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Review

Uniqueness and versatility of iminopyrrolyl ligands for transition metal complexes ☆

Kazushi Mashima *, Hayato Tsurugi

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

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Abstract

Nitrogen-based ligands containing an iminopyrrole unit have recently attracted attention because of their flexible complexation to transition metals. Since steric and electronic demands can be readily introduced to the iminopyrrole unit, a wide variety of ligand has been designed and synthesized. In this contribution, we briefly review synthetic and structural features of transition metal complexes with the multidentate iminopyrrolyl ligands and their catalytic activity, especially polymerization of α-olefins.

Contents

1. Introduction

Nitrogen-based polydentate ligands such as phenoxyimine [1–4], 2,6-bis(*N*-aryliminomethyl)pyridine [5], and α-diimine derivatives [6] have attracted recent interest because of their advantageous feasibility and flexibility in design to introduce sterically and electronically demanding features on the ligand as required for polymerization catalysts [7]. Compared to those ligands, iminopyrrole ligands have not drawn much attention. However, recent exploration of the nitrogen-based ligand modification has promoted the synthetic application of the iminopyrrolyl ligands for preparing many kinds of transition metal complexes. Iminopyrrole ligands are readily prepared by condensations of 2-form-

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* Corresponding author. Fax: +81 6 6850 6245.
E-mail address: mashima@chem.es.osaka-u.ac.jp (K. Mashima).

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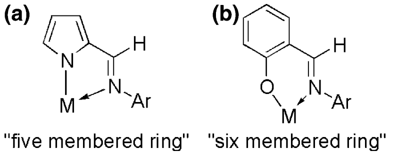


Fig. 1. Schematic drawings of iminopyrrolyl and phenoxyimine complexes.

ylpyrrole or 2,5-diformylpyrrole with amines, and accordingly many kinds of ligands from bidentate system to hexadentate system have been prepared. Particular achievements are that some iminopyrrolyl complexes were able to catalyze α-olefin polymerization.

Both iminopyrrole and phenoxyimine ligands have quite similar steric feature by tuning the substituents at the imine-nitrogen of the ligand. The differences of those ligand systems are size of chelate rings: the iminopyrrolyl ligand forms five-membered ring (**A**), while the phenoxyimine ligand forms six-membered ring (**B**) (Fig. 1).

Since mono(phenoxyimine)nickel complexes and bis(phenoxyimine)-titanium and -zirconium complexes have been found to catalyze α-olefin polymerization, some transition metal complexes with iminopyrrolyl ligands have also been expected to have a potentiality to be catalysts for polymerization of α-olefin. In this contribution, we briefly review the synthesis and catalytic performance of transition metal complexes supported by the iminopyrrolyl ligands and their higher homologues.

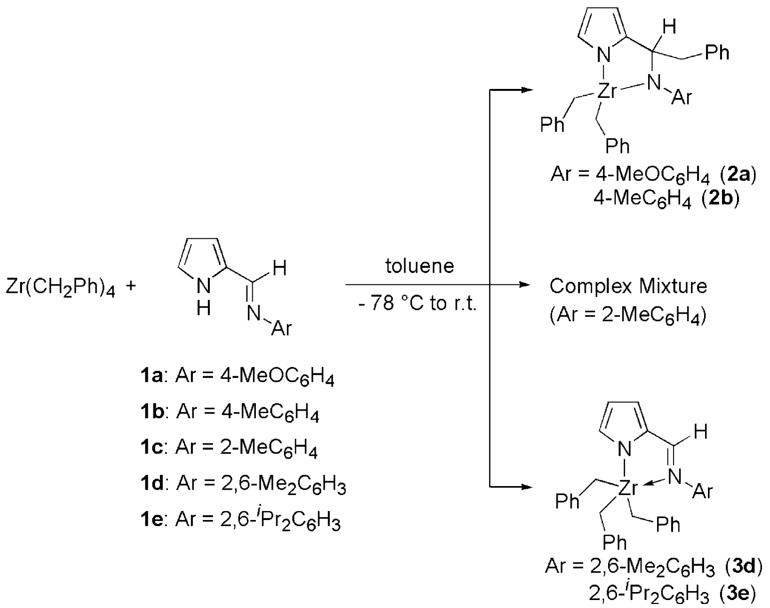
2. Iminopyrrolyl complexes

Various complexes bearing bidentate iminopyrrolyl ligands have been reported. These complexes were classified into two categories; mono(iminopyrrolyl) and bis(iminopyrrolyl) complexes.

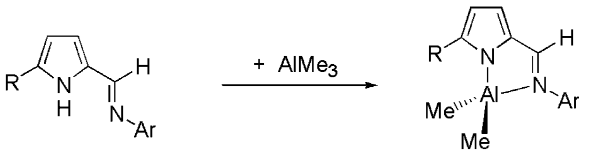
2.1. Mono(iminopyrrolyl) complexes

We recently prepared zirconium mono(iminopyrrolyl) complexes starting from $Zr(CH_2Ph)_4$ (Scheme 1) [8]. The reactions of $Zr(CH_2Ph)_4$ with 1 equiv. of 2-(*N*-aryliminomethyl)pyrrolyl ligands (**1a–e**) in toluene afforded two types of zirconium complexes. In case of less bulky ligands such as **1a** and **1b**, dibenzyl complexes **2a** and **2b** were obtained by the unique intramolecular benzylation of the C=N moiety and the release of 1 equiv of toluene. On the other hand, the reactions with bulky aryl substituents ligands, **1d** and **1e**, afforded tri(benzyl) complexes **3d** and **3e**, respectively, with the release of toluene. In the case of *o*-tolyl ligand **1c**, the reaction did not give any isolable product. Thus, the introduction of bulky substituents at *ortho*-positions delicately prevented the intramolecular alkylation of the imino group. All these zirconium complexes have found to show catalytic activity for ethylene polymerization under atmospheric pressure of ethylene in the presence of excess (1000 equiv) amounts of MMAO. Noteworthy was that catalytic activity of the pyrrolyl-amido complexes **2a** (0.8×10^3 kg-PE/mol-cat h) and **2b** (1.08×10^3 kg-PE/mol-cat h at 0 °C) are higher compared with that of **3c** (19 kg-PE/mol-cat h) and **3d** (51 kg-PE/mol-cat h).

Similar reactions of bulky ligands, **1e** and **1f**, with $AlMe_3$, respectively giving **4e** and **4f**, were reported by Roesky and co-workers (Eq. (1)) [9]. Those aluminum complexes have four-coordinate tetrahedral geometry around the Al atoms. They did not use those complexes for any catalytic processes.



Scheme 1.

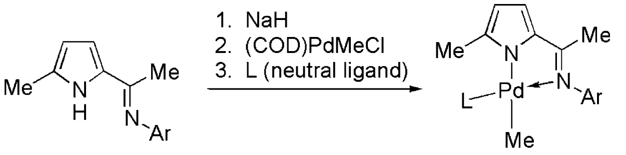


1e: R = H, Ar = $2,6\text{-}{}^{i}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$
1f : R = ^{t}Bu, Ar = $2,6\text{-}{}^{i}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$

4e, 4f

(1)

The iminopyrrolyl ligand has been used for the preparation of late transition metal complexes. Novak and co-workers [10] prepared neutral palladium complexes (**5g–7g**) by the reaction of the sodium salt of ligand **1g** with (COD)PdMeCl in the presence of $\mathrm{PPh_3}$, $\mathrm{PMe_3}$ or pyridine (Eq. (2)). Those complexes were reported to initiate the polymerization of methyl acrylate, but they were inactive for polymerization of both ethylene and 1-hexene in the presence of phosphine scavenger. Copolymerization of methyl acrylate and olefins such as norbornene and 1-hexene proceeded by using complex **5g**, presumably acting as a radical initiator, to give acrylate-rich polymer.

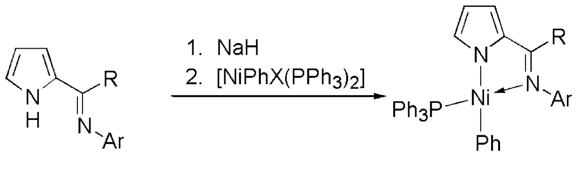


1g: Ar = $2,6\text{-}{}^{i}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$

5g: L = $\mathrm{PPh_3}$
6g: L = $\mathrm{PMe_3}$
7g: L = pyridine

(2)

The neutral Ni(II) complexes were also prepared by the similar reactions of the sodium salt of iminopyrrolyl ligands with *trans*-$[\mathrm{NiBr(Ph)(PPh_3)_2}]$ or *trans*-$[\mathrm{NiCl(Ph)(PPh_3)_2}]$ (Eq. (3)) [11]. The imine group of **8e** and **8l** occupied the position *trans* to the triphenylphosphine ligand, the same as neutral-Ni(II) salicylaldiminato complexes reported by Grubbs and co-workers [4]. The complex **8l** could catalyze the oligomerization of ethylene in the presence of $[\mathrm{Ni(COD)_2}]$, which is a scavenger for the triphenylphosphine ligand, but the catalyst activity (1.25×10^3 g oligomer (mol Ni)$^{-1}$ h^{-1} bar^{-1}) of **8l** was much lower than that of the salicylaldiminato Ni(II) complex/$[\mathrm{Ni(COD)_2}]$ system [4] or diimine Ni(II) complex/MAO system [6e,6g]. In the case of the complexes **8e** and **8h–j**, these did not polymerize ethylene in the presence of phosphine scavenger or MMAO.

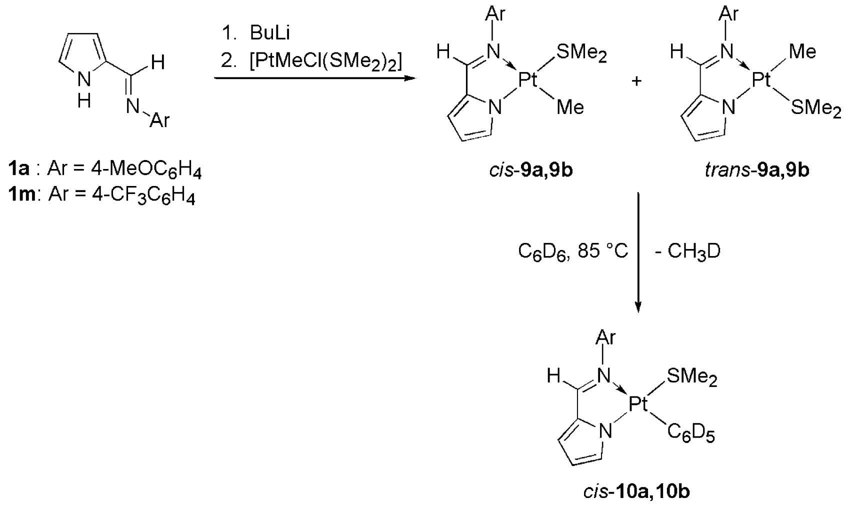


8e, 8h-l

1e: Ar = $2,6\text{-}{}^{i}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$,
R = H
1h: Ar = $2\text{-}{}^{i}\mathrm{Pr}\text{-}6\text{-}\mathrm{MeC}_6\mathrm{H}_3$,
R = H
1i : Ar = $2,6\text{-}\mathrm{Et}_2\mathrm{C}_6\mathrm{H}_3$,
R = H
1j : Ar = $2\text{-}{}^{t}\mathrm{BuC}_6\mathrm{H}_4$,
R = H
1k: Ar = $2,4,6\text{-}\mathrm{Me}_3\mathrm{C}_6\mathrm{H}_2$,
R = H
1l : Ar = $2,4,6\text{-}\mathrm{Me}_3\mathrm{C}_6\mathrm{H}_2$,
R = Me

(3)

The neutral Pt(II) complexes, having one iminopyrrolyl ligand, showed C–H bond activation reaction (Scheme 2) [12]. Reaction of iminopyrrolyl ligand **1a** and **1m** with *n*-BuLi followed by *trans*-$\mathrm{PtMeCl(SMe_2)_2}$ afforded a mixture of *cis* and *trans* isomer, **9a** and **9b**. Both isomers were heated in $\mathrm{C_6D_6}$ at 85 °C to give the *cis* isomer of the corresponding phenyl complexes **10a** and **10b**, with generating $\mathrm{CH_3D}$.



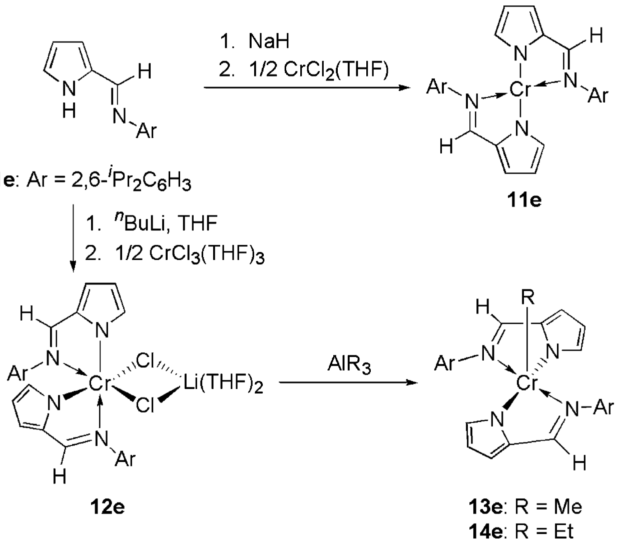
1a : Ar = $4\text{-}\mathrm{MeOC}_6\mathrm{H}_4$
1m: Ar = $4\text{-}\mathrm{CF}_3\mathrm{C}_6\mathrm{H}_4$

cis-**9a,9b**

trans-**9a,9b**

cis-**10a,10b**

Scheme 2.

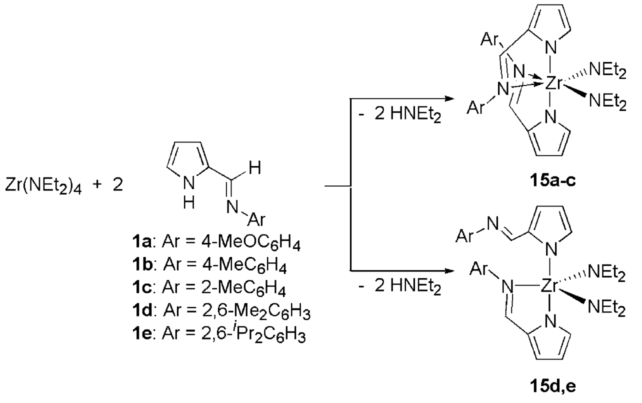


Scheme 3.

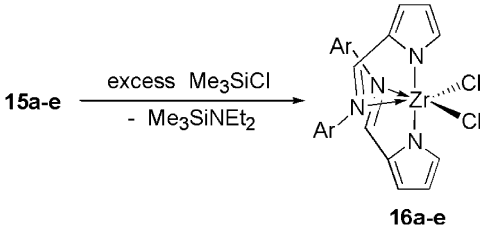
2.2. Bis(iminopyrrolyl) complexes

The first bis(iminopyrrolyl) complexes were reported by Gibson et al. [13] for Cr(II) and Cr(III) complexes, which were derived from the reaction of the alkaline salts of **1e** with $CrCl_2$ as shown in Scheme 3. The structure of Cr(II) complex **11e** is distorted square planar, while the structure of Cr(III) complex **12e** is octahedral surrounded by two iminopyrrolyl ligands and two *cis*-chloro atoms bridged by a solvated Li atom. Alkylations of **12e** by AlR_3 (R = Me and Et) gave rise to five coordinated square pyramidal complexes **13e** and **14e**, respectively. These chromium complexes were found to become active catalysts for ethylene polymerization upon addition of dialkylaluminum chlorides, Me_2AlCl and Et_2AlCl.

Some research groups have reported the synthesis of bis(iminopyrrolyl) complexes of Group 4 metals; we [14] and Bochmann and co-workers [15] for zirconium-dichloro and -diamido complexes, Fujita and co-workers [16] for titanium-dichloro complexes, and Okuda and co-workers [17] for zirconium- and hafnium-dibenzyl complexes. We reported that the reaction of $Zr(NEt_2)_4$ with 2 equiv. of iminopyrrolyl ligands **1a–e** afforded the corresponding zirconium-diamido complexes **15a–e** accompanied with the release of 2 equiv. of $HNEt_2$ (Eq. (4)) [14]. Complexes **15d** and **15e**, with bulky substituents on the imine nitrogen of the ligand, exhibited one set of signals assignable to a trigonal bypyramidal geometry. On the other hand, the ^1H NMR spectra of complexes **15a–c** with less bulky ligand showed signals assignable to two geometric isomers **15a–c**-tbp and **15a–c**-oh, and then at 70 °C two signals coalesced, presumably due to the rapid interconvertion between Δ- and Λ-complexation through a similar trigonal bypyramidal species as observed for **15d,e**. Treatment of complexes **15a–e** with trimethylsilyl chloride in toluene afforded the corresponding dichloro complexes **16a–e** (Eq. (5)). For ethylene polymerization, the catalytic activities of **15a–e**/MMAO systems (17 (**15a**), 20 (**15b**), 18 (**15c**), 32 (**15d**), 18 (**15e**) kg-PE/mol-cat h) were found to be almost the same as those found for **16a–e**/MMAO systems (12 (**16a**), 31 (**16b**), 33 (**16c**), 38 (**16d**), 46 (**16e**) kg-PE/mol-cat h), indicating that both amido- and chloro-zirconium complexes were converted to the same catalytically active species.

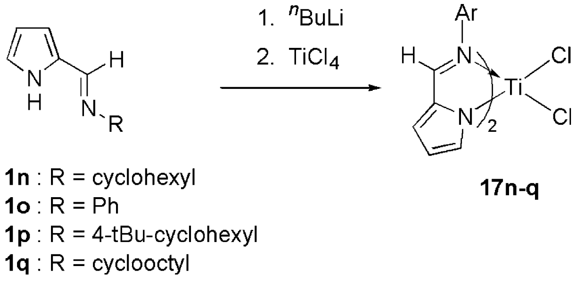


(4)



(5)

Titanium-dichloro complexes $[2\text{-}(R\text{–}N{=}CH)pyr]_2\text{-}TiCl_2$ (**17n**: R = cyclohexyl, **17o**: R = phenyl, **17p**: R = 4-^{t}Bu-cyclohexyl, **17q**: R = cyclooctyl) were prepared by the metathesis reaction of $TiCl_4$ and 2 equiv. of iminopyrrolyl lithium salt (Eq. (6)) [16].

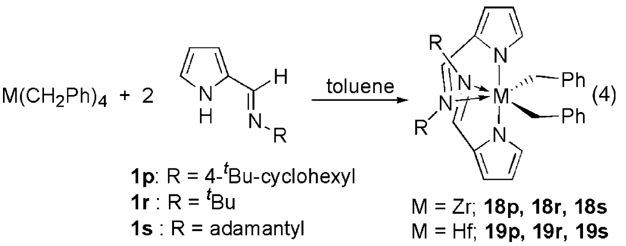


(6)

The complexes **17n** and **17o** showed extremely high activity for ethylene polymerization upon activation with MAO (**17n**; 14100 kg-PE/mol-cat h, **17o**; 6000 kg-PE/mol-cat h) [16b]. In the case of $Ph_3CB(C_6F_5)_4/^iBu_3Al$ as cocatalysts, these complexes afforded polyethylene with exceptionally high molecular weight (M_w > 4,000,000). Titanium complexes were found to catalyze the living copolymerization of ethylene/norbornene upon activation with MAO, giving polymers with very high catalyst activities (**17n**; 2472–3240 kg-PE/mol-cat h, **17o**; 540–576 kg-PE/mol-cat h, **17p**; 2154–2280 kg-PE/mol-cat h,

17q; 3186–3360 kg-PE/mol-cat h) and narrow molecular weight distribution (**17n**; M_w/M_n = 1.07–1.16, **17o**; M_w/M_n = 1.08–1.15, **17p**; M_w/M_n = 1.08–1.24, **17q**; M_w/M_n = 1.09–1.23) [16c,16d]. Recently, Ziegler and co-workers [18] reported the theoretical study for ethylene polymerization by using these titanium-bis(iminopyrrolyl) systems. They suggested that the rate-determining step in the insertion processes is ethylene uptake rather than insertion into Ti–C bond due to the increased electron density at the metal and the steric crowding around the metal coordination sphere. They also pointed out that first insertion barriers are higher for the titanium complexes than zirconium complexes, thus indicating that zirconium-bis(iminopyrrolyl) systems would be better catalysts.

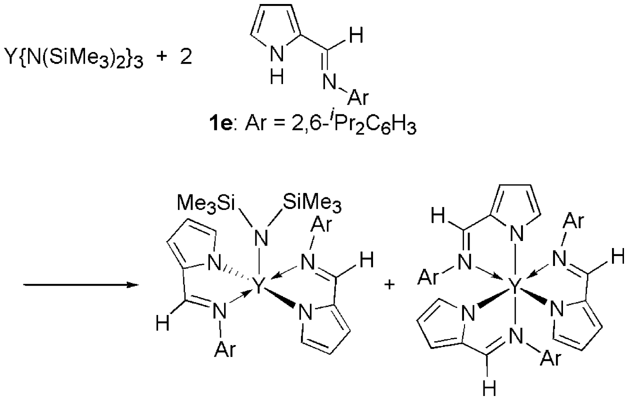
Dibenzyl complexes of zirconium and hafnium were prepared by Okuda and co-workers [17]. The selection of the substituent at imine nitrogen of the ligand sensitively affected not only the stability of dibenzyl complexes but also the activity for ethylene polymerization. In the reaction of tetrabenzyl-zirconium and hafnium with 2 equiv. of iminopyrrolyl ligand (R = 4-^{i}PrC$_6$H$_4$, Et, ^{i}Pr), the products were mixture or easily decomposed. On the other hand, the dibenzyl complexes **18p**, **18r**, **18s** and **19p**, **19r**, **19s** were solated by using much bulkier ligands **1p**, **1r**, **1s** (Eq. (7)).



(7)

Ethylene polymerization activity of the zirconium complexes was affected not only by the substituent at the imine nitrogen of the ligand, but also by the choice of the cocatalyst, MAO or Ph$_3$CB(C$_6$F$_5$)$_4$/^{i}Bu$_3$Al. The activities of **18r** (17952 kg-PE/mol-cat h) and **18s** (22944 kg-PE/mol-cat h) using MAO were higher than those (746 kg-PE/mol-cat h for **18r** and 1760 kg-PE/mol-cat h for **18s**) using Ph$_3$CB(C$_6$F$_5$)$_4$/^{i}Bu$_3$Al. The hafnium complexes showed a similar trend for the substituent, but catalysts combined with Ph$_3$CB(C$_6$F$_5$)$_4$/^{i}Bu$_3$Al were much more effective than the corresponding catalysts combined with MAO (2242 kg-PE/mol-cat h for **19r**/Ph$_3$CB(C$_6$F$_5$)$_4$/^{i}Bu$_3$Al; 1273 kg-PE/mol-cat h for **19r**/MAO; 2096 kg-PE/mol-cat h for **19s**/Ph$_3$CB(C$_6$F$_5$)$_4$/^{i}Bu$_3$Al; 616 kg-PE/mol-cat h for **19s**/MAO). These observations suggested that the hafnium complexes had a higher ion pair character than the zirconium complexes.

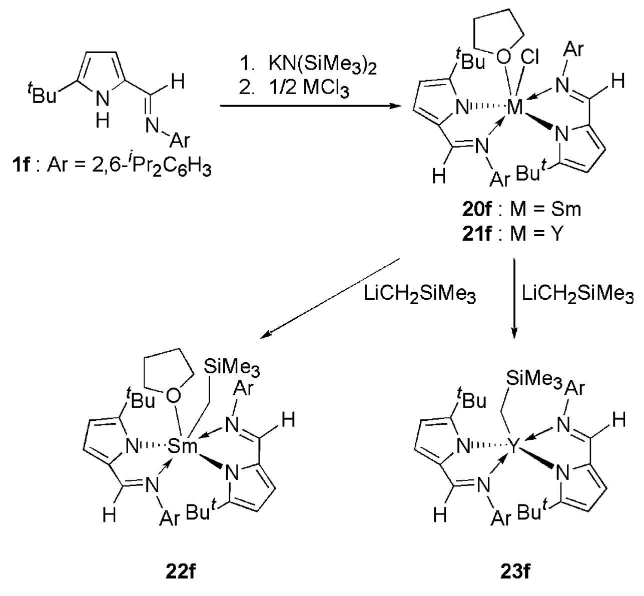
We [19] and Arnold and co-workers [20] independently reported bis(iminopyrrolyl) complexes of rare earth metal. The reaction of Y{N(SiMe$_3$)$_2$}$_3$ with 2 equiv. of iminopyrrole ligand **1e** bearing a bulky 2,6-diisopropyphenyl group at the imino nitrogen afforded a mixture of bis(iminopyrrolyl)Y{N(SiMe$_3$)$_2$} and a homoleptic complex, tris(iminopyrrolyl)Y; the latter complex was obtained quantitatively upon treating Y{N(SiMe$_3$)$_2$}$_3$ with 3 equiv. of iminopyrrole ligand (Eq. (8)) [19].



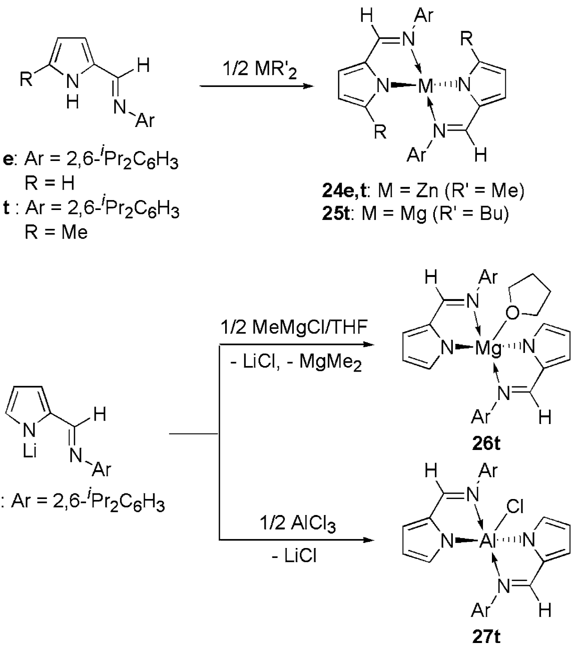
(8)

On the other hand, metathesis reactions of MCl$_3$ (M = Sm and Y) with the potassium salt of a more sterically bulky iminopyrrolyl ligand **1f**, which has a *tert*-butyl group at 5-position of pyrrole ring gave the corresponding bis(iminopyrrolyl) complexes, (iminopyrrolyl)$_2$MCl(thf) (**20f**: M = Sm; **21f**: M = Y) (Scheme 4) [20]. Monoalkyl complexes, **22f** and **23f**, were prepared by treating these chloro complexes with LiCH$_2$SiMe$_3$. Complex **22f** was found to be highly active catalysts for isospecific polymerization of methyl methacrylate (MMA), giving high molecular weight isotactic PMMA (*mm* triad: up to 97.8%; $M_n = 1.41 \times 10^6$, PDI = 1.31).

Bochmann and co-workers [15] reported some late transition metal complexes: cobalt(II) and nickel(II)



Scheme 4.



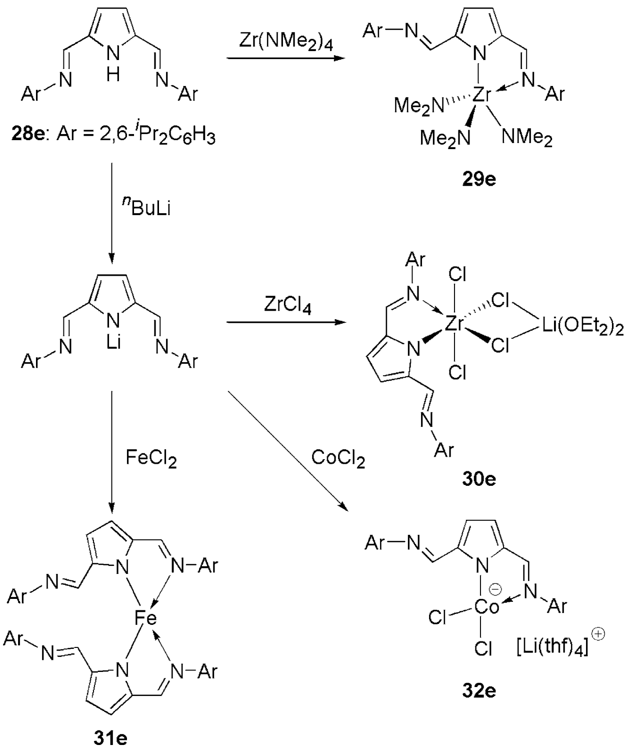
Scheme 5.

complexes, [2-(Ar–N=CH)pyr]$_2$Co and [2-(Ar–N=CH)-pyr]$_2$Ni (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), were prepared by the reactions of 2 equiv. of the lithium salt of the iminopyrrolyl ligand **1e** with CoCl$_2$ and NiBr$_2$(dme), respectively. The cobalt and nickel complexes did not show any catalytic activity toward polymerization and oligomerization of ethylene. As shown in Scheme 5, bis(iminopyrrolyl) complexes of main group elements such as aluminum, zinc, and magnesium were prepared and crystallographically characterized by Roesky and co-workers [9]. Those complexes were not applied as catalysts.

3. Tridentate bis(imino)pyrrolyl complexes

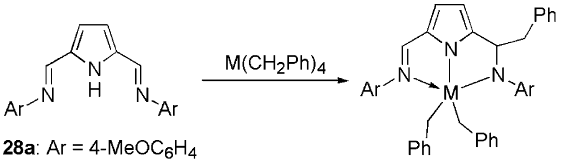
Bis(imino)pyrrole ligands, 2,5-bis(*N*-aryliminomethyl)-pyrroles, which were prepared by the condensation of 2,5-diformylpyrrole with the corresponding anilines, have two imino groups and thus act as bidentate or tridentate ligands, being in comparison to the fixed tridentate ligation of the bis(imino)pyridine ligand.

Bochmann and co-workers [15] prepared bis(imino) pyrrolyl complexes **29e–32e** of zirconium, iron, and cobalt (Scheme 6). All complexes were coordinated by two of the three nitrogen atoms of the bis(imino)pyrrolyl ligand. The metathesis reaction of the lithium salt of **28e** with ZrCl$_4$ afforded a tetrachlorozirconate, {bis(imino)pyrrolyl}ZrCl$_2$(μ-Cl)$_2$Li(OEt$_2$)$_2$ (**30e**), was obtained. The reaction with FeCl$_2$ afforded a halide-free product **31e**, which has a distorted tetrahedral geometry around the iron atom. On the other hand, the lithium salt of **28e** reacted with anhydrous CoCl$_2$ to give an ionic complex, [Li(thf)$_2$][{bis(imino)pyrrolyl}CoCl$_2$] (**32e**). The zirconate complex **30e** showed a moderate activity (42 kg-PE/mol-cat h) for ethylene polymerization, while the cobalt complex **32e** catalyzed the oligomerization of ethylene and propene.



Scheme 6.

We have recently reported that reactions of Zr(CH$_2$Ph)$_4$ and Hf(CH$_2$Ph)$_4$ with bis(imino)pyrrolyl ligands **28a–e** afforded unique tridentate amido-imino-pyrrolyl complexes **33c–e** and **34a–e**, respectively (Eq. (9)) [21]. These reactions involved a selective benzylation of one of two imino moieties of the tridentate bis(imino)pyrrolyl ligands. The reaction of Zr(CH$_2$Ph)$_4$ with 1 equiv. of tridentate 2,5-bis(*N*-aryliminomethyl)pyrrolyl ligands **28c–e** in toluene afforded the corresponding dibenzyl complexes of zirconium (**33c–e**) along with the release of 1 equiv. of toluene. In contrast, reaction with 1 equiv. of *p*-substituted pyrrolyl ligands **28a** and **28b** resulted in the complicated mixtures, from which none of the products could be isolated. The reaction of tetrabenzyl hafnium with 1 equiv. of **28a–e** gave the corresponding hafnium complexes **34a–e** as air- and moisture-sensitive yellow solids. These zirconium and hafnium complexes, upon activation with MMAO, became active ethylene polymerization catalyst (14–447 kg-PE/mol-cat h for Zr complexes **33c–e**; 0.1–6.4 kg-PE/mol-cat h for Hf complexes **34c–e**). Monobenzyl cations were possible intermediates, which were detected on the reaction of the neutral dibenzyl complexes **33d**, **33e**, **34d**, and **34e** with Ph$_3$CB(C$_6$F$_5$)$_4$.

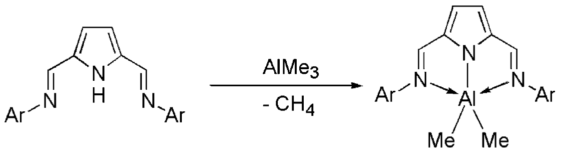


(9)

28a: Ar = 4-MeOC$_6$H$_4$
28b: Ar = 4-MeC$_6$H$_4$
28c: Ar = 2-MeC$_6$H$_4$
28d: Ar = 2,6-Me$_2$C$_6$H$_3$
28e: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

33c-e: M = Zr
34a-e: M = Hf

Tridentate bis(imino)pyrrole ligands **28a–e** reacted with AlMe$_3$ to give the corresponding mononuclear aluminum dimethyl complexes (**35a–e**) along with the release of 1 equiv. of methane [22] (Eq. (10)).



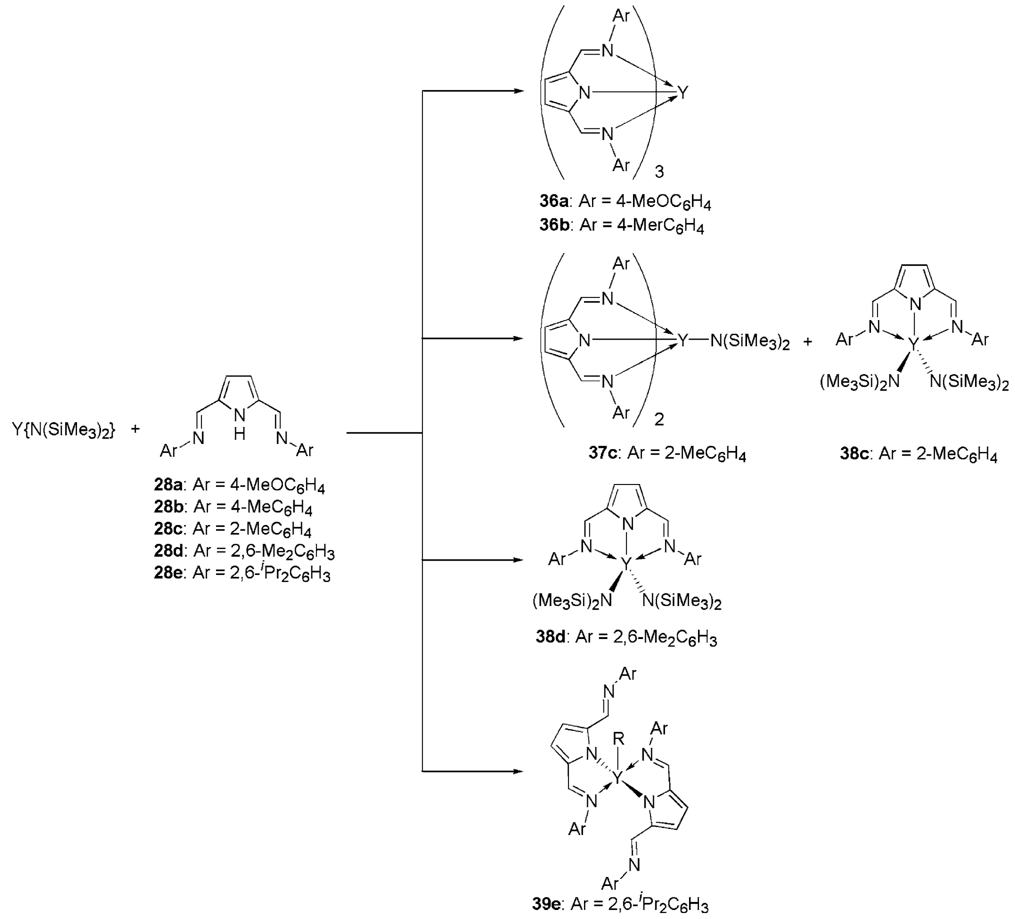
(10)

28a: Ar = 4-MeOC$_6$H$_4$
28b: Ar = 4-MeC$_6$H$_4$
28c: Ar = 2-MeC$_6$H$_4$
28d: Ar = 2,6-Me$_2$C$_6$H$_3$
28e: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

35a-e

In solution, NMR measurements revealed that bis(imino)pyrrolyl anion coordinated in a tridentate fashion to the aluminum atom; while in solid state the bis(imino)pyrrolyl ligand chelated the aluminum metal in a bidentate fashion. Catalyst **35e** showed lower catalytic activity (80 g-PE/mol-cat h) for the ethylene polymerization, when activated by 1 equiv. of B(C$_6$F$_5$)$_3$ in toluene under 1 atom of ethylene, than those of imidinate-aluminum system (700 g-PE/mol-cat h) [23] and aminotroponiminate-aluminum system (2600 g-PE/mol-cat h) [24].

We also explored the synthesis of yttrium complexes and their application for ε-caprolactone polymerization [19]. The number of bis(imino)pyrrolyl ligands introduced to an yttrium atom as well as the coordination mode of the ligands could be controlled by varying the bulkiness on the aryl group of the ligands (Scheme 7). Reaction of Y{N(SiMe$_3$)$_2$}$_3$ with 2,6-dimethyl substituted ligand **28d** afforded **38d**, in which one pyrrolyl ligand coordinated in a tridentate fashion to the yttrium center and two N(SiMe$_3$)$_2$ remained intact. The reaction of Y{N(SiMe$_3$)$_2$}$_3$ with a much bulkier *ortho*-diisopropy substituted ligand **28e** resulted in the selective formation of bis(pyrrolyl) complex **39e**, in which the two pyrrolyl ligands coordinated in a bidentate fashion to the yttrium metal. On the other hand, reaction with *ortho*-methyl substituted ligand **28c** afforded a 4:1 mixture of mono(pyrrolyl) complex **38c** and bis(pyrrolyl)complex **37c**. Reactions with *para*-substituted ligands **28a** and



28a: Ar = 4-MeOC$_6$H$_4$
28b: Ar = 4-MeC$_6$H$_4$
28c: Ar = 2-MeC$_6$H$_4$
28d: Ar = 2,6-Me$_2$C$_6$H$_3$
28e: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

36a: Ar = 4-MeOC$_6$H$_4$
36b: Ar = 4-MerC$_6$H$_4$

37c: Ar = 2-MeC$_6$H$_4$

38c: Ar = 2-MeC$_6$H$_4$

38d: Ar = 2,6-Me$_2$C$_6$H$_3$

39e: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

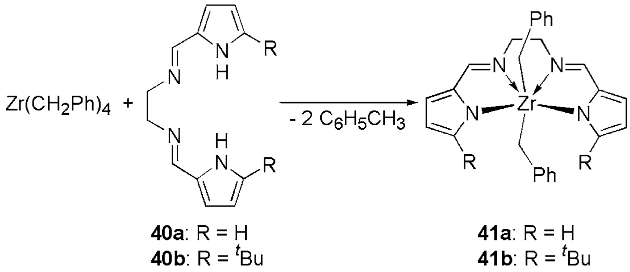
Scheme 7.

28b led to the formation of homoleptic tris(pyrrolyl) complexes **36a** and **36b**, respectively. Bis(pyrrolyl) complex **39e** was found to catalyze polymerization of ε-caprolactone, giving polymer with narrower PDI ($M_w/M_n = 1.3$) compared with the polymer obtained by **38d**, while homoleptic pyrrolyl complexes showed no catalytic activity.

4. Multidentate iminopyrrolyl complexes

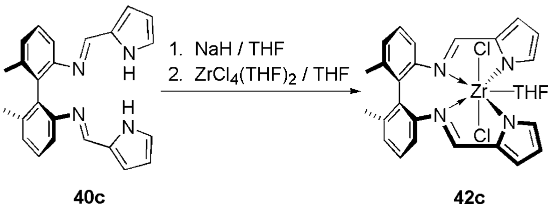
4.1. Tetradentate diimino-dipyrrolyl complexes

Tetradentate ligands such as diimino-dipyrroles were prepared by the condensation of 2 equiv. of 2-formylpyrrole with the corresponding diamine. Bochmann and co-workers [25] reported a dibenzyl zirconium complex **41a** bearing diimino-dipyrrolyl ligand, [2-(C_4H_3N)CH=NCH_2]$_2$ (**40a**) (Eq. (11)). Catalyst system **41a**/MAO was inactive for ethylene polymerization, presumably due to the *trans* orientation of two alkyl groups in the complex. Liang et al. [26] also prepared a dibenzyl complex **41b** by using a modified tetradentate ligand **40b**.



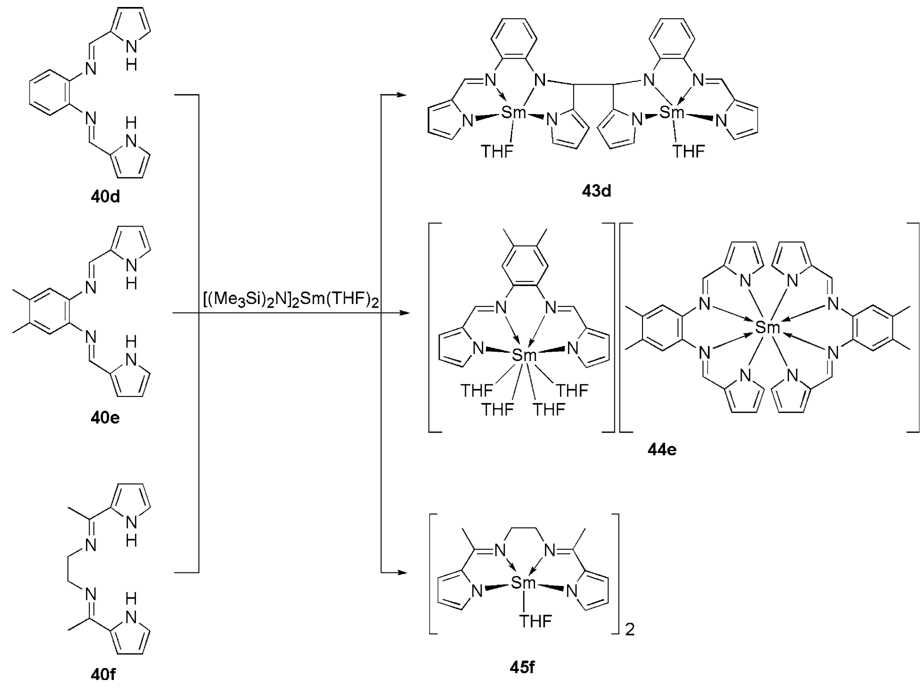
(11)

Brintzinger and co-workers [27] reported the preparation of diimino-dipyrrole ligand **40c** with a chiral 6,6′-dimethyl-bianiline backbone and prepared its zirconium complex, (diimino-dipyrrolyl)$ZrCl_2$(thf) (**42c**) (Eq. (12)). This complex, upon activation with MAO, was found to polymerize ethylene (6.2 kg-PE/mol-cat h) and propene (7.8 kg-PE/mol-cat h; 55% *mmmm*), though two chloride atoms of **42c** occupied *trans*-positions. Scott and co-workers [28] reported the preparation of titanium and zirconium complexes bearing tetradentate imino-phenolate ligand with a chiral backbone, and co-ligands of those complexes occupied *cis*-coordination site.



(12)

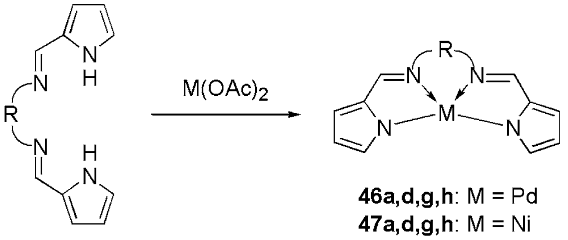
Gambarotta and co-workers [29] attempted to prepare divalent samarium complexes by using **40d–f**; however, **43d**, **44e**, and **45f** were obtained depending on modification of the ligand (Scheme 8). In the reaction of Sm[N($SiMe_3$)$_2$]$_2$(thf)$_2$ with **40d**, a coupling reaction of imino group proceeded to give a trivalent samarium complex **43d**, while the introduction of methyl groups at the 3,4-positions of phenyl ring led to the formation of a trivalent samarium ionic complex **44e**, due to a disproportionation process. Compared with using **43d** and **44e**, ketimine ligand **40f** prevented reductive coupling of the imino group and disproportionation of samarium



Scheme 8.

complex to give a divalent samarium complex **45f**. The structure of **45f** is a dimeric and the dinuclear aggregation is constructed by the π-interaction of the samarium center with the pyrrolyl ring of the second unit.

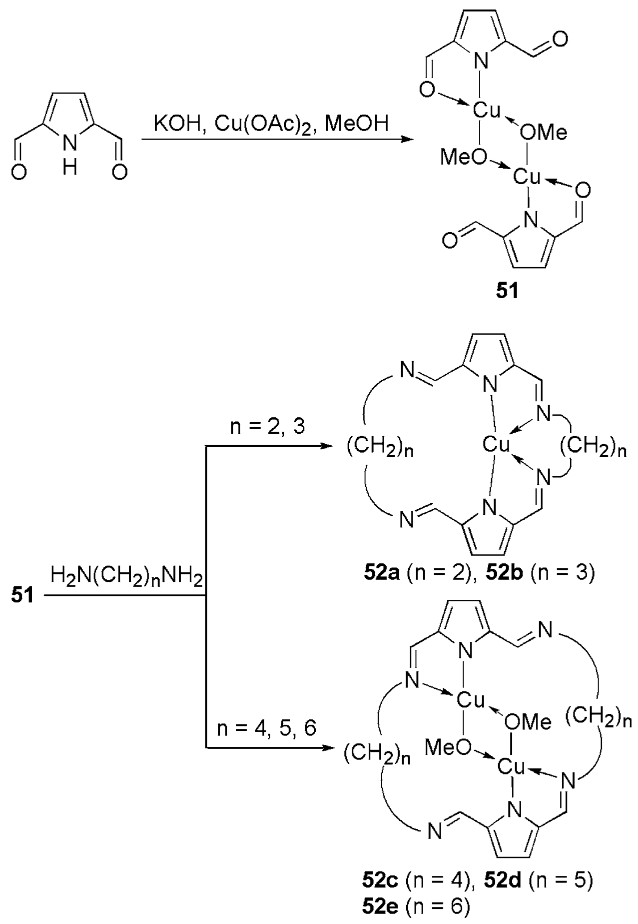
Palladium and nickel complexes bearing tetradentate diimino-dipyrrole ligands were prepared by Carcelli and co-workers [30]. The reaction of $Pd(OAc)_2$ or $Ni(OAc)_2$ with tetradentate ligand **40a**, **40d**, **40g**, and **40h** afforded the corresponding four-coordinated Pd- and Ni-complexes, respectively (Eq. (13)). The coordination geometry around palladium center was crystallographically characterized to be square-planar. These complexes were tested as catalysts for the hydrogenation of phenylacetylene.



46a,d,g,h: M = Pd
47a,d,g,h: M = Ni

(13)

40a: R = $(CH_2)_2$
40d: R = C_6H_4
40g: R = $(CH_2)_3$
40h: R = *trans*-C_6H_{10}



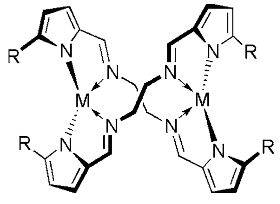
51

52a (n = 2), **52b** (n = 3)

52c (n = 4), **52d** (n = 5)
52e (n = 6)

Scheme 9.

Such tetradentate ligands have flexibility to support dinuclear complexes. Double helical dinuclear complexes bearing these tetradentate ligands, i.e., dinuclear copper (**48a**) [31a], manganese (**49a**) [31b], and magnesium (**50b**) [26] have been crystallographically characterized.

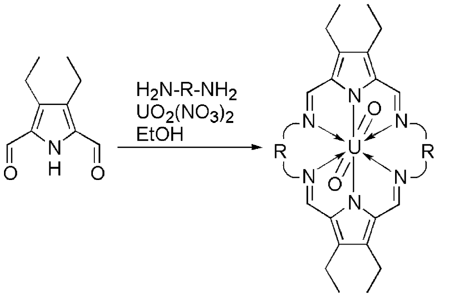


48a: M = Cu, R = H
49a: M = Mn, R = H
50b: M = Mg, R = ^{t}Bu

4.2. Hexadentate tetraimino-dipyrrolyl complexes

Hexadentate tetraimino-dipyrrole ligands were prepared by using template reactions. For example, copper macrocyclic compounds **52a–e** were prepared by the reaction of copper complex **51** with corresponding diaminoalkanes (Scheme 9) [32]. Depending on the chain length of diaminoalkanes, mononuclear complexes **52a,b** and dinuclear complexes **52c–e** were selectively prepared.

Macrocyclic uranyl(VI) complexes **53a–c** were prepared in the presence of uranyl nitrate via template condensation between 3,4-diethyl-2,5-diformylpyrrole and corresponding diamines (Eq. (14)) [33]. The uranyl(VI) cation was thus supported by all six nitrogen atoms of the ligand, as revealed by X-ray analysis.



(14)

53a: R = $(CH_2)_2$
53b: R = $(CH_2)_3$
53c: R = 1,2-$MeO_2C_6H_2$

5. Conclusion

Iminopyrrole and its derivatives have been shown to be versatile supporting ligands for various transition metals, though these have attracted less attention compared to phenoxyimine and porphyrine complexes. Among them, chemistry of metal complexes with bidentate iminopyrrolyl ligand is of particular interest because of their applicability as highly active polymerization catalysts. Attractive features such as flexible in design and practical in synthesis of such nitrogen-based ligands would have high potentiality to open new coordination chemistry as well as new catalysts.

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References

[1] (a) H. Makio, N. Kashiwa, T. Fujita, Adv. Synth. Catal. 344 (2002) 477;
(b) M. Mitani, T. Nakano, T. Fujita, Chem. Eur. J. 9 (2003) 2396;
(c) Y. Suzuki, H. Terao, T. Fujita, Bull. Chem. Soc. Jpn. 76 (2003) 1493.
[2] (a) J. Tian, G.W. Coates, Angew. Chem., Int. Ed. 39 (2000) 3626;
(b) J. Tian, P.D. Hustad, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 5134.
[3] (a) V.C. Gibson, S. Mastroianni, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. (2000) 1969;
(b) D.J. Jones, V.C. Gibson, S. Green, P.J. Maddox, Chem. Commun. (2002) 1927.
[4] (a) C. Wang, S. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149;
(b) T.R. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Babsleben, Science 287 (2000) 460.
[5] (a) B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049;
(b) G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849;
(c) B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143;
(d) G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Stroemberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728;
(e) G.J.P. Britovsek, S. Mareoinni, G.A. Solan, S.P.D. Baugh, C. Redshaw, V.C. Gibson, A.J.P. White, D.J. Williams, M.R.J. Elsegood, Chem. Eur. J. 6 (2000) 2221.
[6] (a) L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414;
(b) L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267;
(c) C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664;
(d) C. Pellecchia, A. Zambelli, Macromol. Rapid Commun. 17 (1996) 333;
(e) C.M. Killan, L.K. Johnson, M. Brookhart, Organometallics 16 (1997) 2005;
(f) S. Mecking, L.K. Johnson, L. Wang, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 888;
(g) S.A. Svejda, M. Brookhard, Organometallics 18 (1999) 65.
[7] (a) R. Kempe, Angew. Chem., Int. Ed. 39 (2000) 468;
(b) L.H. Gade, Chem. Commun. (2000) 173.
[8] H. Tsurugi, T. Yamagata, K. Tani, K. Mashima, Chem. Lett. 32 (2003) 756.
[9] H. Hao, S. Bhandari, Y. Ding, H.W. Roesky, J. Magull, H.G. Schmidt, M. Noltemeyer, C. Cui, Eur. J. Inorg. Chem. (2002) 1060.
[10] G. Tian, H.W. Boone, B.M. Novak, Macromolecules 34 (2001) 7656.
[11] (a) Y.S. Li, Y.R. Li, X.F. Li, J. Organomet. Chem. 667 (2003) 185;
(b) R.M. Bellabarba, P.T. Gomes, S.I. Pascu, Dalton Trans. (2003) 4431.
[12] C.N. Iverson, C.A.G. Carter, R.T. Baker, J.D. Scollard, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 125 (2003) 12674.
[13] (a) V.C. Gibson, P.J. Maddox, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 1651;
(b) V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. (2002) 4017.
[14] Y. Matsuo, K. Mashima, K. Tani, Chem. Lett. (2000) 1114.
[15] D.M. Dawson, D.A. Walker, M. Thornton-Pett, M. Bochmann, J. Chem. Soc. Dalton Trans. (2000) 459.
[16] (a) Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, M. Nitabaru, T. Nakano, H. Tanaka, T. Fujita, Chem. Lett. (2000) 1270;
(b) Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, Organometallics 20 (2001) 4793;
(c) Y. Yoshida, J. Saito, M. Mitani, Y. Takagi, S. Matsui, S. Ishii, T. Nakano, N. Kashiwa, T. Fujita, Chem. Commun. (2002) 1298;
(d) Y. Yoshida, J. Mohri, S. Ishii, M. Mitani, J. Saito, S. Matsui, H. Makio, T. Nakano, H. Tanaka, M. Onda, Y. Yamamoto, A. Mizuno, T. Fujita, J. Am. Chem. Soc. 126 (2004) 12023.
[17] (a) S. Matsui, T.P. Spaniol, Y. Takagi, Y. Yoshida, J. Okuda, J. Chem. Soc., Dalton Trans. (2002) 4529;
(b) S. Matsui, Y. Yoshida, Y. Takagi, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 689 (2004) 1155.
[18] K. Vanka, Z. Xu, T. Ziegler, Organometallics 23 (2004) 2900.
[19] Y. Matsuo, K. Mashima, K. Tani, Organometallics 20 (2001) 3510.
[20] C. Cui, A. Shafir, C.L. Reeder, J. Arnold, Organometallics 22 (2003) 3357.
[21] H. Tsurugi, Y. Matsuo, T. Yamagata, K. Mashima, Organometallics 23 (2004) 2797.
[22] Y. Matsuo, H. Tsurugi, T. Yamagata, K. Tani, K. Mashima, Bull. Chem. Soc. Jpn. 76 (2003) 1965.
[23] M.P. Coles, R.F. Jordan, J. Am. Chem. Soc. 119 (1997) 8125.
[24] E. Ihara, V.G. Young Jr., R.F. Jordan, J. Am. Chem. Soc. 120 (1998) 8277.
[25] N.A.H. Male, M. Thornton-Pett, M. Bochmann, J. Chem. Soc. Dalton Trans. (1997) 2487.
[26] L.C. Liang, P.Y. Lee, W.L. Lan, C.H. Hung, J. Organomet. Chem. 689 (2004) 947.
[27] M. Kettunen, C. Vedder, F. Schaper, M. Leskela, I. Mutikainen, H.-H. Brintzinger, Organometallics 23 (2004) 3800.
[28] P.D. Knight, A.J. Clarke, B.S. Kimberley, R.A. Jackson, P. Scott, Chem. Commun. (2002) 352.
[29] C.D. Berube, S. Gambarotta, G.P.A. Yap, P.G. Cozzi, Organometallics 22 (2003) 434.
[30] A. Bacchi, M. Carcelli, L. Gabba, S. Ianelli, P. Pelagatti, G. Pelizzi, D. Rogolino, Inorg. Chim. Acta 342 (2003) 229.
[31] (a) T. Kikuchi, C. Kabuto, H. Yokoi, M. Iwaizumi, W. Mori, Chem. Commun. (1983) 1306;
(b) F. Franceschi, G. Guillemot, E. Solai, C. Floriani, N. Re, H. Birkedal, P. Pattison, Chem. Eur. J. 7 (2001) 1468.
[32] H. Adams, N.A. Beiley, D.E. Fenton, S. Moss, C.O.R. Barbarin, G. Jones, J. Chem. Soc., Dalton Trans. (1986) 693.
[33] (a) J.L. Sessler, T.D. Mody, V. Lynch, Inrog. Chem. 31 (1992) 529;
(b) J.L. Sessler, T.D. Mody, M.T. Dulay, R. Espinoza, V. Lynch, Inorg. Chim. Acta 246 (1996) 23.