Discrete metal complexes from $N$-heterocyclic ferrocenes: structural diversity by ligand design

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ABSTRACT
The aim of this review is to provide an overview of the structures of discrete metal complexes with $N$-heterocyclic ferrocenes, based on their crystal structures. These $N$-heterocyclic ferrocenes act as versatile ligands for the construction of metal complexes with unique structures, owing to the $\pi\cdots\pi$ interaction between the $N$-heterocycles and conformational flexibility of the ferrocenyl moiety. $N$-Heterocyclic ferrocenes coordinate to metal ions in monodentate, C,N-bidentate, multidentate, and bridging fashions, which results in metal complexes with various M:L stoichiometry. The ligands and their metal complexes have been recently employed for applications including chemical sensors, homogeneous catalysts, and redox-driven conformational switching.

Keywords: $N$-Heterocyclic ferrocene; Coordination mode; Crystal structure

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Abbreviations: Ac, acetyl; acac, acetylacetonato; bpy, 2,2’-bipyridine; \textit{t}-Bu, tertiary-butyl; cod, 1,5-cyclooctadiene; Cp, cyclopentadienyl; Cy, cyclohexyl; dcpab, 2-dicyclohexylphosphanylidene-2’-(N,N-dimethylamino)biphenyl; dppe, diphenylphosphinoethane; dppf, 1,1-diphenylphosphinoferrocene; dppp, diphenylphosphinopropane; dppz, dipyrrophenazine; hfac, 1,1,1,5,5,5-hexafluoroacetylacetone; OTf, trifluoromethanesulfonate; PEG, poly(ethylene glycol); Ph, phenyl; phen, 1,10-phenanthroline; PPN, bis(triphenylphosphine)iminium cation; \textit{i}PrNHC, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; H-\textit{ptpy}, 2-(4-tolylpyridine); TBAB, tetra-	extit{normal}-butylammonium bromide; [14]aneS₄, 1,4,8,11-tetrathiacyclotetradecane.
1. Introduction

Ferrocene derivatives have been widely utilized in various fields, mainly owing to their unique structural, electronic, and magnetic properties [1–3]. In particular, synthesis and applications of ferrocene derivatives as ligands have been reported extensively [1–3]. However, N-heterocyclic ferrocenes, defined here as ferrocenes with N-heterocyclic substituents on their cyclopentadienyl rings, have received less attention as ligands. These groups are rich in synthetic chemistry and structural chemistry [4–8]; however, they have only recently been employed as ligands in coordination chemistry. There are several advantages for using N-heterocyclic ferrocenes as ligands. First, they show interesting coordination chemistry owing to the variety of N-heterocycles (Fig. 1) and the conformational flexibility of ferrocene rings and N-heterocycles (Fig. 2). Second, functionalized building blocks, especially metal-containing ligands (metalloligands) [9–11], have been the subject of recent attention in crystal engineering [12, 13]. In fact, the introduction of a ferrocenyl group to an N-heterocyclic ring is a rational approach to obtain metalloligands. Third, N-heterocyclic ferrocenes and their metal complexes have proven to act as chemical sensors [14–19], homogeneous catalysts, and conformationally switchable materials, taking advantage of the conformational flexibility and redox ability of the ligands. Finally, many of these systems have well-defined structures, which allows for a better understanding of their properties.

In this review, we discuss the structural variation of the discrete metal complexes with N-heterocyclic ferrocenes based on crystallographic data. Complexes without crystallographic data will be described only when they have remarkable aspects. Omitted from this review are ferrocenes bearing chiral N-heterocycles, saturated N-heterocycles, and mixed donor N-heterocycles, which have considerable use as ligands for asymmetric catalysts, because they have been reviewed in the literature [20–23]. Also omitted are coordination polymer complexes with N-heterocyclic ferrocenes, which are summarized in our previous review [11].
2. Structures of metal complexes

All N-heterocyclic ferrocenes in this review are classified according to their coordination fashion and ring size (Fig. 3). N-Heterocyclic ferrocenes can be prepared by general synthetic procedures, including palladium catalyzed cross-coupling [24–31], cyclodehydration [32–39], azide alkyne Huisgen cycloaddition (Click reaction) [14, 15, 40, 41], and other reactions [42–46].

2.1. N-Heterocyclic ferrocenes that produce monodentate complexes

Structural formulae of N-heterocyclic ferrocenes adopting monodentate ligation are summarized in Fig. 4. The chemical formulas of their complexes are listed in Table 1. Although the N-heterocyclic ferrocenes dealt with in this section are simple, their coordination structures vary, accompanying the variation of the M:L ratios. Ferrocenes with bulky N-heterocycles, such as indole [47], benzimidazole [37], perimidine [48], quinoline [30, 32, 39, 43], and quinoxaline [33–36, 38], also act as monodentate ligands; however, their metal complexes are fewer.

2.1.1. Pyrazole and triazole derivatives (L1–L4)

Although many ferrocenyl pyrazole derivatives have been reported, their coordination complexes are relatively few. The photochemical reaction of L1·H and W(CO)6 affords a 1:1 M:L complex [W(CO)5(L1·H)] (1, Fig. 5) [49]. The crystal structure of 1 reveals that the pyrazole of L1·H coordinates to the tungsten(II) center with the nitrogen atom farther away from the ferrocenyl moiety. The N–H group of 1 forms an intermolecular hydrogen bonding with a carbonyl moiety of an adjacent molecule to construct a 1D network structure.

L2·H, a regioisomer of L1·H, coordinates to a metal(II) ion via the 2-position nitrogen to construct 1:4 or 1:2 M:L complexes, [MX2(L2·H)n] {M = Zn, X = NO3−, n = 4 (2, Fig. 6a); M = Co, X = Cl−, n = 4 (3, Fig. 6b); M = Zn, X = NCS, n = 2 (4, Fig. 6c)} [50]. 2 and 4 possess 1D hydrogen bonding network structures, while 3 shows a discrete structure. 2 has two polymorphs, 2a and 2b. Despite the difference in their packing structures and space groups (P-1 for 2a, P21/c for 2b), their
molecular structures and the hydrogen bonding networks are almost the same. The metal(II) ions in 2a and 3 adopt an octahedral geometry and are occupied by four equatorial nitrogen atoms from four L2-H ligands and two axial heteroatoms from counter anions. In 2a, two of the four L2-H ligands form intramolecular N−H···O hydrogen bonds with two NO3− anions, while the others form intermolecular N−H···O hydrogen bonds with two NO3− anions from two adjacent molecules, affording a 1D network structure. The zinc(II) ion in 4 shows a tetrahedral coordination geometry, surrounded by four nitrogen atoms from two L2-H ligands and from two NCS− anions. Each unit is linked by intermolecular N−H···S hydrogen bonds between two ligands and two counter anions, forming a 1D network structure.

Several ferrocenyltriazole derivatives and their coordination complexes have been prepared during the development of the Click reaction [14, 40]. By treating with PdCl2(PhCN)2, L3 and L4 afford [PdCl2(L)2] {L = L3 (5, Fig. 7) [51] and L4 (6) [52], respectively}. The palladium(II) centers in both 5 and 6 show square planar coordination geometry, in which the N-donor ligands occupy the trans positions. In both complexes, the ligands coordinate to the metal center with the nitrogen atom farthest away from the benzyl group. A trinuclear ferrocenyltriazole derivative can be also prepared using the Click reaction of the trifunctionalized benzene derivative and ethynylferrocene, and this derivative reacts with β-cyclodextrin to form an encapsulated complex (Fig. 8). The complex can stabilize and solubilize palladium nanoparticles, which catalyze both the Suzuki and Heck reactions in aqueous media [53].

2.1.2. Pyridine, pyrimidine, and pyrazine derivatives (L5–L9)

The most widely investigated class of N-heterocyclic ferrocenes has been those with six-membered rings. Many complexes with L5 and L6 are crystallographically characterized. Most studies on the complexes with L6 deal with their electrochemical properties, which have revealed that there is little electronic communication between the ferrocenyl group and the metal center [54–58]. Because of the similarity of the complexes, we will limit our discussion to certain interesting 1:2 and 2:2 M:L complexes with L5, [MCl2(L5)2] {M = Pd (7, Fig. 9a) [59], Pt (8, Fig.
The two L5 ligands in 7 occupy the trans-positions of the palladium(II) center, while those in 8 coordinate to the cis-positions of the platinum(II) center. The assembled structure of 9 can be regarded as a 2:2 M:L dimer, in which the gold(I) centers adopt a slightly distorted T-shaped geometry and are bounded by a nitrogen atom from L5, a carbon atom from C₆F₅, and an adjacent gold(I) ion (Au···Au = 3.301(2) Å). In the dimer, the pyridyl moiety of L5 and the adjacent C₆F₅ ring lie approximately parallel and are separated by 3.58 Å, which is an acceptable distance for π···π stacking interaction [62]. The structures of [RhCl(cod)(L5)] [63], [Au(L5)(PPh₃)] [61], [Au(C₆F₅)₃(L5)n] (n = 2, m = 2; n = 3, m = 1) [61], and [RuCl(L6){[14]aneS₄}]Cl [54] are similar to the above ones.

The reaction of PdCl₂(CH₃CN)₂ and the diferrocene L7 generates the 1:2 M:L complex [PdCl₂(L7)₂] (10, Fig. 10) [64], in which the square planar palladium(II) center is coordinated by the trans nitrogen atoms from two L7 ligands and two chlorine atoms. The two L7 ligands adopt a head-to-head conformation around the palladium(II) center in which the ferrocene groups adopt the anti conformation with respect to the central pyridine ring. The angles between the pyridyl and Cp rings in the complexes with L5–L7 vary between 3.3 and 52.3°. A similar variation is found in the complexes with L8.

L8 is a versatile ligand that coordinates to a variety of metal ions to generate discrete complexes or coordination polymers [11, 65, 66]. In the 2:2 M:L complex [Cu(OAc)₂(L8)]₂ (11, Fig. 11a) [65], one of the two pyrimidine rings shows intermolecular π···π interactions (3.59 Å). The 1:2 M:L complex [Zn(NCS)₂(L8)₂] (12, Fig. 11b) also possesses a dimer-like structure with an effectual π···π interaction between the Cp ring and pyrimidine ring of an adjacent molecule (3.58 Å) [65]. The choice of solvent for the complexion of L8 and [Ni(hfac)₂] is critical; the reaction in diethyl ether generates a 1:2 M:L discrete complex, [Ni(hfac)₂(L8)]₂ (13, Fig. 11c) [67], while the reaction in pentane leads to a zigzag side chain polymer, [Ni(hfac)₂(L8)]ₙ [66], having an M:L ratio of 1:1, regardless of the initial M:L ratio during synthesis. Two L8 ligands in 13 act as monodentate ligands and occupy the cis positions of the nickel(II) center. This contrasts with the result of [Ni(hfac)₂(L8)]ₙ, in which L8 behaves as a bidentate bridging ligand and occupies the trans
positions of the nickel(II) center. The 1:3 M:L complex [Zn(NO$_3$)$_2$(L8)$_3$] (14, Fig. 11d) possesses a five-coordinated distorted square pyramidal zinc(II) center [65], in which two nitrogen atoms from two L8 ligands, two oxygen atoms from two counter anions occupy the equatorial positions, and a nitrogen atom from the remaining L8 occupies the axial position. The 1:4 M:L pinwheel-like complex [Ni(NCS)$_2$(L8)$_4$] (15, Fig. 11e) contains a nickel(II) ion with a distorted octahedral geometry in which four L8 ligands occupy the equatorial position [67], and the two NCS$^-$ groups are in the axial positions. The reaction of cis-Pt(NH$_3$)$_2$Cl$_2$ and L8 in the presence of AgPF$_6$ generates [cis-Pt(NH$_3$)$_2$(L8)$_2$](PF$_6$)$_2$ (16), which transforms to [trans-Pt(NH$_3$)$_2$(L8)$_2$](PF$_6$)$_2$ (17) on heating [68]. The NH$_3$ groups in the crystal of 16-ethanol (Fig. 12a) form intermolecular hydrogen bonds with a non-coordinated nitrogen atom of adjacent L8 and with two oxygen atoms of two ethanol molecules, constructing a quasi-2D structure. The NH$_3$ groups in the crystal of 17·2(CH$_3$)$_2$CO (Fig. 12b) form hydrogen bonds with the oxygen atoms of the solvate molecules. The angles between the pyrimidyl groups and the Cp rings of L8 in 11–17 vary in the range of 0.6 to 44.5°, which provides their coordination complexes with structural variety.

L9 coordinates to a metal ion only via the 4-nitrogen atom of the pyrazine ring, constructing discrete complexes. In the 1:2 M:L complex [Cu(hfac)$_2$(L9)$_2$] (18, Fig. 13a) [67], the geometry around the copper(II) center is a six-coordinate octahedron in which two nitrogen atoms from two L9 ligands occupy the trans positions. A related complex [Cu(NO$_3$)$_2$(L9)$_2$] (19, Fig. 13b) has a square planar copper(II) center coordinated with two trans nitrogen atoms from two L9 ligands [67]. The angles between the pyrazyl and Cp rings of the ligands in 18 and 19 are 3.7 and 26.3°, respectively.

2.1.3. Naphthyridine derivative (L10)

Ferrocenes with 8-naphthyridinyl substituents show unique coordination chemistry with metal ions. L10 can coordinate to metal ions in a monodentate or bidentate chelate fashion to produce a series of unique complexes with various M:L stoichiometries. Metal complexes with L10 are discussed in Bera's review [69]; hence we omit discussion on some of their complexes. The
reaction of PdCl₂(CH₃CN)₂ and L₁₀ generates the 1:1 M:L complex [PdCl₂(L₁₀)] (20) [70], which catalyzes the methoxycarbonylation of styrene; however, the performance in terms of activity and selectivity is very low compared with related complexes. The reaction of [Ir(cod)(L₁₀)]₂BF₄ (21) and CO in CH₂Cl₂ results in the formation of a dimer complex, [IrCl₂(CO)₂(L₁₀)]₂ (22, Fig. 14) [70, 71]. The chlorides are from the solvent molecules. In this complex, the monomer units are linked by an unsupported iridium(II)–iridium(II) bond (2.7121(8) Å).

2.2. N-Heterocyclic ferrocenes that produce metallacycle complexes

Structural formulae of N-heterocyclic ferrocenes producing metallacycle complexes are summarized in Fig. 15. The chemical formulas of their complexes are listed in Table 2. N-heterocycles with a ferrocenyl group attached to the next carbon atom to the nitrogen atom have the ability to produce metallacycle complexes via ortho-metalation (Fig. 16). Some of the complexes show good catalytic activity.

2.2.1. Imidazoline derivatives (L₁₁, L₁₂)

The reactions of ferrocenylimidazoline L₁₁ or L₁₂ and palladium salts in the presence of a base generate chloride-bridged palladacycle dimers [Pd(μ-Cl)(L)]₂ {L = L₁₁’ (23), L₁₂’ (24)} [72, 73], where the prime indicates that the ligand is deprotonated at the α-carbon atom of the ferrocenyl moiety; hereinafter the same meaning is applied. Although their crystal structures have not been determined, their PPh₃ adducts [PdCl(L)PPh₃] {L = L₁₁’ (25), L₁₂’ (26, Fig 17)} have been crystallographically characterized [72]. They are stable in air and moisture, which offers advantages to catalytic processes. The coordination geometries around the palladium(II) centers of 25 and 26 are similar to each other, where the phosphine atom is trans to the nitrogen atom.

23 has been employed for aza-Claisen rearrangement of N-p-methoxyphenylbenzimidate to generate N-allyl-N-(p-methoxyphenyl)benzamide [74]. The complex catalyzes the coupling reaction of 4-bromotoluene and phenylboronic acid to give 4-methy-1,1’-biphenyl. The reaction is achieved at low catalyst loading and short reaction time; however, a high temperature is required. 26 activates
the C–Cl bond in aryl chlorides and is employed as the catalyst for the coupling reaction of 4-nitrochlorobenzene and phenylboronic acid in aqueous media to give 4-nitro-1,1′-biphenyl [71]. This catalyst, however, requires a higher temperature and longer reaction time than the water soluble Pd(II)–diimine catalyst [75].

2.2.2. Pyridine and pyrimidine derivatives (L13–L15)

L13 usually behaves as a monodentate ligand and generates discrete metal complexes; however, their crystal structures have not been reported to the best of our knowledge. In contrast, many metallacycle complexes with L13′ have been crystallographically studied. The reaction of L13 with Li2PdCl4 generates a 1:2 M:L complex [PdCl2(L13)2] (27) [60]. When a similar reaction is carried out in the presence of NaOAc, ortho-metalation occurs at the Cp ring, and a 2:2 M:L chloride-bridged palladacycle dimer [Pd(μ-Cl)(L13′)]2 (28) is generated [76]. 28 is the precursor of palladacycle complexes [PdCl(L13′)PPh3] and [Pd(acac)(L13′)] [76]. The reaction of L13 and a polymeric complex [RuCl2(CO)2]n in the presence of Na2CO3 leads to the formation of a 2:2 M:L chloride-bridged ruthenocycle dimer complex, [Ru(μ-Cl)(L13′)(CO)2]2 (29, Fig. 18) [77, 78], which has a planar chirality at the ruthenocycle. The two ruthenocycle units in 29 are perpendicular to each other. This contrasts with other relevant complexes such as cis-[Ru(μ-Cl)(ptpy)(CO)2]2, in which the ruthenocycle units show a parallel arrangement [79]. 29 is also a precursor of related complexes, [PPN][RuCl2(L13′)(CO)2] and [Ru(N^N)(L13′)(CO)2] (N^N = chiral bidentate ligands) [77].

A palladacycle complex [PdCl(L14′)(iPrNHC)] (30, Fig. 19) [80], having the advantage of being air-stable, has been tested as a catalyst for both the Suzuki coupling and the Buchwald–Hartwig amination reactions in a PEG media. High activities have been observed when high temperatures and long reaction time are applied. The catalyst can be recycled and reused three times without lessening of activity.

The reactivity and structure of a palladacycle dimer [Pd(μ-Cl)(L15′)]2 (31) are similar to that found in 28 [81]. In 31, one of the two nitrogen atoms of the pyrimidine ring remains vacant. The
complex is a precursor for several phosphine complexes, such as \([\text{PdCl(L15')}](P\text{-donor})\) \(P\text{-donor} = \text{PPh}_3, \text{PCy}_3, \text{PCy}_2(2\text{-biphenyl}), \text{dcpab} (32, \text{Fig. 20})\) [81]. The coordination environment around the metal center of 32 is similar to that in 26. Compound 32 shows a catalytic activity for the Buchwald–Hartwig amination, catalyzing the coupling of 2-chloroanisole and 2,5-dimethylaniline.

2.2.3. Bipyridine, quinoline, and phenanthroline derivatives (L16–L19)

Many ferrocenyl-bipyridine derivatives and their metal complexes have been prepared; however, their crystal structures are rather limited [82–85].

L16 undergoes an ortho-metalation when reacted with PdCl\(_2\)(cod), and subsequently produces a 1:1 M:L palladacycle complex, \([\text{PdCl}(L16')]\) (33) [86], in which L16' behaves as a CNN ligand. Although ortho-metalation generally requires a base to remove the \(\alpha\) proton, this reaction proceeds without a base. When treated with \(\tau\)-BuNC, 33 produces \([\text{Pd}(L16')(\tau\text{-BuNC})]\text{Cl} (34)\) [87], showing no successive isocyanide insertion (Fig. 21). The reaction of PdCl\(_2\)(cod) and L17 affords a 1:1 M:L palladacycle complex, \([\text{PdCl}(L17')]\) (35, Fig. 22) [86]. In 35, the ferrocenyl rings adopt a synclinal conformation and the two bipyridine rings are approximately parallel to each other. One of the two bipyridyl groups is nearly planar and coordinates to a square planar palladium(II) ion in a CNN fashion, while the other is twisted and without coordination.

L18 acts as a bidentate ligand in the 1:1 M:L complex \([\text{ZnCl}_2(L18)]\) (36, Fig. 23) [88], which exhibits a metallacycle structure. The ligand coordinates to the zinc(II) ion via the nitrogen atom of the quinoline ring and a carbon atom of the Cp ring, where the Zn–C distance is 2.407(2) Å. The metal center adopts a distorted tetrahedral coordination geometry. The spacing between adjacent naphthalene rings is 3.39 Å, which falls within a \(\pi\cdots\pi\) interaction distance.

The reaction of Pd(OAc)\(_2\) and L19 in the presence of CF\(_3\)CO\(_2\)H affords a palladacycle complex, \([\text{Pd(O}_2\text{CCF}_3)(L19')]\) (37, Fig. 24) [89]. This complex is used for the preparation of \([\text{Pd}(L19')(\text{MeCN})]\text{PF}_6, [\text{Pd}(L19')(\text{PPh}_3)](\text{O}_2\text{CCF}_3)\text{Cl}, \text{and }\{[\text{Pd}(L19')]_2(\mu-P\text{P})](\text{O}_2\text{CCF}_3)\text{Cl}\) \(P\text{P} = \text{dppe, dppp})\), owing to the lability of the CF\(_3\)CO\(_2\) anion. The reaction of K\(_2\)PdCl\(_4\) and L19 generates the palladacycle complex \([\text{PdCl}(L19')]\) (38) [90]. The coordination geometries around the metal
centers in 37 and 38 are similar to each other.

2.3. *N*-Heterocyclic ferrocenes that produce chelate complexes

Structural formulae of *N*-heterocyclic ferrocenes producing chelate complexes are summarized in Fig. 25. The chemical formulas of their complexes are listed in Table 3. These complexes have been studied mainly in terms of structural chemistry; however, several metal complexes with polypyridinyl ferrocenes have been employed for DNA binding and DNA photocleavage reagents.

2.3.1. Pyrazole and triazole derivatives (L20–L23)

The heptanuclear wheel-like complex [Ni7(OH)4(L20)8](ClO4)2·6CH3CN (39, Fig. 26) is obtained by the reaction of L20 and Ni(ClO)4·6H2O in the presence of a base [91]. This complex is composed of nickel(II) ions with four different types of coordination geometries, including a NiN2O4 octahedron, a NiN3O octahedron, two NiN2O2 square pyramids, and two NiN3O square planes. The NiN2O4 octahedron is located at the center of the wheel, while the other nickel(II) ions are linked by six L20 ligands to construct a macrocycle. The temperature dependence of the magnetic susceptibility shows the presence of antiferromagnetic interactions (θ = −22.5 K) between the nickel(II) ions.

An *N*-alkylated ligand L21 has been obtained by the treatment of L20 with NaH and BrCH2COOC2H5. The reaction of L21 and Mo(CO)4(piperidine)2 affords the 1:1 M:L complex [Mo(CO)4(L21)] (40, Fig. 27), in which the ligand coordinates to the molybdenum(0) center in an NN bidentate chelate fashion [92].

A tridentate ligand L22 can be prepared from L2. The reaction of L22 and Fe(BF4)2·6H2O in acetonitrile affords a pentanuclear complex, [Fe(L22)2](BF4)2·3CH3CN (41, Fig. 28) [93]. The coordination geometry around the iron(II) center is a highly distorted octahedron, in which L22 occupies the meridional positions of the iron(II) ion. The Fe–N lengths of the complex are relatively long, being characteristic for a high spin state of iron(II) ion. The complex does not show a spin
conversion even at low temperature, owing to the distorted geometry that stabilizes the high spin state.

A nitrogen-rich ligand L23 acts as a chemical sensor for toxic heavy metal ions [94]. Addition of cadmium(II), lead(II), and mercury(II) to an acetonitrile solution of L23 increases the half-wave redox potential \( E_{1/2} \) of the ferrocenyl moiety. The reaction of L23 with Zn(OTf)\(_2\) yields the 1:2 M:L complex [Zn(OTf)\(_2\)(L23)\(_2\)]·CHCl\(_3\) (42, Fig. 29) [94], in which the distorted octahedral zinc(II) ion is coordinated with four equatorial nitrogen atoms from two L23 and axial oxygen atoms of OTf\(^-\) anions.

2.3.2. Bipyridine and pyrimidine derivatives (L16, L24)

As described above, L16 can act as NN-bidentate chelate and CNN-tridentate ligands. The 1:2 M:L complex [Co(L16)\(_2\)(CH\(_3\)CN)\(_2\)](OTf)\(_2\) (43, Fig. 30) possesses an octahedral cobalt(II) center coordinated by two L16 ligands in a chelate fashion and two acetonitrile molecules occupying the cis positions [95].

The complexes [Cu(2,9-dianthryl-1,10-phenanthroline)(L24)]BF\(_4\) (R = p-tolyl, 1-naphthyl, 9-anthracenyl, and t-butyl) (44) contain a tetrahedral copper(I) center coordinated with two bulky ligands in a chelate fashion [96, 97]. In the solution state, the ferrocene group in 44 is located near the copper(I) center in the neutral state (Fig. 31a), whereas it is placed far away from the copper(I) center in the oxidized state owing to the electrostatic repulsion between the copper(I) center and the ferricinium moiety (Fig. 31b). Therefore, these complexes exhibit redox-driven conformational switching, which may further lead to interesting molecular functions.

2.3.3. Terpyridine and polypyridine derivatives (L25, L26)

Similar to the ferrocenyl-bipyridine derivatives, several positional isomers of ferrocenyl-terpyridine derivatives have been prepared [84, 98]; however, only L25 has been extensively studied as a ligand [99–101]. The 1:1 M:L complex [Cu(dppez)(L25)](ClO\(_4\))\(_2\) (45) shows DNA binding and photoinduced DNA cleavage activities [102]. The analogues [M(N^N)(L25)]X\(_2\)
(M = Cu, N^N = dppz, X = ClO₄⁻ (46, Fig. 32) [102]; M = Cu, N^N = bpy, X = BF₄⁻ (47) [103]; M = Cu, N^N = phen, X = ClO₄⁻ (48) [104]; M = Zn, N^N = phen, X = ClO₄⁻ (49) [105]; M = VO, N^N = bpy, X = PF₆⁻ (50) [106]) have been crystallographically characterized. 46 has a distorted square pyramidal copper(II) center. In 46, L₂₅ and one of the two pyrido nitrogen atoms of dppz occupy the equatorial plane of the metal center, while the remaining pyrido nitrogen atom is located at the axial position. The coordination geometries around the metal centers of 47–50 resemble that of 46. In 50, the coordination geometry of vanadium(IV) is approximately octahedral, in which the three nitrogen atoms from L₂₅ occupy the meridional positions. L₂₅ can also coordinate to three different metal ions using its three pyridyl nitrogen atoms. The reaction of three equivalents of Au(C₆F₅)(THF) and L₂₅ affords a 3:1 M:L complex, [{Au(C₆F₅)}₃(L₂₅)] (51, Fig. 33) [107], in which the three pyridyl nitrogen atoms coordinate to three different gold(I) ions. The three gold(I) ions are linked by L₂₅ and aurophilic interactions of themselves, in which the central gold(I) ion adopts a distorted square planar coordination and the outer two gold(I) ions adopt a T-shaped coordination geometry. The outer two pyridyl nitrogen atoms point in almost opposite directions.

The polypyridine ligand L₂₆ may behave as either a multidentate or a bridging ligand to produce complexes with 1:1, 2:2, and 2:1 M:L ratios. The 2:2 M:L complex [Ag(L₂₆)]₂(OTf)₂ (52, Fig. 34) has a double-helical structure in which the two silver(I) ions have different coordination environments [108]. One is an elongated trigonal bipyramid, and the other has a geometry intermediate between tetrahedron and square plane. The distance between the silver(I) ions is 3.089(2) Å, which is an acceptable distance for argentophilic interactions [109–111]. A similar double-helical structural motif is found in [M(solv)(L₂₆)]₂(PF₆)₆ [112] [M = Cu, solv = none, n = 3 (53, Fig. 35a); M = Ni, solv = H₂O, n = 4 (54)], in which one of the two metal centers adopts a six-coordinate geometry and the other shows a four coordinate geometry. The six- and four-coordinate metal centers in 53 are copper(II) and copper(I) ions, respectively; thus the complex is in a mixed valence state. The metal centers in 1:1 M:L complexes [M(H₂O)₂(L₂₆)](PF₆)₂ [M = Fe (55), Co (56)] (Fig. 35b) adopt a hepta-coordinate geometry [113], which is occupied by five nitrogen atoms from L₂₆ and two oxygen atoms from two water molecules. A helical complex
[Ru₂Cl(L25)_2(L26)](PF₆)_3 (57, Fig. 35c) includes two different six-coordinate ruthenium(II) centers [112]. One of the two ruthenium centers is coordinated by three nitrogen atoms from L25 and three nitrogen atoms from L26, while the other is surrounded by two nitrogen atoms from L25, three nitrogen atoms from L26 and a chloride anion.

2.3.4. Hydroxyquinoline and phenanthroline derivatives (L27, L19)

The reaction of hydroxyquinoline derivative L27 and metal salts produces [M(L27)_2(H₂O)_2] [M = Ni (58), Cu (59)] [113]. They adopt a six-coordinate octahedral geometry, in which two nitrogen atoms and two phenoxy oxygen atoms are from the ligands and two oxygen atoms are from two coordinated water molecules.

The reaction of phenanthroline derivative L19 and a palladium(II) salt produces a complex with chelate bidentate or CNN tridentate coordination modes depending on experimental conditions. A chelate complex [PdCl₂(L19)] is obtained by the reaction of L19 and PdCl₂(cod) [86], while the palladacycle complex [PdCl(L19')] (38) is generated by the reaction of L19 and K₂PdCl₄ [90]. The treatment of [PdCl(CH₃)(L19)] (60) with AgPF₆ in CH₃CN leads to the formation of [Pd(CH₃)(CH₃CN)(L19)] (61) [89], which shows excellent catalytic activity in the Heck reaction of iodobenzene and methylacrylate to afford methyl-trans-cinnamate.

2.4. N-Heterocyclic ferrocenes that produce macrocyclic complexes

Structural formulae of N-heterocyclic ferrocenes producing macrocyclic complexes are summarized in Fig. 36. The chemical formulae of their complexes are listed in Table 4. 1,1'-Bis substituted ferrocenes with N-heterocycles of six-membered rings and condensed aromatic rings are likely to adopt the syn conformation and therefore afford discrete metal complexes, although they are capable of adopting other conformations. This is associated with the intramolecular π···π interaction between the N-heterocyclic rings.

In 1,1'-bis substituted ferrocenes, the torsion angle τ is used to express the conformation, which is defined as the torsion angle of X¹⁻Cp¹⁻Cp²⁻X², where X¹ and X² are carbon atoms bonded
to \(N\)-heterocycles, and \(\text{Cp}^1\) and \(\text{Cp}^2\) are the centroids of the \(\text{Cp}\) rings (Fig. 37) [11]. The variety of torsion angles of the ferrocene backbone provides \(N\)-heterocyclic ferrocene complexes with structural versatility.

2.4.1 Pyrazole derivative (L1)

The reaction of \(L1\cdot\text{H}\) and \([\text{Rh}(\mu-\text{Cl})(\text{cod})]_2\) in the presence of a base generates the macrocyclic complex \([\text{Rh}(\mu-L1)(\text{cod})]_2\) (62, Fig. 38) [114]. The complex adopts a head-to-tail structure in which the –\(\text{Rh}–N–N–\text{Rh}–N–N–\) metallacycle exhibits a boat conformation.

2.4.2. Pyridine and pyrazine derivatives (L28-L31)

Ditopic ligands \(L28\) and \(L29\) show either chelating or bridging coordination modes to construct 2:2, 1:1, and 2:1 M:L complexes. The 2:2 M:L dimeric complex \([\text{Ag}(\mu-\text{ClO}_4)(L28)]_2\) (63, Fig. 39a) contains two \(\text{Ag}(L28)\) units which are linked by two \(\text{ClO}_4^-\) counter anions [115]. The \(L28\) ligand in 63 adopts a synclinal conformation \((\tau = 84.2^\circ)\) and coordinates to silver(I) ion with the \textit{trans} chelating mode \((N–\text{Ag}–N = 163.1^\circ)\). The \(L28\) ligand in 1:1 M:L \([\text{Pd}(\text{CH}_3\text{Cl})(L28)]\) (64, Fig. 39b) adopts a synclinal conformation \((\tau = 0.4^\circ)\) and chelates to palladium(II) ion in the \textit{cis} mode \((N–\text{Pd}–N = 84.5^\circ)\) [116]. The complex shows C=O insertion into the \(\text{Pd}–\text{CH}_3\) bond to generate \([\text{Pd}(\text{COCH}_3\text{Cl})(L28)]\) (65) [116]. The coordination chemistries of octamethylated \(L29\) are similar to those of \(L28\). The ligand conformations in 2:1 M:L \([\text{Cu}(L29)][\text{CuCl}_2]\) (66, Fig. 39c) and 1:1 M:L \([\text{Cu}(L29)]\text{BF}_4\) (67) are similar to that in 61 [117,118] In contrast to 63 and 64, in the 2:1 M:L complex \([\{\text{PtCl}_2(\text{C}_2\text{H}_4)\}_2(\mu-L28)]\) (68, Fig. 39d) [116], \(L28\) bridges metal ions. The two pyridine rings of \(L28\) in the complex lie approximately parallel and are separated by 3.65 Å, which is an acceptable distance for \(\pi\cdots\pi\) interactions. The molecular structure of 2:1 M:L \([\{\text{PtCl}_2(\text{C}_2\text{H}_4)\}_2(\mu-L29)]\) (69) is almost identical to that of 68 [118].

\(L30\) cannot chelate to a metal ion and has a tendency to adopt the \textit{syn} conformation, causing its complex to form 2:2 M:L metallomacrocyclic structures. Indeed, coordination polymer complexes containing \(L30\) with an \textit{anti} conformation have not been reported. In the
metallomacrocycle \([\text{AgNO}_3(L30)]_2\cdot1.5\text{H}_2\text{O (70, Fig. 40a) [119, 120]}, \) the two pyridine rings of \(L30\) are in a face-to-face orientation, with the distance between the two pyridine rings being 3.44 Å. The silver(I) ions are coordinated in a highly distorted tetrahedral geometry by two nitrogen atoms from two \(L30\) ligands and two oxygen atoms from the \(\text{NO}_3^-\) anion. One of the two anions links adjacent macrocyclic units. The macrocyclic complex \([\text{Zn(OAc)}_2(L30)]_2 (71, \text{Fig. 40b})\) contains two zinc(II) ions with a distorted square pyramidal geometry and two \(L30\) ligands with a synperiplanar conformation \((\tau = 3.6^\circ) [119]\). Two of the four OAc\(^-\) anions bridge the two zinc(II) ions in the macrocycle with a monoatomic \(\mu^2\)-bridging mode, while the others coordinate to the ions with a monodentate \(\text{syn}\) fashion. The crystal structure of \([\text{Cd(OAc)}_2(L30)]_2 \cdot \text{CH}_3\text{OH} \cdot 0.5\text{C}_6\text{H}_6 (72)\) is somewhat similar to that of \(71 [119].\) The butterfly shaped complex \([\text{ZnCl}_2(L30)]_2 (73, \text{Fig. 40c})\) is composed of two zinc(II) ions with a tetrahedral geometry and two \(L30\) ligands with a synclinal conformation \((\tau = 35.1^\circ) [119, 120].\) In \(70–72,\) the pyridine rings in \(L30\) are approximately parallel and are twisted with respect to the attached Cp rings by 3.5–14.8\(^\circ\). Comparison of the zinc(II) complexes \(71\) and \(73\) reveals the correlation between the Zn···Zn and Fe···Fe distances and the conformation of \(L30.\) The Zn···Zn and Fe···Fe distances of \(71\) with a synperiplanar \(L30\) are 3.9 and 15.0 Å, respectively, whereas those of \(73\) with a synclinal \(L30\) are 6.1 and 11.9 Å, respectively.

The 1,1′-di-substituted ligand \(L31\) tends to adopt the synperiplanar conformation, probably owing to an intramolecular π···π interaction between the two pyrazine rings. The pyrazine rings in \(L31\) may lie in the same direction or different directions; hence the ligand can afford macrocyclic or polymer complexes when reacted with metal salts. The copper(I) complex \([(\text{CuI})_2(L31)]_2 \cdot L31 (74, \text{Fig. 41a})\) contains a ladder-like \((\text{CuI})_2(L31)_2\) unit and a free \(L31 [121].\) The ladder-like unit consists of three \((\text{CuI})_2\) cyclic units and two \(L31\) ligands with a synperiplanar conformation. In the crystal, the free \(L31\) adopts an antiperiplanar conformation and occupies the space between the ladder-like units. The reaction of Ag\(X\) and \(L31\) affords a series of metallomacrocycles \([\text{AgX}(L31)]_2\cdot(\text{solv}) [X = \text{ClO}_4^-, \text{solv} = 2\text{C}_6\text{H}_6 (75, \text{Fig. 41b}); X = \text{ClO}_4^-, \text{solv} = \text{none}; X = \text{NO}_3^-, \text{solv} = \text{C}_6\text{H}_6; X = \text{NO}_3^-, \text{solv} = \text{PhCl}; X = \text{NO}_3^-, \text{solv} = \text{PhCH}_3; X = \text{PF}_6^-, \text{solv} = \text{none}]\) with various Ag···Ag distances [121]. The macrocyclic unit in \(75\) is composed of two silver(I) ions with a highly distorted tetrahedral
geometry, which are bridged by the two $\text{L31}$ ligands and two counter anions, constructing a paddle-windmill-like structure. The other macrocyclic complexes exhibit almost identical structures. The Ag···Ag distances in these units can be changed by changing the counter anions ($\text{PF}_6^−$ = ca. 3.4 Å; $\text{ClO}_4^−$ = ca. 3.4–3.3 Å; $\text{NO}_3^−$ = ca. 3.2 Å). The difference in the Ag···Ag distances between the $\text{ClO}_4^−$ and $\text{NO}_3^−$ complexes is ascribable to the differences in the negative charge density on the oxygen atoms of the counter anions.

2.4.3. Quinoline and naphthyridine derivatives ($\text{L32, L33}$)

The 1,1-disubstituted ligand $\text{L32}$ acts as a tridentate ligand in $\left[\text{ZnCl(}\text{L32}\text{)}\right]_2\text{[Zn}_2\text{Cl}_6\text{]}$ (76, Fig. 42) [122], with the ligand coordinating to a zinc(II) ion by the two nitrogen atoms of the quinoline rings and the iron(II) atom in the ferrocenyl group. The complex consists of two 1:1 M:L cation $\left[\text{ZnCl(}\text{L32}\text{)}\right]^+$ units and a dianion $\left[\text{Zn}_2\text{Cl}_6\right]^{2−}$ unit. The zinc(II) center in the cation adopts a distorted tetrahedral geometry and is coordinated by $\text{L32}$ in a tridentate fashion and by a chlorine atom. The zinc(II)–iron(II) distance is 2.562(1) Å. The ferrocenyl moiety adopts a synclinal conformation.

The tetramer complex $\left[\text{ZnCl}_2(\text{L33})\right]_4$ (77, Fig. 43) possesses a macrocyclic structure [123, 124], in which $\text{L33}$ behaves as a bridging ligand and adopts a synclinal conformation ($τ = 2.5°$). In 77, the two naphthyridine rings of $\text{L33}$ form $\pi$···$\pi$ interactions (3.37 Å) and coordinate to two different zinc(II) ions with the nitrogen atoms far from ferrocene group. The reaction of $\text{Cu(CH}_3\text{CN})_4\text{ClO}_4$ and $\text{L33}$ affords complexes with various M:L stoichiometries $\left[\text{Cu(}\text{L33}\text{)}\right]_2(\text{ClO}_4)_2$ (78), $\left[\text{Cu(}\text{L33}\text{)}\right]\text{ClO}_4$ (79), and $\left[\text{Cu}_2(\text{ClO}_4)_2(\text{L33})\right]\text{ClO}_4$ (80) [123, 124], depending on the initial ratio of M:L. The crystal structure of 78·4CH$_3$NO$_2$ reveals that it adopts a 2:2 M:L macrocyclic structure (Fig. 44a), in which the copper(I) ions show a linear coordination geometry occupied by two nitrogen atoms farthest from the ferrocene groups of two $\text{L33}$ ligands. The intramolecular Cu···Cu distance is 3.27 Å, suggesting no significant interaction between them. In the complex, the ferrocenyl moiety adopts a synclinal conformation ($τ = 3.7°$) and the two naphthyridine rings of $\text{L33}$ stack in a head-to-head orientation (3.53 Å). 80 shows a 2:1 M:L macrocyclic structure (Fig. 44b), in which one of the copper(I) ions, coordinated by the nitrogen atoms near the ferrocenyl group of
L33, adopts a nearly linear geometry. The other copper(I) ion has a T-shaped coordination geometry, surrounded by two nitrogen atoms farther from the ferrocenyl group in L33 and a oxygen atom from the ClO$_4^-$ anion. There is no significant interaction between the copper(I) ions (2.47 Å). L33 adopts a synclinal conformation (τ = 80.2°) in the complex.

3. Summary and future outlook

The structural aspects of N-heterocyclic ferrocene complexes have been discussed in detail in this review. Many N-heterocyclic ferrocenes have been known for years; however, it is only rather recently that they have been exploited as ligands and chemical sensors. These N-heterocyclic ferrocenes show interesting coordination chemistry, in which they act as monodentate, bidentate, multidentate, or bridging ligands depending mainly on the ligand design, namely the size, shape, and number of nitrogen atoms of the N-heterocycles. In addition, we have briefly discussed applications of these complexes for catalysts and redox-driven conformational switching.

In the future, the design and use of ferrocene derivatives bearing nitrogen-rich N-heterocycles will in future become a more active area because of their potential to produce metallacycle and hetero-polynuclear complexes with unique properties. As described above, such complexes have played roles in many important areas from catalysis chemistry to material chemistry. In addition, the development of redox-switchable materials, such as electrochromic dyes, or catalysts which can be tuned “on/off” by an external potential, is also an interesting research target.

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References


J.R. Wright, K.J. Shaffer, C.J. McAdam, J.D. Crowley, Polyhedron 36 (2012) 73–78.


Table 1

Metal complexes with monodentate N-heterocyclic ferrocenes.

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### Table 2

Metallacycle complexes from N-heterocyclic ferrocenes.

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Table 3
Chelate complexes with N-heterocyclic ferrocenes.

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<td>[Ag(L26)]₂OTf</td>
<td>34</td>
<td>[108]</td>
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<tr>
<td>53</td>
<td>[Cu(L26)]₂PF₆₃</td>
<td>35a</td>
<td>[112]</td>
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<tr>
<td>54</td>
<td>[Ni(H₂O)(L26)]₂PF₆₄</td>
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<tr>
<td>55</td>
<td>[Fe(H₂O)₂(L26)]PF₆₂</td>
<td>35b</td>
<td>[113]</td>
</tr>
<tr>
<td>56</td>
<td>[Co(H₂O)₂(L26)]PF₆₂</td>
<td>-</td>
<td></td>
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<tr>
<td>57</td>
<td>[Ru₂Cl₂(L25)₂(L26)]PF₆₃</td>
<td>35c</td>
<td>[112]</td>
</tr>
<tr>
<td>58</td>
<td>[Ni(L27)₂(H₂O)₂]</td>
<td>-</td>
<td>[113]</td>
</tr>
<tr>
<td>59</td>
<td>[Cu(L27)₂(H₂O)₂]</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>[PdClCH₃(L19)]</td>
<td>-</td>
<td>[89]</td>
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<tr>
<td>61</td>
<td>[Pd(CH₃)(CH₃CN)(L19)]</td>
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Table 4

Macro cyclic complexes with \(N\)-heterocyclic ferrocenes.

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<th>Number</th>
<th>Complex</th>
<th>Figure</th>
<th>Reference</th>
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<tr>
<td>62</td>
<td>([\text{Rh}(\mu-L1)(\text{cod})]_2)</td>
<td>38</td>
<td>[114]</td>
</tr>
<tr>
<td>63</td>
<td>([\text{Ag}(\mu-\text{ClO}_4)(L28)]_2)</td>
<td>39a</td>
<td>[115]</td>
</tr>
<tr>
<td>64</td>
<td>([\text{Pd}(\text{CH}_3)\text{Cl}(L28)])</td>
<td>39b</td>
<td>[116]</td>
</tr>
<tr>
<td>65</td>
<td>([\text{Pd}(&lt;\text{COCH}_3)\text{Cl}(L28)])</td>
<td>-</td>
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<tr>
<td>66</td>
<td>([\text{Cu}(L29)][\text{CuCl}_2])</td>
<td>39c</td>
<td>[117,118]</td>
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<tr>
<td>67</td>
<td>([\text{Cu}(L29)]\text{BF}_4)</td>
<td>-</td>
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<tr>
<td>68</td>
<td>([{\text{PtCl}_2(\text{C}_2\text{H}_4)}_2(\mu-L28)])</td>
<td>39d</td>
<td>[116]</td>
</tr>
<tr>
<td>69</td>
<td>([{\text{PtCl}_2(\text{C}_2\text{H}_4)}_2(\mu-L29)])</td>
<td>-</td>
<td>[118]</td>
</tr>
<tr>
<td>70</td>
<td>([\text{AgNO}_3(L30)]_2\cdot1.5\text{H}_2\text{O})</td>
<td>40a</td>
<td>[119,120]</td>
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<tr>
<td>71</td>
<td>([\text{Zn(OAc)}_2(L30)]_2)</td>
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<td>[119]</td>
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<td>72</td>
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<td>73</td>
<td>([\text{ZnCl}_2(L30)]_2)</td>
<td>40c</td>
<td>[119,120]</td>
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<tr>
<td>74</td>
<td>([{\text{CuI}}_2(L31)]_2\cdot L31)</td>
<td>41a</td>
<td>[121]</td>
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<td>75</td>
<td>([\text{AgX}(L31)]_2\cdot2\text{C}_6\text{H}_6)</td>
<td>41b</td>
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<td>76</td>
<td>([\text{ZnCl}(L32)]_2[Zn_2\text{Cl}_6])</td>
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<td>[122]</td>
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<td>[123,124]</td>
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<td>78</td>
<td>([\text{Cu}(L33)]_2(\text{ClO}_4)_2)</td>
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<tr>
<td>79</td>
<td>([\text{Cu}(L33)]\text{ClO}_4)</td>
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<td>80</td>
<td>([\text{Cu}_2(\text{ClO}_4)(L33)]\text{ClO}_4)</td>
<td>44b</td>
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</table>
Figure Captions

Fig. 1. Representative $N$-heterocycles that are used as substituents to ferrocenes.

Fig. 2. Conformational flexibility of ferrocene rings and $N$-heterocycles (e.g. 1,1’-bis(2-pyridyl)ferrocene).

Fig. 3. Possible coordination modes of $N$-heterocyclic ferrocenes.

Fig. 4. $N$-Heterocyclic ferrocenes that adopt monodentate coordination.

Fig. 5. 1D hydrogen bonding network structure of 1. Dotted lines indicate hydrogen bonds. Hydrogen atoms bonded to carbon atoms are omitted for clarity, similarly hereinafter.

Fig. 6. (a) 1D hydrogen bonding network structure of 2a, (b) molecular structure of 3, and (c) 1D hydrogen bonding network structure of 4. Dotted lines indicate hydrogen bonds.

Fig. 7. Molecular structure of 5.

Fig. 8. Schematic illustration of the complexation of ferrocenyltriazole and $\beta$-cyclodextrin.

Fig. 9. Molecular structures of (a) 7, (b) 8, and (c) 9. Dotted line indicates Au···Au aurophilic interactions.

Fig. 10. Schematic drawing of the molecular structure of 10.

Fig. 11. Molecular structures of (a) 11, (b) 12, (c) 13, (d) 14, and (e) 15.

Fig. 12. Molecular structures of (a) 16-ethanol and (b) 17·2(CH$_3$)$_2$CO. Solvate molecules are also shown. Dotted lines indicate hydrogen bonds.

Fig. 13. Molecular structures of (a) 18 and (b) 19.

Fig. 14. Molecular structure of 22.

Fig. 15. $N$-Heterocyclic ferrocenes that produce metallacycle complexes.

Fig. 16. Ortho-metalation of $N$-heterocyclic ferrocenes.
Fig. 17. Molecular structure of 26.

Fig. 18. Molecular structure of 29.

Fig. 19. Molecular structure of 30.

Fig. 20. Molecular structure of 32.

Fig. 21. Formation of 34 from 33 and t-BuNC.

Fig. 22. Molecular structure of 35.

Fig. 23. Molecular structure of 36.

Fig. 24. Molecular structure of 37.

Fig. 25. N-Heterocyclic ferrocenes that produce chelate complexes.

Fig. 26. Molecular structure of 39. Coordination geometries around the nickel ions are highlighted.

Fig. 27. Molecular structure of 40.

Fig. 28. Molecular structure of 41. Counter anions and solvent molecules are omitted for clarity.

Fig. 29. Molecular structure of 42. Solvent molecules are omitted for clarity.

Fig. 30. Molecular structure of 43. Counter anions are omitted for clarity.

Fig. 31. Redox-driven conformational change of 44: (a) neutral and (b) oxidized states.

Fig. 32. Molecular structure of 46. Counter anions are omitted for clarity.

Fig. 33. Molecular structure of 51.

Fig. 34. Schematic drawing of the molecular structure of 52. Dashed line indicates Ag···Ag argentophilic interactions.

Fig. 35. Schematic drawing of the molecular structures of (a) 53, (b) 55 and 56, and (c) 57.
**Fig. 36.** $N$-Heterocyclic ferrocenes that produce macrocyclic complexes.

**Fig. 37.** Schematic illustrations of the torsion angle $\tau$ and conformational flexibility of 1,1′-disubstituted ferrocenes.

**Fig. 38.** Molecular structure of 62.

**Fig. 39.** Molecular structures of (a) 63 and (b) 64, (c) 66, and (d) 68. Dotted line indicates weak Ag···O interactions.

**Fig. 40.** Molecular structures of (a) 70, (b) 71, and (c) 73. Solvent molecules are omitted for clarity. Dotted lines indicate weak Ag···O interactions.

**Fig. 41.** Molecular structures of (a) 74 and (b) 75. Solvent molecules are omitted for clarity. Dotted lines indicate weak Ag···O interactions.

**Fig. 42.** Molecular structure of 76. Counter anions are omitted for clarity.

**Fig. 43.** Molecular structure of 77.

**Fig. 44.** Molecular structures of (a) 78·4CH$_3$NO$_2$ and (b) 80. Solvent molecules and non-coordinated counter anions are omitted for clarity.