these applications, yet the direction of this tuning seems to be in the opposite direction: the complexes with small substituents at the phenyl rings attached to the imine nitrogen atom are promising for potential industrial applications in the olefin hydrosilylation with tertiary silanes.[162]

It was also demonstrated that diiminopyridyl complexes catalyze C−C bond-forming processes, including cycloaddition of dienes,[163] the Mukaiyama aldol reaction,[164] and the Suzuki−Miyaura reaction.[71] In the latter case, the diiminopyridine ligand may provide an alternative to the phosphines.

Diiminopyridine compounds have also found some applications in electrochemistry. Their complexes with the first-row group 8−10 metals are known to diminish the highly negative potential of CO_2 reduction owing to the electron storage capability of the ligand.[165] Electrochemically polymerized diiminopyridyl iron complexes were useful in the oxygen reduction process.[166]

Certain group-12 diiminopyridyl complexes exhibit blue luminescence due to the ligand centered $\pi^* \rightarrow \pi$ transitions;[60,78] hence, they may find potential application in optoelectronics.

Finally, it should be mentioned that there exist both intra-[68] and intermolecular interactions[60,78,167,168] exhibited by the diiminopyridyl complexes bearing certain functionalized substituents. The latter contribute to the self-assembly process and the formation of network structures.

4. PERSPECTIVES AND OUTLOOK

Several decades after their first synthesis and characterization, diiminopyridine late-transition metal complexes emerged as potent catalysts of coordinative olefin polymerization. This finding triggered intensive research that still maintains its pace. Much effort has been put into the modification of the original catalyst in order to improve its properties, and there are considerable achievements in this field that resulted in highly active and thermally stable catalytic systems.

Diiminopyridines probably combine the “ideal” proportions of donor strength, Lewis basicity, and the bite angle; therefore, the attempts to modify the size of the central ring, the kind of heteroatom, and the length of the chelating arms to find improved catalytic systems were largely futile.[41] The contribution of the ligand’s unique electronic and steric properties into the performance of the catalytic system was recognized immediately by Brookhart and by Gibson, but the intricate redox and acid−base chemistry pertaining to the diiminopyridine ligands was understood only much later. Insight into the properties of the diiminopyridine derivatives and their complexes, acquired in some cases serendipitously over the years, still does not allow clear articulation of the role of a ligand in the coordinative polymerization; the clear picture is obscured by both the multitude and complexity of the interactions within the catalytic system.

Low-valent transition metal complexes, usually based on precious metals, are often applied in the activation of small molecules. The literature indicates many examples in which the diiminopyridine ligand can support inexpensive, abundant elements (such as aluminum) to provide cost-efficient alternatives to the catalysts relying on expensive materials.[169] Diiminopyridine, the ligand whose presence was once restricted to the organometallics containing the transition metal atoms, receives more and more attention in the chemistry of main group elements, and there are spectacular examples indicating that it can also ligate nonmetal atoms. Future research will show whether such exotic compounds remain only a scientific curiosity or find practical applications difficult to anticipate at this time.

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Notes

The authors declare no competing financial interest.

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