

Functional pyrazolylpyridine ligands in the design of metal complexes with tunable properties

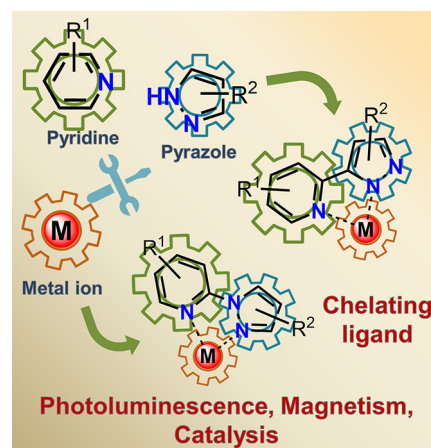
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(1*H*-Pyrazolyl)pyridines are highly demanded ligands in coordination chemistry. Compounds of this class are analogues of 2,2'-bipyridine ligands. They possess a number of benefits such as ready availability and the ease of synthesis. They can function as bridging counter-ions because of deprotonation of the NH group. This review summarizes the general methods for the synthesis of pyrazole derivatives substituted with pyridine in position 1 or 3(5). The approaches to the preparation of (1*H*-pyrazolyl)pyridine ligands, arranged according to the type of coordination, are integrated and analyzed. The coordination compounds of various metals, including noble and coinage metals, formed on the basis of these ligands, are described. It was shown that the structure of pyrazolylpyridine determines the photophysical and chemical properties of the metal complex. The results can be used to establish the functional ligand — structure of the complex — property relationships.

The bibliography includes 119 references.

Keywords: pyridine-pyrazole, 2-(1*H*-pyrazol-3-yl)pyridine, 2-(1*H*-pyrazol-1-yl)pyridine, coordination chemistry, photoluminescence, cyclometallated complexes, pyrazolate complexes.



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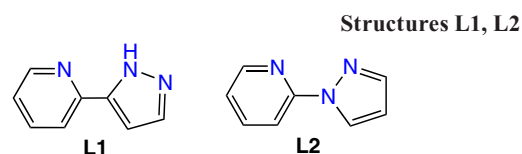
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1. Introduction

Five-membered nitrogen-containing heterocycles are frequently used ligands in the coordination chemistry. Among azole systems, an important place belongs to pyrazoles containing nitrogen atoms in adjacent positions. The interest in pyrazoles is due to the fact that they can act as counter-ion bridging ligands in the deprotonated form. This opens up the way to convert them to neutral mono-, bi-, or polynuclear metal complexes and cyclic coordination compounds.^{1–4} By functionalization of the starting ligand, it is possible to tune the properties of the metal complex based on this ligand.^{5–7} An example of pyrazole-derived chelating ligands are pyrazolylpyridines. The structure and coordination properties of compounds of this class are similar to those of 2,2'-bipyridine ligands, but they have a number of advantages. First, owing to rather simple methods of synthesis of pyrazolylpyridines, it is possible to vary the steric and electronic factors and thus to influence the structure and properties (photophysical, magnetic, catalytic, *etc.*) of metal complexes. Second, the possibility of obtaining neutral complexes is useful, for example, for the production of thin films for organic light-emitting diodes (OLEDs).

The development of pyrazolylpyridine chemistry is closely related to luminescent noble metal complexes,^{8,9} including those designed for the use as chemosensors.¹⁰ The greater part of publications in which these ligands are described address ruthenium,¹¹ osmium, iridium^{12–18} and platinum complexes.¹⁹ In recent years, there was increasing interest in pyrazolylpyridine complexes with rare earth metals and group 11 metals (copper, silver and gold).^{20–24} Analysis of the published data demonstrates that the heteroligand complexes of these metals with 2,2'-bipyridine derivatives and bis-phosphines do not show high photoluminescence efficiency (photoluminescence quantum yields are typically < 50%); therefore, they cannot be used in the design of OLED and LEEC devices (LEEC is a light-emitting electrochemical cell). Meanwhile, luminescence quantum yields for copper(I) complexes with pyrazolylpyridine ligands can be nearly quantitative. Neutral trinuclear copper(I) and silver(I) complexes exhibiting luminescent properties were obtained from unsaturated 2-(1*H*-pyrazol-3(5)-yl)pyridine.²⁵ Despite the presence of quite a few publications addressing metal complexes with pyrazolylpyridine derivatives,^{26,27} the role of the ligand environment, which determines the structure and properties of the coordination compound, is virtually neglected. These studies are mainly published in journals specializing in inorganic chemistry and materials science. The ligand synthesis is often described in Supplementary Materials or is presented as references to earlier publications, which considerably complicates handling of this information. The search through databases usually does not bring references to original procedures for the synthesis of pyrazolylpyridines. Until recently, methods for the synthesis of such ligands and pathways for ligand modification for the preparation of metal complexes have not been integrated or systematized. This review is devoted to pyrazole derivatives containing a pyridine ring at the carbon atom in position 3(5)[†] or at the pyrrole nitrogen atom. The simplest representatives of this class of compounds are 2-(1*H*-pyrazol-3(5)-yl)pyridine (**L1**) and 2-(1*H*-pyrazol-1-yl)

pyridine (**L2**). The key methods for the synthesis of these compounds as platforms for the design of metal complexes and materials possessing various physical (luminescent, magnetic) and chemical (catalytic) properties are discussed and analyzed.



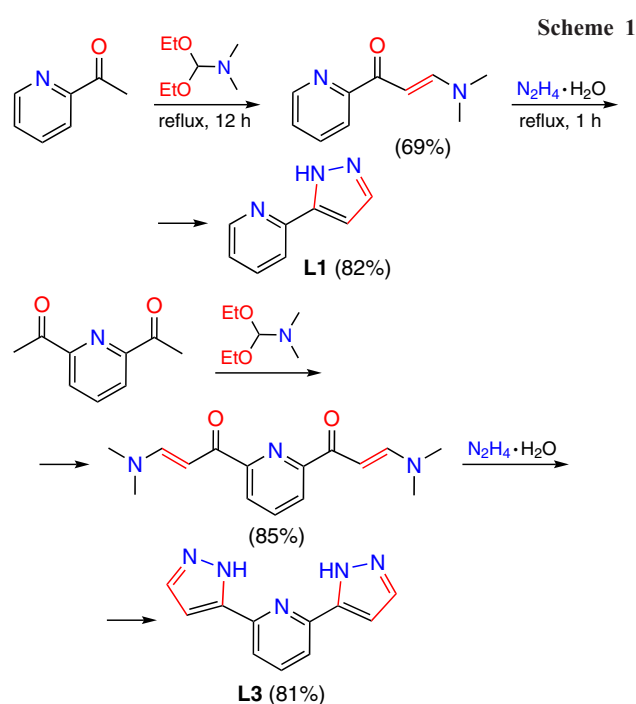
This review is intended to help researchers who do not specialize in organic synthesis to establish the relationship between the method of synthesis and structure of a functionalized ligand and the properties of the obtained metal complex.

2. General synthetic routes to 1*H*-pyrazol-3(5)-ylpyridines

2.1. Preparation of unsubstituted 2-(1*H*-pyrazol-3(5)-yl)pyridine

2.1.1. Condensation of 2-acetylpyridine with *N,N*-dimethylformamide dimethyl acetal

The synthesis of unsubstituted 2-(1*H*-pyrazol-3(5)-yl)pyridine (**L1**) was first described in 1992 by German researchers, Brunner and Scheck,²⁸ and consisted in condensation of 2-acetylpyridine with *N,N*-dimethylformamide diethyl acetal followed by cyclization in the presence of hydrazine (Scheme 1). In that study, 2,6-diacetylpyridine was also proposed as a platform for the preparation of a tridentate ligand, 2,6-bis(1*H*-pyrazol-3(5)-yl)pyridine (**L3**). Several optically active derivatives were prepared by *N*-alkylation of the pyrazole ring in compound **L1**; these products were used as enantioselective catalysts.²⁸



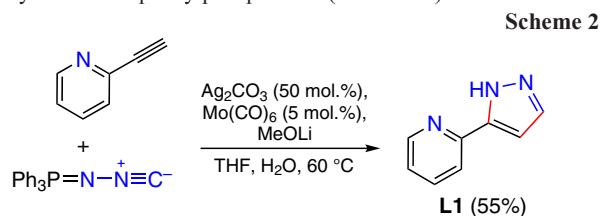
[†] Prototropic tautomerism of NH pyrazoles containing a substituent near to a heteroatom leads to equivalence of positions 3 and 5, *i.e.*, to the absence of isomerism; therefore, the structural formulae of such compounds presented in the review coincide with those given in original sources.

Subsequently, unsubstituted 2-(1*H*-pyrazol-3(5)-yl)pyridine was studied in detail by Professor Thiel and co-workers, who used this compound as a ligand in metal-catalyzed reactions of

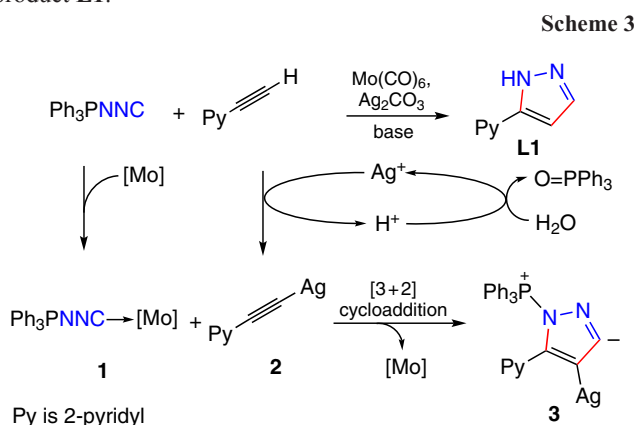
olefins,^{29,30} hydrosilylation,³¹ CO₂ hydrogenation,³² and photoinduced proton transfer reactions.³³

2.1.2. Catalytic [3+2]-cycloaddition of alkyne to (*N*-isocyanimino)triphenylphosphorane

Unsubstituted pyrazolylpyridine **L1** has also been prepared by catalytic [3+2]-cycloaddition of the appropriate alkyne to *N*-isocyanimino-triphenylphosphorane (Scheme 2).³⁴



The authors proposed the following reaction mechanism (Scheme 3). The first step includes two parallel reactions: generation of molybdenum isocyanide complex (**1**)[‡] by the reaction of (*N*-isocyanimino)triphenylphosphorane with Mo(CO)₆ and σ -activation of 2-pyridylacetylene *via* the reaction with Ag₂CO₃. The subsequent [3+2]-cycloaddition of intermediate **1** to silver acetylide **2** affords pyrazole zwitter-ion **3**. In the final step, base-induced hydrolysis takes place to give product **L1**.



2.2. Synthesis of substituted pyrazol-3(5)-ylpyridines

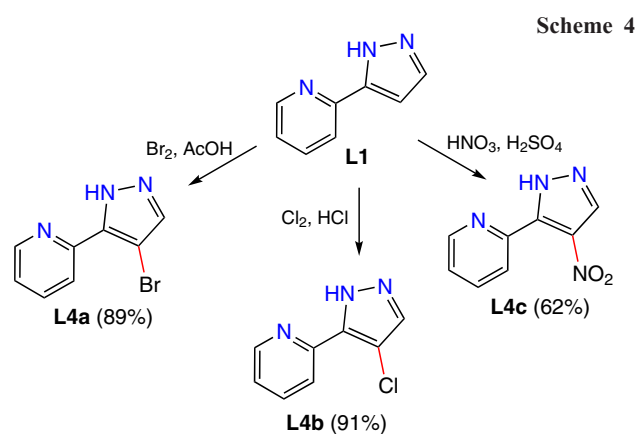
2.2.1. Introduction of a substituent into position 4 of the pyrazole ring

Direct introduction of functional groups into unsubstituted 2-(1*H*-pyrazol-3(5)-yl)pyridine (**L1**) opens up the possibility of subsequent modification of this ligand. Thiel and co-workers^{31,32} described the preparation of 4-halo and 4-nitro derivatives **L4a–c** (Scheme 4).

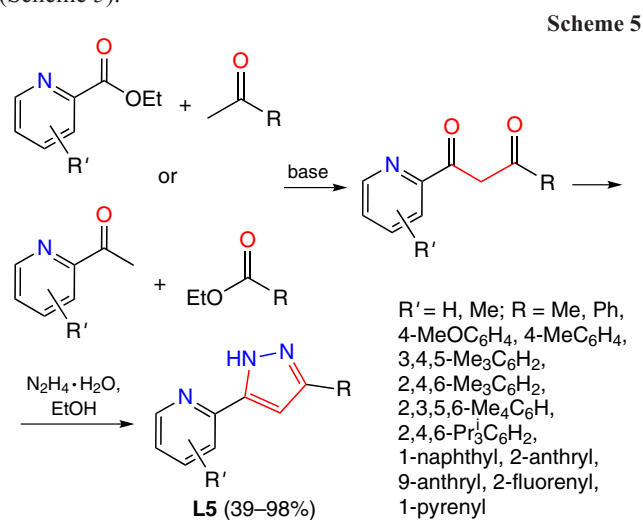
2.2.2. Reactions of diketones with hydrazine hydrate

A key method for the preparation of substituted pyrazoles is the reaction of diketones with hydrazine hydrate. Pyrazolylpyridines substituted in position 3 of the pyrazole ring were obtained in the 1970s–1980s by the Claisen condensation followed by

[‡] Two types of numbering are used in the review: the numbers preceded by letter **L** refer to the main investigation objects, pyrazolylpyridine ligands, while auxiliary compounds such as reaction substrates and intermediates and metal complexes are numbered by Arabic numerals.

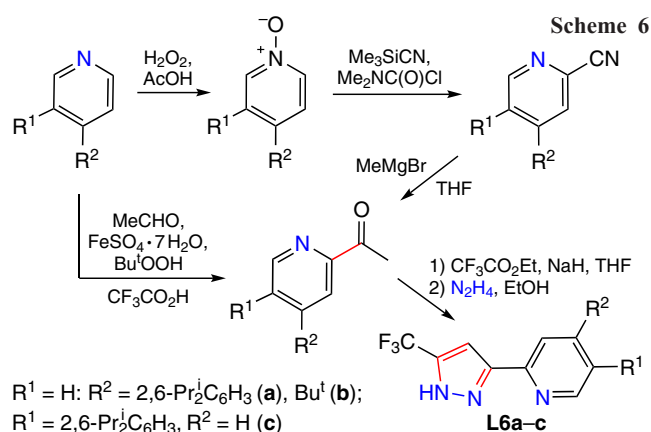


cyclization induced by hydrazine.^{35,36} Particularly this approach is currently used most often to prepare 2-(1*H*-pyrazol-3(5)-yl)pyridines **L5** substituted in both the pyridine and pyrazole rings (Scheme 5).^{32,37}



2.2.3. Introduction of a substituent into the pyridine ring

(5(3)-Trifluoromethylpyrazol-3(5)-yl)pyridines **L6a–c** with substituents in position 3 or 4 of the six-membered ring are obtained from appropriate pyridine derivatives along two pathways (Scheme 6).³⁸ One path consists in direct acylation of substituted pyridine at position 2 on treatment with acetaldehyde in the presence of a mixture of FeSO₄·7H₂O, Bu^tOOH and CF₃COOH. The other alternative is a three-step synthesis that implies successive oxidation of substituted pyridine, cyanation



of the resulting pyridine *N*-oxide and the methylation with the Grignard reagent (see Scheme 6).³⁸

This synthetic sequence makes it possible to introduce bulky substituents into ligand **L6** and prevents the appearance of intermolecular contacts in the complexes. Platinum(II) complexes with the deprotonated form of this ligand are efficient blue phosphorescent emitters, which were used to fabricate white light emitting diodes.³⁸

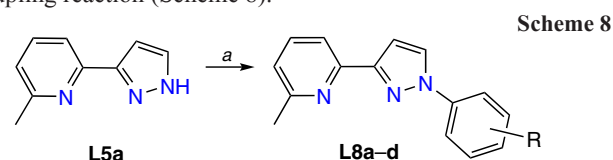
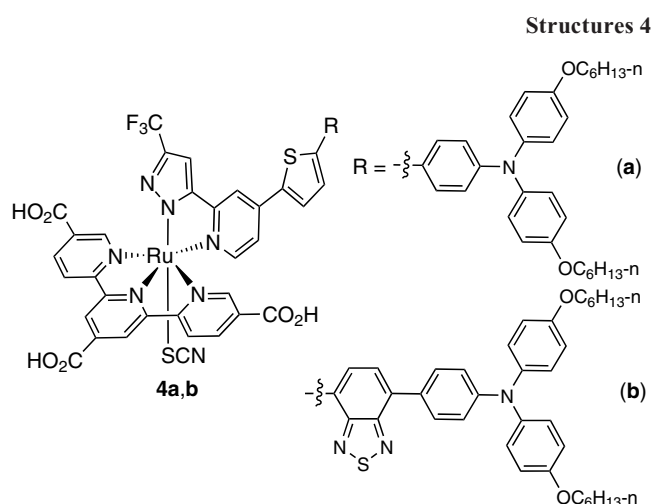
(1*H*-Pyrazol-3(5)-yl)pyridine derivatives **L7a,b** containing a thiophene ring with bulky amino groups in the pyridine moiety were prepared from ethyl 4-chloro- α -picolinate (Scheme 7).³⁹ In the first step, the starting reactant was subjected to the Stille cross-coupling with 2-(tri-*n*-butylstannyl)thiophene to give ethyl 4-(2-thienyl)picolinate, in which the thiophene ring was brominated at position 5. After conversion of the ester group to the acetyl group, the bromine atom was replaced by the CF₃ group, and the free NH group of pyrazole was protected. Finally, Suzuki cross-coupling with pre-synthesized pinacol esters of arylboronic acids was carried out. It is noteworthy that the tetrahydropyran protection of the pyrazole NH group proved to tolerate the cross-coupling

conditions and was easily removed on treatment with trifluoroacetic acid.

It was shown³⁹ that the efficiency of solar batteries based on Ru^{II} complexes **4a,b** containing compound **L7** as an auxiliary ligand substantially increased upon introduction of electron-donating amino groups, especially when they were linked *via* a benzothiazole bridge (Scheme 8). In the presence of these substituents, the extinction coefficient of the resulting dyes and their complexes increased several-fold, in particular in the visible region. The influence of the electron-donating or -withdrawing properties of the substituent on energy conversion efficiency was demonstrated.

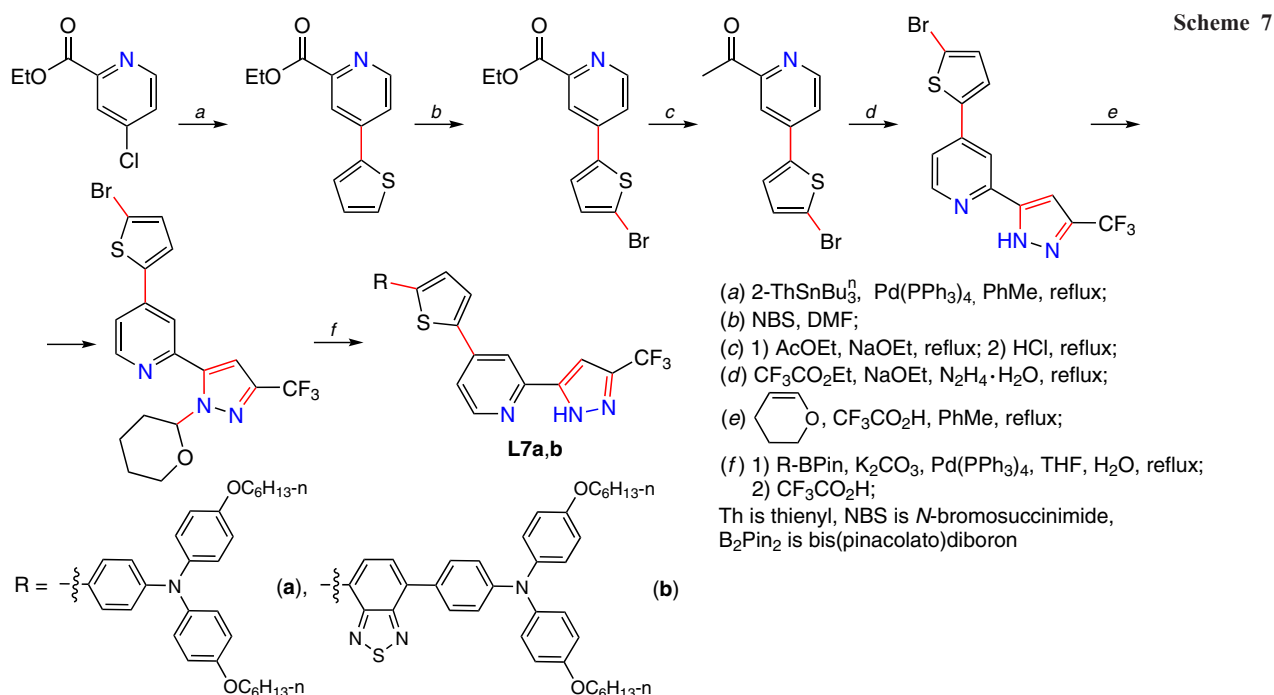
2.2.4. Arylation of the NH group of pyrazole

The introduction of an aryl moiety into the free NH group of the pyrazole ring may considerably enhance the steric effects in the ligand. A number of *N*-aryl-substituted 2-(1*H*-pyrazol-3(5)-yl)pyridines (**L8a–d**) were prepared by the copper-catalyzed C–N coupling reaction (Scheme 8).⁴⁰



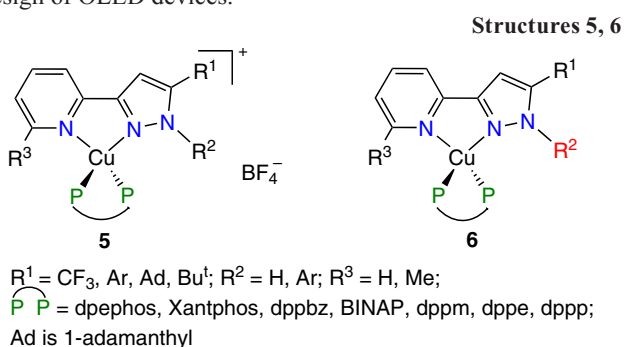
(a) RC₆H₄Hal (1 equiv.), CuI (0.2 equiv.), 1,10-phenanthroline (0.4 equiv.), CsCO₃ (2 equiv.), 100 °C, 24 h;
L8: R = H (**a**), 2-Me (**b**), 2-CF₃ (**c**), 4-CF₃ (**d**)

Complexes of group 11 monovalent metals (so-called coinage metals) with pyrazolylpyridine derivatives are rather poorly addressed in the literature.^{40–46} For example, targeted modification of 2-(1*H*-pyrazol-3(5)-yl)pyridines to be used as ligands in copper(I) complexes has barely been reported. The initial ligands were usually prepared by a standard procedure, including the condensation of the appropriate esters and ketones (see Scheme 3). The effect of the ligand structure on the photophysical properties of the complexes was mainly determined by varying steric properties. It was shown that



substituents in the pyrazolylpyridine ligands^{40,41} or in bis-phosphine⁴⁶ prevent the structural changes that may take place during electron transitions upon excitation or emission, thus decreasing the contribution of non-radiative relaxation and retaining the high efficiency of emission.

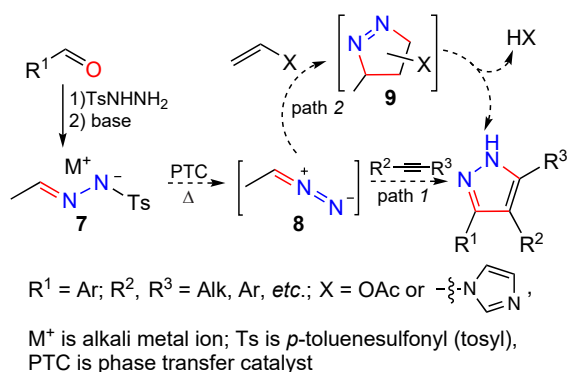
Copper(I) complexes **5** and **6** with bis-phosphine bridging or chelating ligands were prepared using compounds **L8** or their NH analogues, particularly bis(2-diphenylphosphinophenyl) ether (dpephos), 9,9-dimethyl-4,5-bis(diphenylphosphino)-xanthene (Xantphos), 1,2-bis(diphenylphosphino)benzene (dppbz), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp). The key feature of these complexes is bright luminescence with a quantum efficiency much exceeding that observed for analogous heteroligand 2,2'-bipyridine complexes;¹³ these compounds are applicable for the design of OLED devices.⁴⁰



2.2.5. 1,3-Dipolar cycloaddition reaction involving diazo compounds

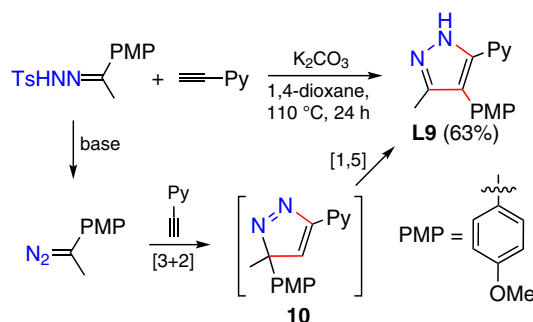
A popular method for the synthesis of pyrazoles is 1,3-dipolar cycloaddition of diazo compounds to a triple bond.⁴⁷ The reaction of tosylhydrazones with acetylenes in the presence of a base provides *in situ* generation of diazo derivatives, which undergo cycloaddition reactions with unsaturated compounds. A putative mechanism of this reaction was described in 2003 (Scheme 9).⁴⁸ In the first step, substituted aldehyde reacts with tosylhydrazine in the presence of a strong base (alkali metal hydroxide) to give intermediate salt **7**, which is converted to reactive diazo derivative **8**. This is followed by 1,3-cycloaddition reaction of **8** with substituted acetylene (see path 1 in Scheme 9). Meanwhile, the addition of olefin with a good leaving group to the obtained diazo derivative **8** furnishes 3,5-substituted pyrazole after elimination of HX (aromatization) from cycloaddition intermediate **9** (see path 2).

Scheme 9



This approach served as the basis for developing a preparation procedure for a broad range of substituted pyrazoles;^{48–51} in some cases, gaseous acetylene was used in the synthesis.⁵² It is noteworthy that the above-cited studies do not describe the synthesis of 2-pyridyl derivatives. In 2015, Perez-Aguilar and Valdes⁵³ reported a one-step method for the preparation of substituted pyrazoles, including 2-[3(5)-methyl-4-(2-methoxyphenyl)-1*H*-pyrazol-5(3)-yl]pyridine (**L9**), by the dipolar cycloaddition of aryl-substituted acetylenes and proposed the mechanism of the reaction. Important achievements of this study are the discovery of an additional intermediate of [1,5]-sigmatropic rearrangement (**10**) and the possibility of synthesizing trisubstituted pyrazoles (Scheme 10).

Scheme 10



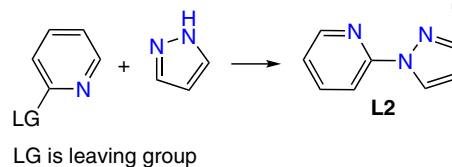
It can be seen that the above methods provide the synthesis of a moderate variety of pyrazolylpyridines. The formation of products is mainly presented with the goal to demonstrate the synthetic potential of various approaches. The use of diketones or keto alcohols obtained by Claisen condensation as the reactants opens up synthetic routes to pyrazolylpyridines containing desired substituents or functional groups, because this condensation can proceed for various acetyl derivatives and esters. Analysis of the published data showed that 2-(1*H*-pyrazol-3(5)-yl)pyridine ligands meant for complex formation with metals are obtained, most often, from diketones or keto alcohols.

3. General methods for the synthesis of 1*H*-pyrazol-1-ylpyridines

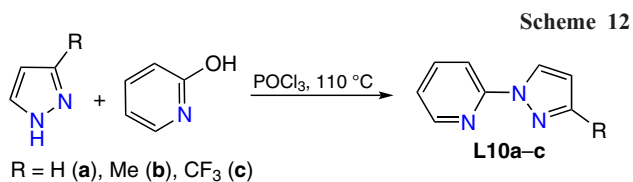
The presence of two nitrogen atoms capable of metal coordination in one five-membered ring accounts for the popularity of 2-(1*H*-pyrazol-1-yl)pyridines as chelating ligands. This part of the review is devoted to the preparation of ligands of this type. The primary attention is paid to modification of 2-(1*H*-pyrazol-1-yl)pyridines in order to vary their coordination capacity and the properties of the transition metal complexes they form.

The simplest approach to the synthesis of 2-(1*H*-pyrazol-1-yl)pyridine (**L2**) is based on coupling of a pyridine containing a leaving group in position 2 with NH pyrazole (Scheme 11).

Scheme 11

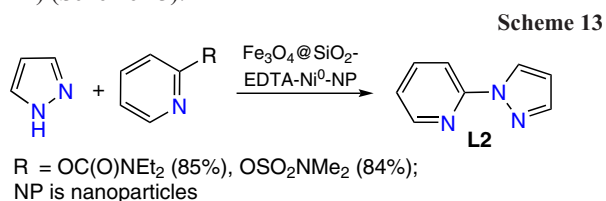


Several procedures for the synthesis of 2-(1*H*-pyrazol-1-yl)pyridines based on this approach have been reported in the literature. The main restrictions are imposed on the nature of substituents in the starting compounds, pyrazole or pyridine. For example, refluxing of 2-hydroxypyridine and substituted

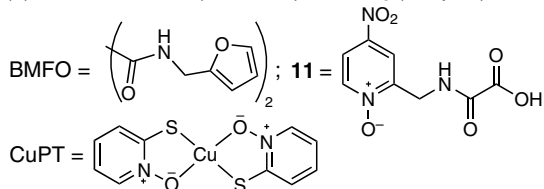
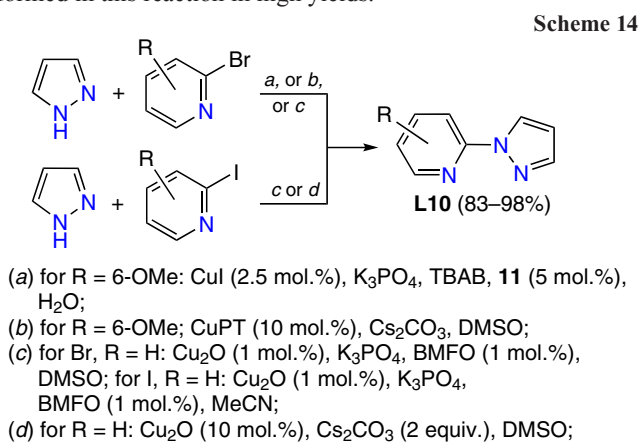


pyrazoles in POCl₃ affords 2-(1*H*-pyrazol-1-yl)pyridine derivatives **L10a-c** (Scheme 12).⁵⁴

Ligand **L2** was prepared in a high yield by coupling pyrazole with pyridinecarbamate or -sulfamate. The reaction was carried out in the presence of a catalyst, nickel nanoparticles, supported on Fe₃O₄@SiO₂ modified with ethylenediaminetetraacetic acid (EDTA) (Scheme 13).⁵⁵



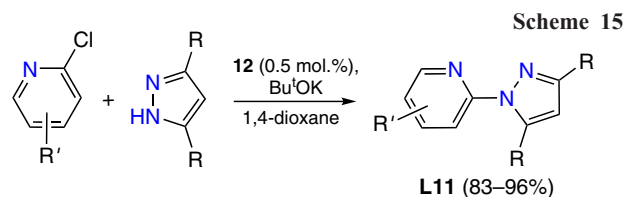
The most popular method for the synthesis of *N*-pyridine-substituted pyrazoles is copper-catalyzed reaction of 2-halopyridines with pyrazoles (Scheme 14).^{56–59} There are a few versions of conditions for this reaction, including the use of a phase transfer catalyst, tetra-*n*-butylammonium bromide (TBAB), in the presence of pyridine oxide **11**. Ligands **L10** are formed in this reaction in high yields.



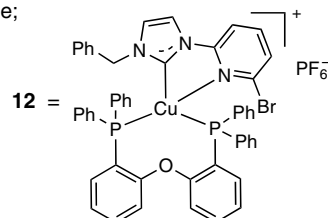
2-(1*H*-Pyrazol-1-yl)pyridines **L11** containing substituents in the pyridine ring were prepared by amination of 2-chloropyridines with pyrazole in the presence of copper carbene complex **12** as a catalyst (Scheme 15).⁶⁰

Iridium,⁶¹ cadmium,⁶² zinc and nickel⁶³ complexes with *N*-pyridyl-substituted pyrazoles **L10** and **L11** were used as photoactive compounds. Mononuclear iron complexes obtained from these ligands exhibited spin crossover⁶⁴ and cytotoxic activity.⁶⁵

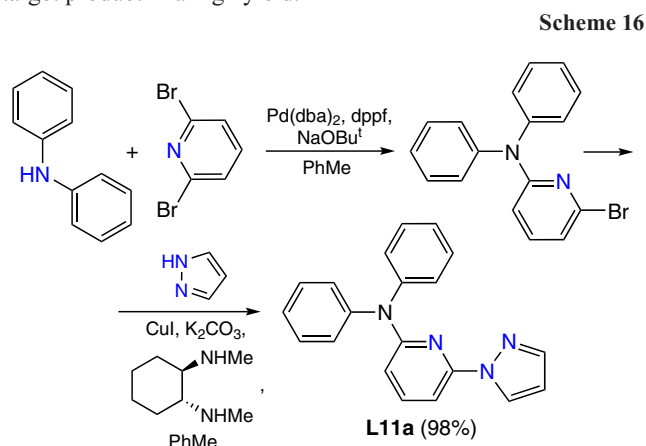
The introduction of luminophore groups into the ligand can change the emission wavelength and efficiency for a metal complex. For example, 2-(1*H*-pyrazol-1-yl)-6-diphenylamino-



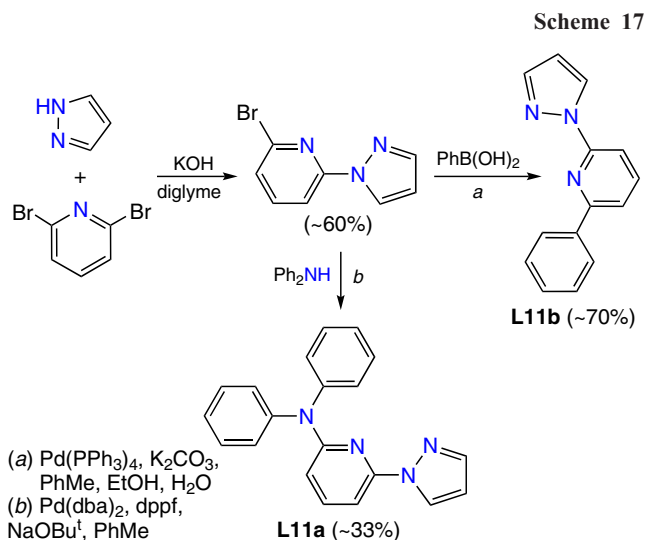
R' = H, 6-Me, 5-Me, 4-OMe, 6-OMe, 5-CF₃, 4-CF₃, 5-Cl;
R = H, Me;



pyridine (**L11a**) was prepared from 2,6-dibromopyridine (Scheme 16).⁶⁶ Cyclometallated Pt^{II} complex with ligand **L11a** showed a bright green phosphorescence in solution. The ligand was synthesized by cross-coupling of amine with bromide in the presence of Pd(dba)₂ (dba is dibenzylideneacetone) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) to give 2-bromo-6-diphenylaminopyridine, which was introduced into a copper-catalyzed reaction with unsubstituted pyrazole to afford the target product in a high yield.



An alternative method for the synthesis of ligand **L11a** was also proposed.¹⁹ In the first step, unsubstituted pyrazole was



allowed to react with 2,6-dibromopyridine on treatment with KOH in diglyme. The C–N or C–C coupling of intermediate 2-bromo-6-(1*H*-pyrazol-1-yl)pyridine with diphenylamine or phenylboronic acid, respectively, catalyzed by palladium complexes furnished ligands **L11a,b** (Scheme 17).

Orrego-Hernandez *et al.*^{67,68} synthesized 3-aryl-1-(2-pyridyl)-4-styrylpyrazoles **L12**, which emitted in the blue region with high quantum yields (up to 66%). The initial condensation of substituted acetophenones with 2-pyridylhydrazine afforded hydrazones **13**, which were converted to 4-formylpyrazoles **14** *via* the Vilsmeier–Haack reaction. Compounds **14** reacted with methyltriphenylphosphonium bromide to give a new C–C bond, and intermediate 4-vinylpyrazoles **15** were converted to target 4-styrylpyrazoles **L12** by the Heck reaction with bromobenzene (Scheme 18).

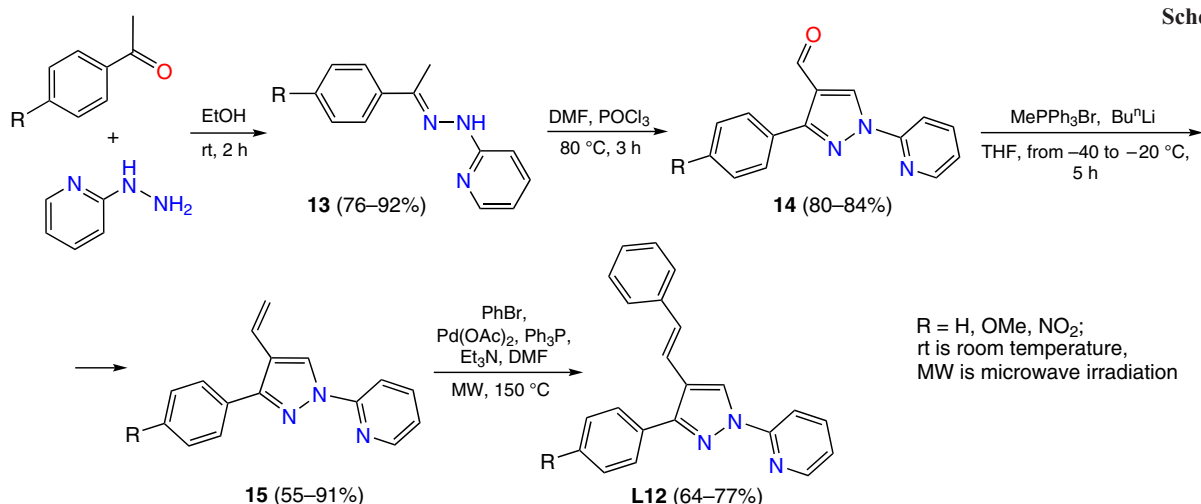
4. 2-Pyrazolypyridines as tridentate CNN ligands

The cyclometallated platinum metal complexes became popular due to their phosphorescence, which determines the scope of their applicability. The photophysical properties of this class of luminophores can be tuned by optimization of the donor–acceptor properties of ligands with a metal–carbon covalent bond and

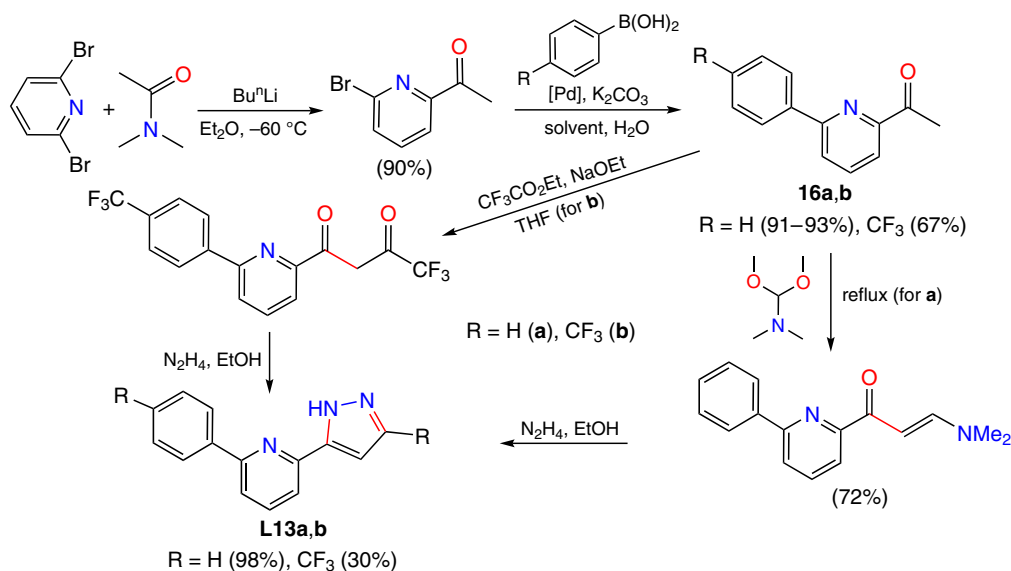
auxiliary ligands, which is attained by variation of substituents. The interest in the use of 2-pyrazolypyridine derivatives as cyclometallating ligands has markedly increased in recent years owing to the broad range of their synthetic modification.

4.1. Introduction of aryl substituent into position 6 of the pyridine ring

In order to obtain chelating ligands from 2-pyrazolypyridines, it is necessary to introduce an alkyl or aryl substituent into position 6 of the pyridine moiety. 2,6-Dibromopyridine is utilized most often as the starting compound for the synthesis of these derivatives.^{69–73} This compound is lithiated, and the product reacts with *N,N*-dimethylacetamide to yield 2-acetyl-6-bromopyridine. This is followed by Suzuki cross-coupling with the corresponding arylboronic acid and the condensation of intermediates **16** with ethyl trifluoroacetate (to introduce a trifluoromethyl group) or with dimethylformamide dimethyl acetal (to obtain 3-unsubstituted pyrazole). The sequence of reactions is completed by formation of the heterocycle *via* the reaction of the obtained carbonyl compound with hydrazine. This flexible synthetic route open up broad opportunities for tuning of luminescent properties of the resulting ligand **L13** (Scheme 19).^{69–73}

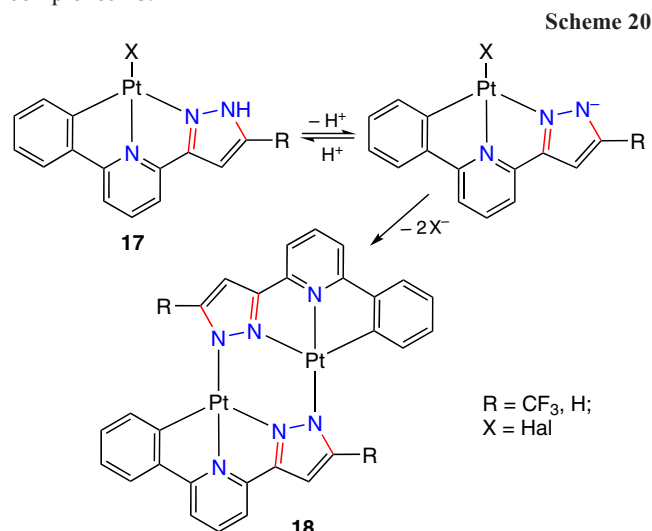


Scheme 18

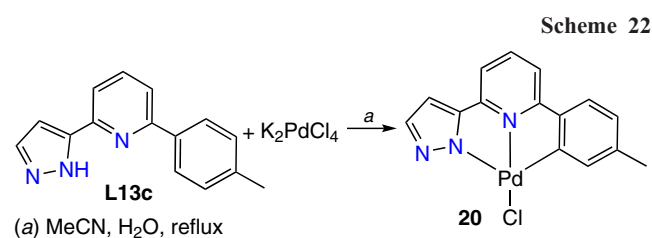
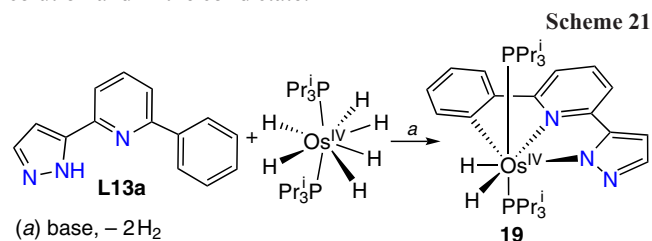


Scheme 19

In these reactions, it is possible to use pinacol esters of arylboronic acids.¹⁷ On the basis of 6-aryl-2-pyrazolypyridines **L13**, cyclometallated platinum(II) complexes **17** were obtained for the first time; a free NH group was retained in the ligand (Scheme 20). In the presence of a base (Et₃N), proton elimination followed by halide ion elimination took place to give dimeric complexes **18**.^{69,74}



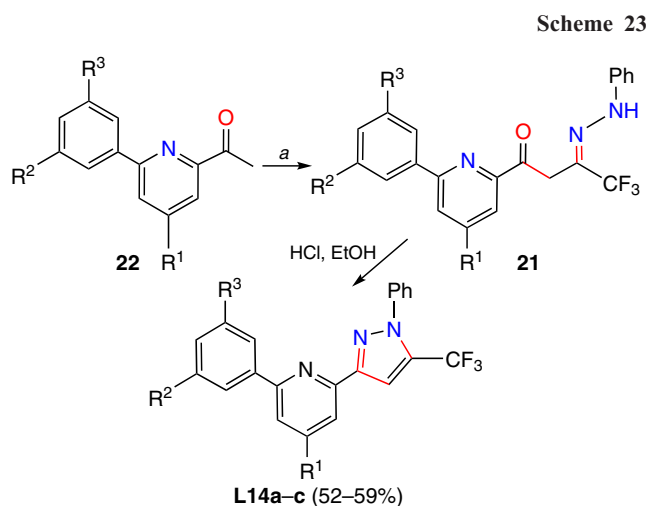
The simplest representative of 6-phenyl-substituted 2-pyrazolypyridines **L13a** was used to prepare osmium(IV) CNN pincer complex **19** (Scheme 21),⁷⁵ while its homologue **L13c** was converted to analogous palladium(II) complex **20** (Scheme 22).⁷⁶ These complexes exhibit phosphorescence in solution and in the solid state.^{75,76}



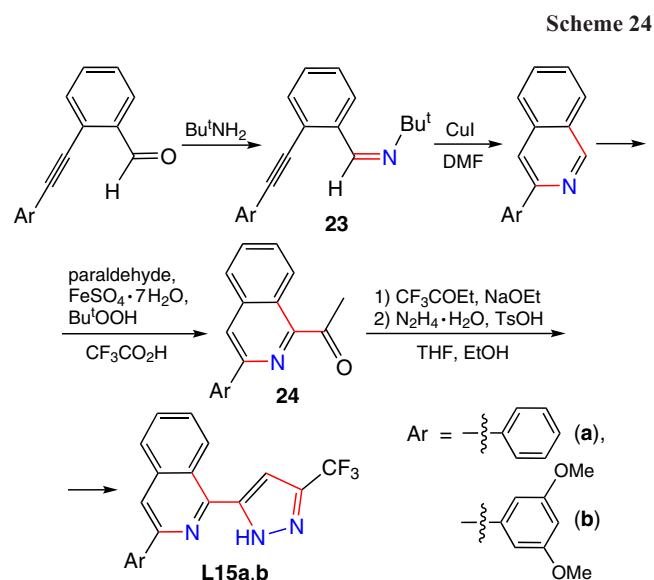
4.2. Introduction of a substituent to the pyrrole nitrogen atom

The introduction of a phenyl group to the pyrazole NH group during cyclization of hydrazones **21** has been reported.⁷⁷ These hydrazones were prepared from substituted 2-acetylpyridine **22**, which was first converted to CF₃-containing diketone, and the product was allowed to react with phenylhydrazine. The cyclization of hydrazones **21** catalyzed by an ethanol solution of HCl resulted in the formation of 2-(1-phenylpyrazol-3-yl)pyridine ligands **L14a–c** (Scheme 23).

Gnanasekaran *et al.*⁷⁷ described an approach to the synthesis of 3-aryl-1-[3-(trifluoromethyl)-1H-pyrazol-5-yl]isoquinolines,



fused analogues of pyrazolypyridine. The synthetic sequence started with the reaction of 2-(phenylethynyl)benzaldehyde with *tert*-butylamine to give imine **23**, which was cyclized by treatment with CuI to afford 3-phenylisoquinoline. This product reacted with acetaldehyde to give acetylisoquinoline **24**, which was converted to pyrazole **L15a** via the condensation with ethyl trifluoroacetate and treatment with hydrazine hydrate (Scheme 24). Product **15b** was synthesized in a similar way.



Ligands **L14** and **L15** were used to prepare iridium(III) complexes. The presence of an aromatic substituent at the pyrazole nitrogen atom additionally stabilizes the structure of bis(tridentate) complexes **25a–e** by forming intramolecular π - π contacts between the phenyl and quinoline moieties; consequently, the luminescence quantum yields may be nearly quantitative (Fig. 1).⁷⁷

Steric crowding of the ligands also gives rise to a stable geometry of the complex, which prevents the vibrational relaxation of its excited state.

Structures 25

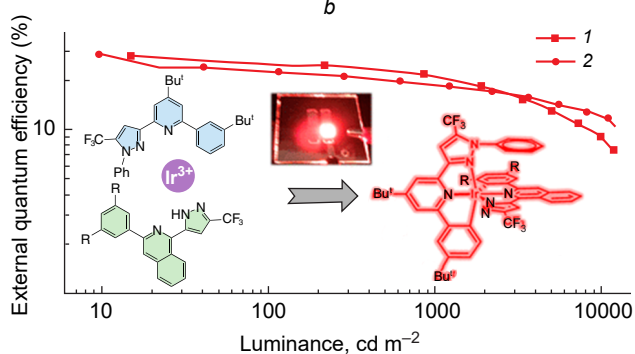
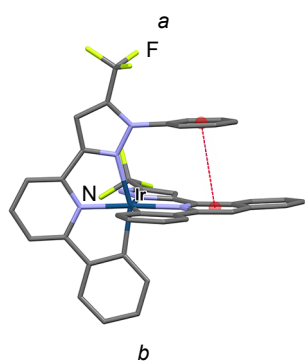
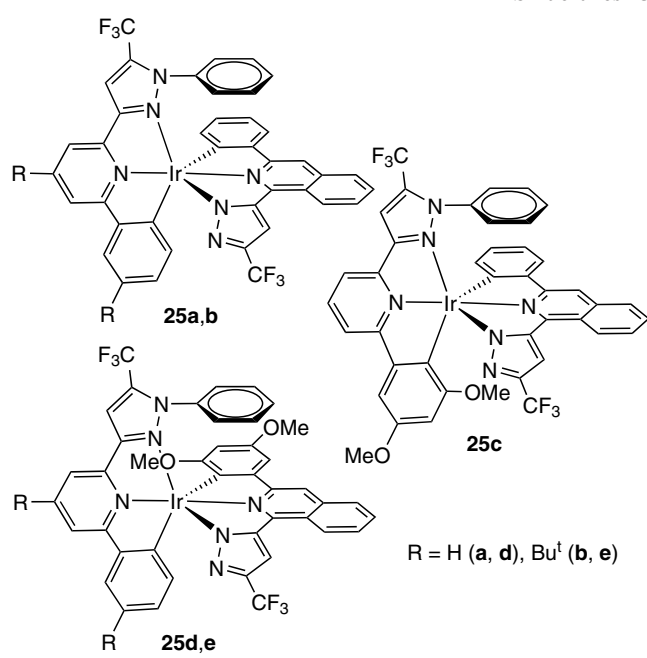


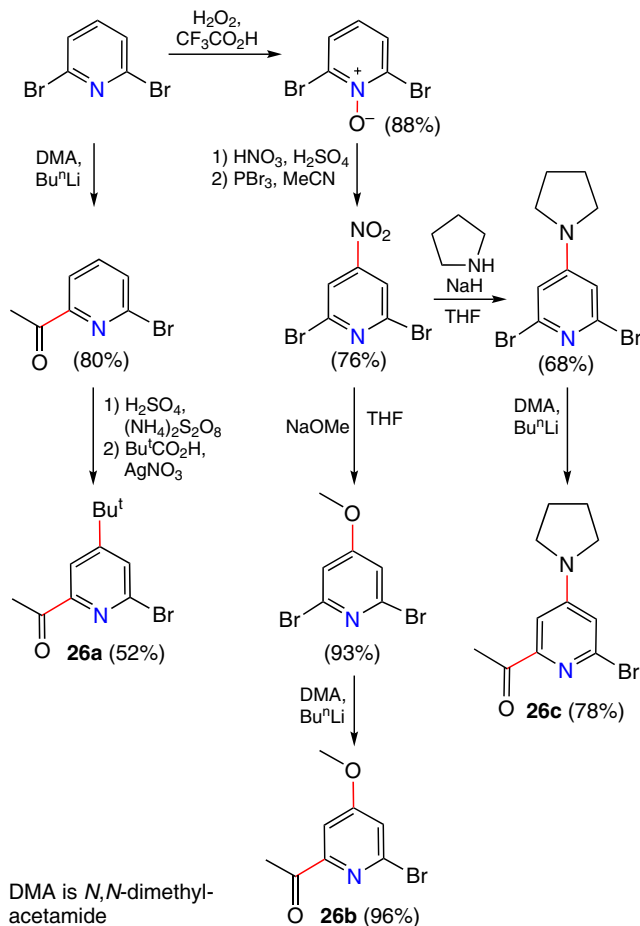
Figure 1. Molecular structure of the Ir[(L14a)(L15a)] complex (25a) according to X-ray diffraction data (the red dashed line marks the intramolecular π - π contacts) (a) and electroluminescence curves of complexes 25a (1) and 25e (2).⁷⁷

4.3. Introduction of substituents into positions 4 and 6 of the pyridine ring

The pyridine moiety of the pyrazolylpyridine ligands directly participates in electron transitions. By varying the electronic properties of substituents in the pyridine ring, one can shift the emission maximum to the blue (electron-donating substituents) or red (electron-withdrawing substituents) spectral ranges. For this reason, to achieve the desired properties of the complex, it is important to modify particularly the pyridine ring. Zhu *et al.*⁷⁸

used 2,6-dibromopyridine to introduce a substituent at position 4. They developed procedures for the synthesis of 4-*tert*-butyl- (26a), 4-methoxy- (26b) and 4-pyrrolidino-6-acyl-2-bromopyridines (26c) (Scheme 25), which were further converted to pyrazolylpyridine ligands.

Scheme 25

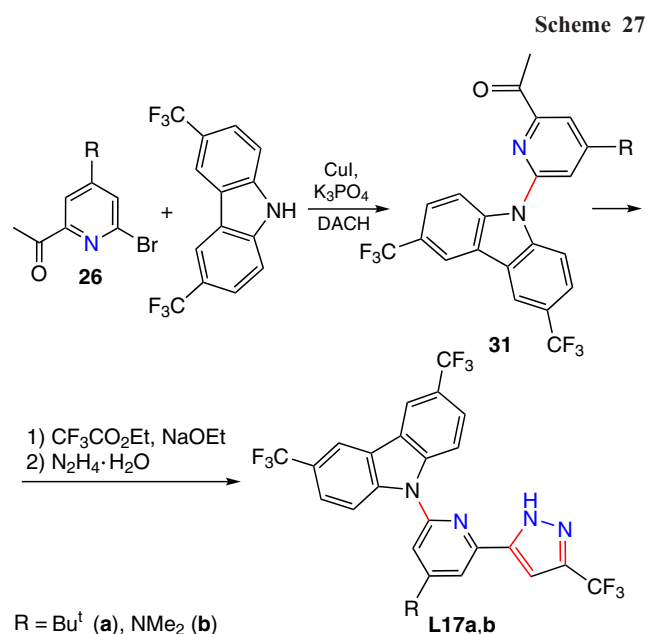
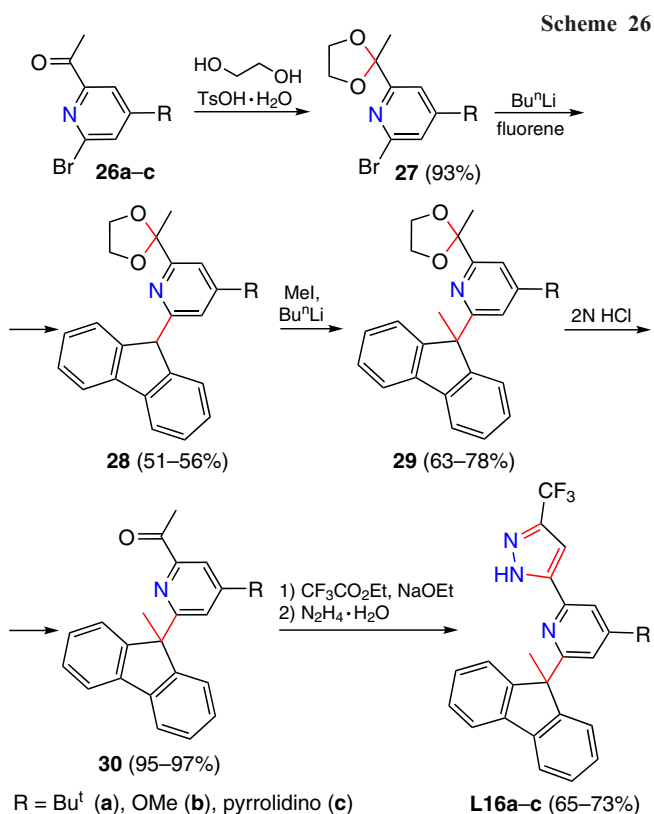


DMA is *N,N*-dimethylacetamide

For the attachment of a *tert*-butyl substituent, 2,6-dibromopyridine was successively acylated and treated with pivalic acid in the presence of silver nitrate. The 4-methoxy- and 4-pyrrolidino-substituted derivatives were prepared by oxidation of the starting substrate to pyrrolidine *N*-oxide followed by nitration at position 4 of the pyridine ring and replacement of the nitro group by the desired moiety.

Compounds 26a–c were converted to pyrazolylpyridine ligands L16a–c containing fluorene in position 6 of the pyridine ring.⁷⁸ For this purpose, first, the carbonyl group in the substrate was protected by treatment with a stoichiometric amount of ethylene glycol in the presence of *p*-toluenesulfonic acid (Scheme 26). The resulting 1,3-dioxolane derivatives 27 were allowed to react with equimolar amounts of *n*-butyllithium and fluorene to give 2-(9*H*-fluoren-9-yl)-6-(2-methyl-1,3-dioxolan-2-yl)pyridines (28), which were then methylated at position 9 of the fluorene substituent. The dioxolane protecting group in intermediate 2-(2-methyl-1,3-dioxolan-2-yl)-6-(9-methyl-9*H*-fluoren-9-yl)pyridines 29 was eliminated by the action of 2 M hydrochloric acid. The subsequent Claisen condensation of keto derivatives 30 followed by cyclization with hydrazine furnished target L16.

2-(1*H*-Pyrazolyl)pyridine ligands L17a,b containing a 3,5-bis(trifluoromethyl)-substituted carbazole ring in position 6 and a *tert*-butyl or dimethylamino group in position 4 of pyridine were obtained *via* a three-step synthesis (Scheme 27).^{79,80} First,



4-substituted 6-acetyl-2-bromopyridines were coupled with 3,6-bis(trifluoromethyl)-9H-carbazole in the presence of CuI and a base, 1,2-diaminocyclohexane (DACH), to give trisubstituted pyridines **31**. The subsequent Claisen condensation involving ethyl trifluoroacetate and hydrazine hydrate-induced heterocyclization afforded ligands **L17**.

The above fluorene- and carbazole-containing (1*H*-pyrazole-5-yl)pyridines **L16**, **L17** were used as auxiliary ligands to obtain iridium(III) bis(tridentate) complexes exhibiting bright blue phosphorescence. Zhu and co-workers^{78–80} showed that substituents in the pyridine ring influence the energy difference between the highest occupied (HOMO) and lowest unoccupied

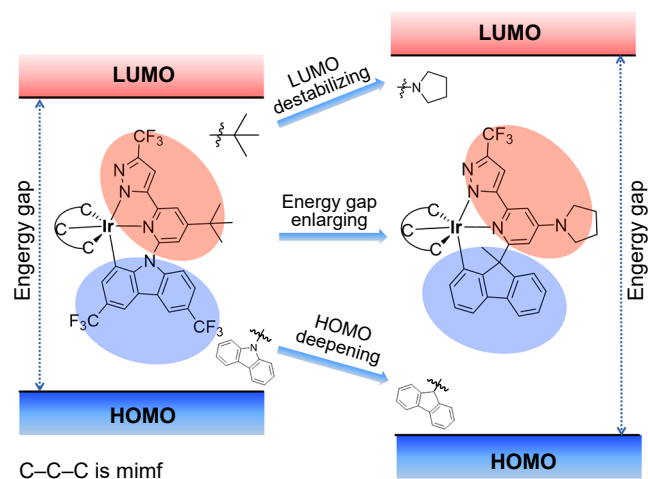
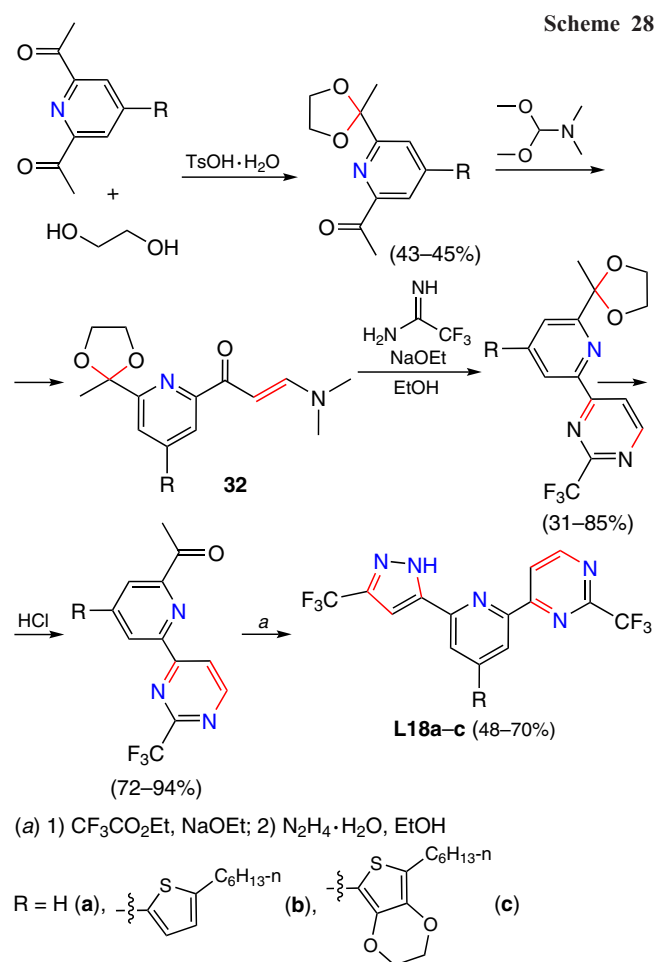


Figure 2. Diagram for the change in the HOMO to LUMO gap in relation to Ir^{III} bis(tridentate) complexes with ligands **L16c** (on the right) and **L17a** (on the left).⁷⁸ mimf is 2,6-bis(1-methylimidazol-3-yl)-4-(trifluoromethyl)phenyl.

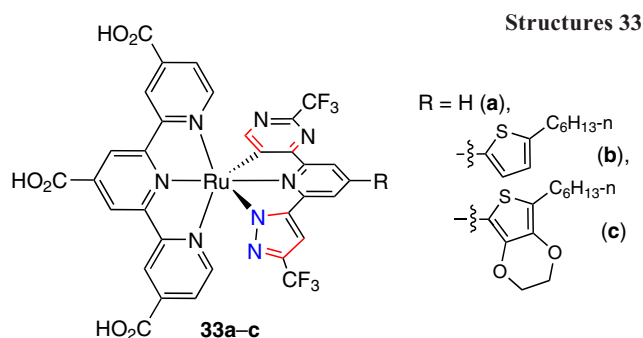
molecular orbitals (LUMO), which opens the way for controlling the emission characteristics for this type of complexes (Fig. 2).

Tridentate 1*H*-pyrazolylpyridine ligands containing a pyrimidine moiety, {4-[6-(3-trifluoromethylpyrazol-5-yl)pyridin-2-yl]-2-trifluoromethylpyrimidines **L18a–c**, were prepared from 2,6-diacetylpyridine and its 4-substituted analogues (Scheme 28).⁸¹ First, the carbonyl group in one acetyl substituent was protected by ethylene glycol. The other acetyl group reacted



in the condensation with *N,N*-dimethylformamide dimethyl acetal. The subsequent heterocyclization of intermediate **32** induced by 2,2,2-trifluoroacetamide in the presence of a base gave a CF₃-substituted pyrimidine moiety in position 6. Then the acetyl group was removed by acid treatment, and the pyrazole ring was formed according to above-described procedures (see Scheme 28).

It is noteworthy that the formation of Ru^{II} complexes **33a–c** with [2,2':6',2''-terpyridine]-4,4',4''-tricarboxylic acid and ligands **L18** did not involve the coordination of the pyrimidine nitrogen atom to the metal. Like in the case of phenyl-substituted pyrazolopyridines, cyclometallated derivatives were formed.

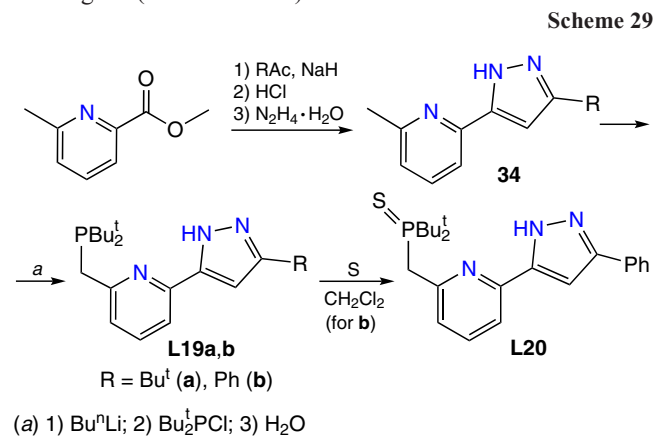


Complexes **33** were shown to be applicable as sensitizers in solar batteries.⁸¹

5. Tridentate ligands based on pyrazolopyridines

5.1. Phosphorus- and sulfur-containing tridentate ligands

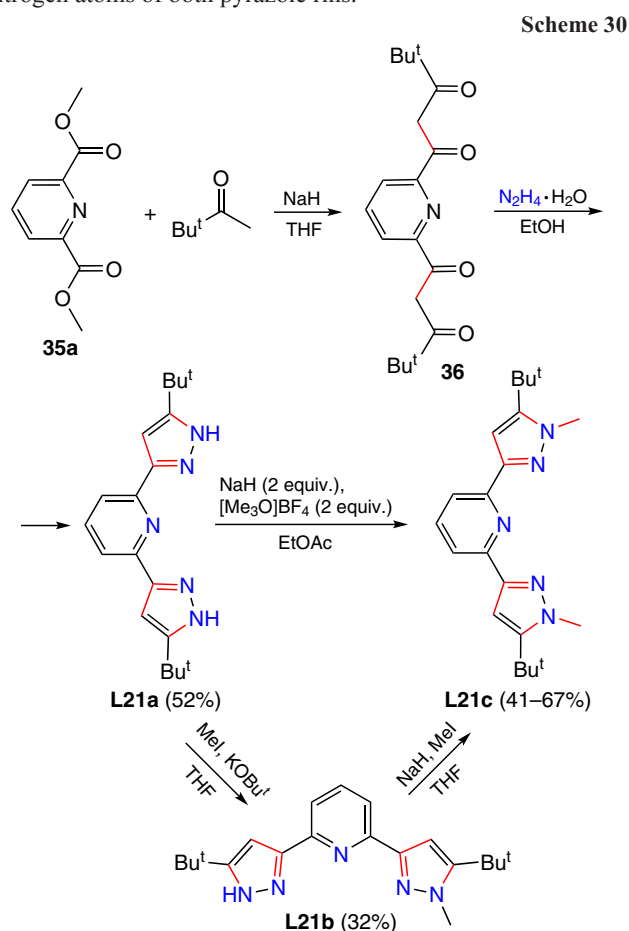
Professor Caulton and co-workers⁸² proposed a modification pathway for the 2-(1*H*-pyrazol-3(5)-yl)-6-methylpyridine molecules to introduce phosphorus and sulfur atoms into the α -methyl substituent and obtain NNP and NNS pincer ligands. Ligands **L19a,b**, containing phenyl or *tert*-butyl group in the pyrazole moiety and di-*tert*-butylphosphine group in the pyridine ring, were prepared by a three-step synthetic route. First the Claisen condensation of methyl 6-methylpicolinate with pinacolone (3,3-dimethylbutan-2-one) or acetophenone followed by treatment with hydrazine was carried out, and then deprotonated intermediates **34** were treated with Bu₂PCl with subsequent hydrolysis (Scheme 29). The addition of elemental sulfur to **L19b** afforded phosphine sulfide **L30**, which is an SNN ligand (see Scheme 29).



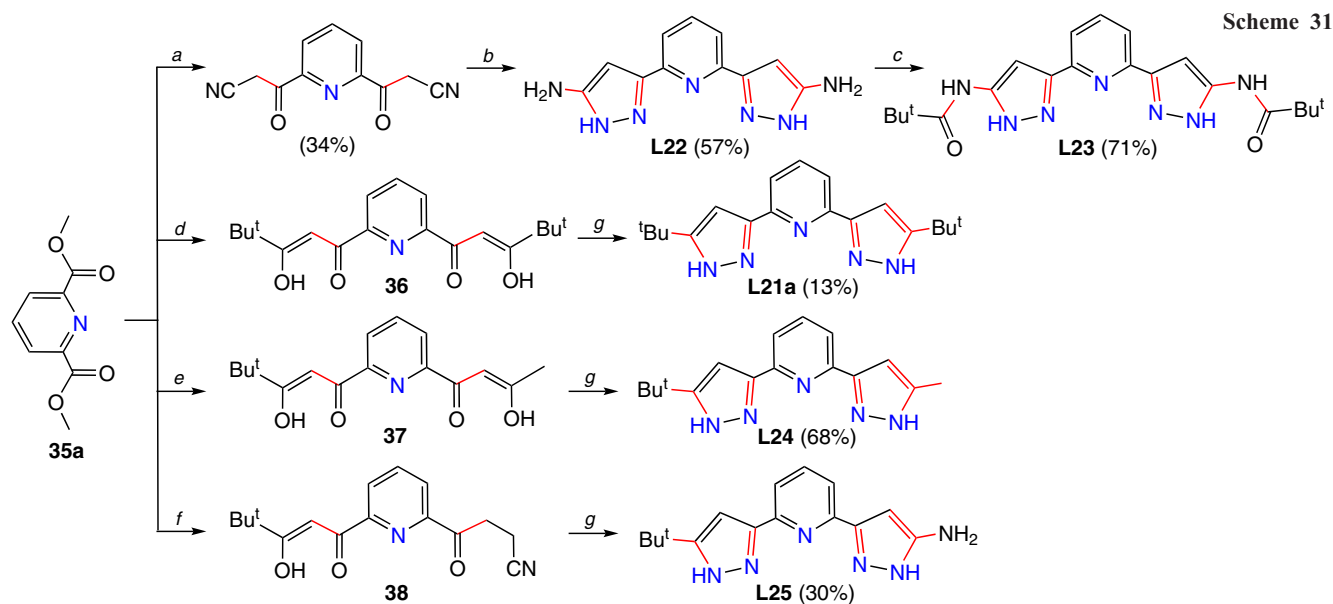
Pyrazolopyridine ligands **L19** and **L20** were used to prepare cobalt,^{82,83} iron,⁸⁴ nickel,⁸⁵ rhodium and zinc⁸⁶ pincer complexes, which have redox activity and catalytic properties.

5.2. NNN ligands with two pyrazole moieties

2,6-Bis(pyrazolyl-3(5)-yl)pyridine derivatives are in fairly wide demand in coordination chemistry. A significant part of studies of these ligands are devoted to the preparation of transition metal complexes that exhibit magnetic properties.^{87,88} Ligands of this type (e.g., compounds **L21a–c**) are synthesized from dimethyl pyridine-2,6-dicarboxylate (**35a**).⁸⁹ The reaction of **35a** with pinacolone in the presence of sodium hydride afforded 1,3-bis(diketone) **36**, which was then cyclized by treatment with hydrazine hydrate (Scheme 30).⁸⁹ The acid protons of pyrazole were replaced by the methyl group by slow addition of two equivalents of trimethyloxonium salt in the presence of NaH.⁹⁰ When an equimolar amount of methyl iodide is added, the NH group of only one five-membered ring is substituted, while the addition of a second equivalent results in the methylation of nitrogen atoms of both pyrazole rings.⁹¹



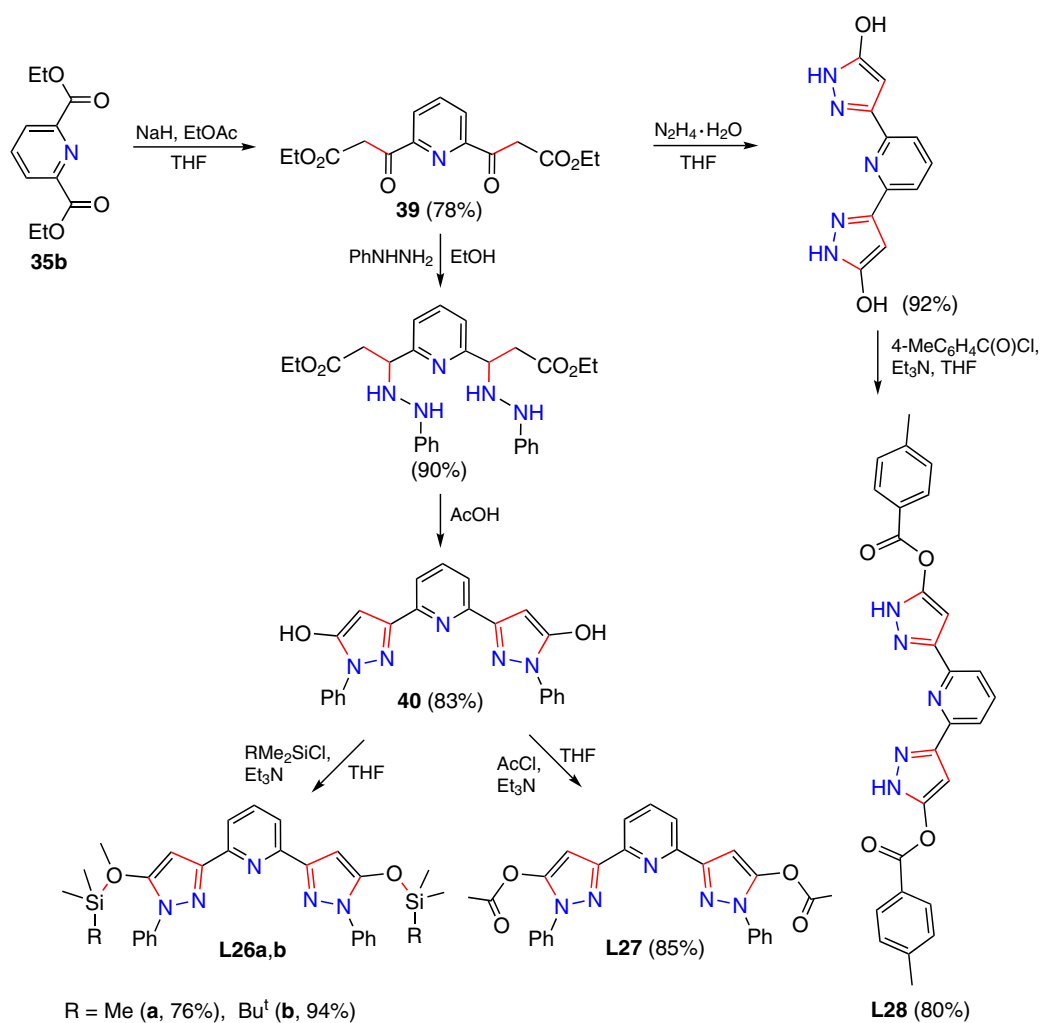
Dimethyl pyridine-2,6-dicarboxylate was also used to synthesize 2,6-bis(pyrazolyl-3(5)-yl)pyridines **L22–L25** with other substituents in the pyrazole ring, including unsymmetrical derivatives (Scheme 31).^{92–94} To introduce an amino group to substrate **35a**, sodium hydride in acetonitrile was added, and then cyclization with hydrazine hydrate was carried out. Treatment of the resulting diamino-bis(pyrazolyl)pyridine **L22** with pivaloyl chloride in acetonitrile gave intermediate hydrochloride, which was converted to free base **L23** upon the addition of Na₂CO₃. The reaction of diamino-substituted ligand **L22** with acyl or benzoyl chloride gave di(methylamino) or



(a) NaH (2 equiv.), MeCN (2 equiv.); (b) $N_2H_4 \cdot H_2O$, EtOH, 78 °C; (c) 1) $Bu^tC(O)Cl$, MeCN; 2) Na_2CO_3 ; (d) 1) Bu^tAc (2 equiv.), NaOEt, PhMe; 2) AcOH, H_2O ; (e) 1) Bu^tAc (1 equiv.), NaOMe (1 equiv.), PhMe; 2) Me_2CO (1 equiv.), NaOMe (1 equiv.), PhMe; (f) 1) Bu^tAc (1 equiv.), NaOMe (1 equiv.), PhMe; 2) MeCN (1 equiv.), NaH (1 equiv.); (g) $N_2H_4 \cdot H_2O$, EtOH, AcOH, rt

di(phenylamido) derivatives. The variation of conditions for the reaction of dimethylpyridine-2,6-dicarboxylate (**35a**) with pinacolone gave bis(β -diketone) **36** (shown in the

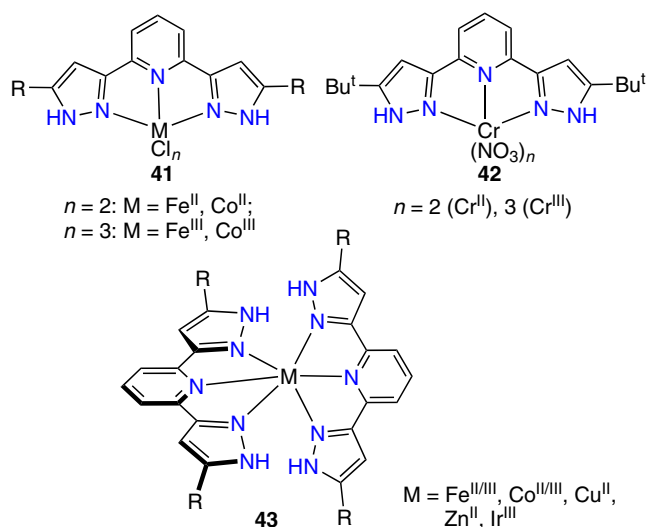
enol form) and unsymmetrical β -diketones **37** and **38**, which reacted with hydrazine hydrate to give ligands **L21a**, **L24** and **L25** (see Scheme 31).



The synthesis of 2,6-bis(1-phenyl-5-hydroxypyrazol-3-yl)pyridines and their silylated derivatives has been reported.⁹⁵ Sterically crowded silylated ligands were used to obtain paramagnetic iron complexes. Ligands **L26–L28** were synthesized by a conventional procedure, which included the initial formation of bis(1,3-ketoester) **35b** via the Claisen condensation and the subsequent cyclization of intermediate **39** with phenylhydrazine in an acid medium (Scheme 32). The silylation of 2,6-bis(5-hydroxy-1-phenylpyrazol-3-yl)pyridine **40** with Me₃SiCl or Me₂Bu^tSiCl was carried out in THF using triethylamine as a base. In addition, the OH groups of the pyrazole ring can be acylated with carboxylic acid chlorides. Using acetyl chloride and *p*-toluic acid chloride, ligands **L27** and **L28**, respectively, were prepared. This type of modification of substituent in the pyrazole ring makes it possible to vary the donor–acceptor properties of the ligand and to markedly increase the steric crowding.^{96,97}

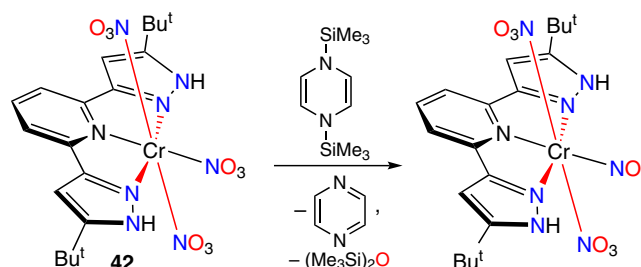
A wide range of transition metal complexes were prepared from ligands **L21–L28**, including complexes of iron,^{90,91,93,94,97–99} cobalt,^{93,100,101} chromium,¹⁰² copper, zinc¹⁰³ and iridium,¹⁰⁴ for example, **41–43**.

Structures 41–43



The interest in these complexes is mainly associated with their magnetic behaviour. In addition, in relation to chromium(III) complex **42**, the possibility of catalytic deoxygenation of the nitrate ion to nitrosyl was demonstrated (Scheme 33).⁷⁹

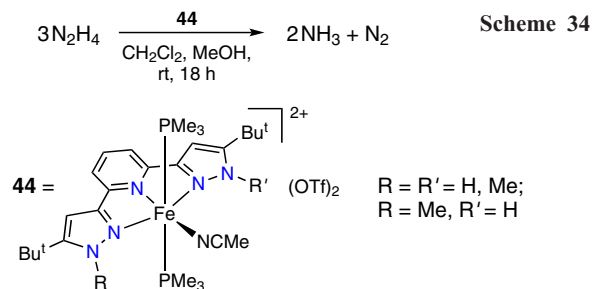
Scheme 33



Iron(II) pincer complexes **44** with ligands **L21a–c** are active catalysts of N–N bond cleavage in hydrazines (Scheme 34).⁹¹

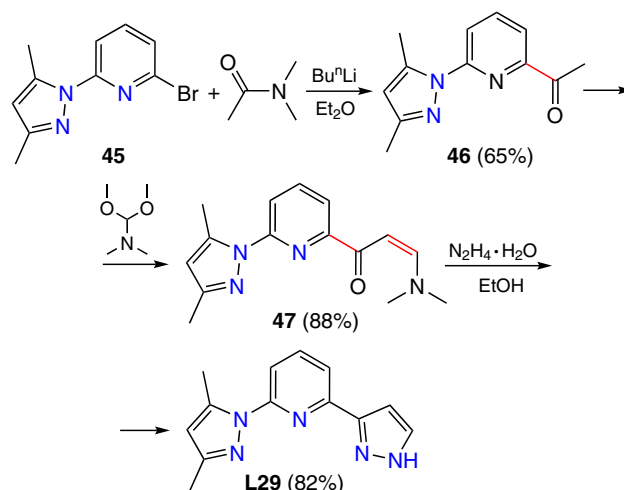
5.3. NNN ligands based on 2-(1*H*-pyrazol-1-yl)pyridine

The synthesis of tridentate ligand **L29**, which contains 1- and 3(5)-substituted pyrazole in the pyridine ring, was reported by



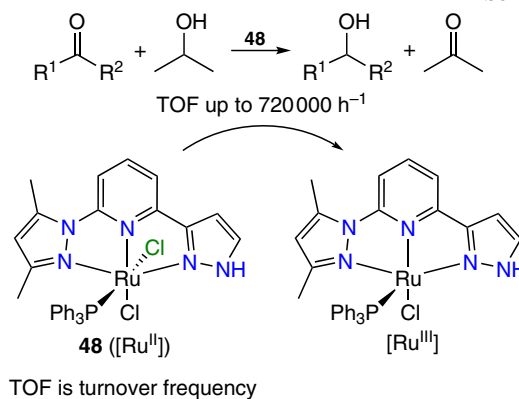
Jin *et al.*¹⁰⁵ The authors used 2-bromo-6-(3,5-dimethylpyrazol-1-yl)pyridine (**45**) as the starting compound; the sequence of transformations included three steps (Scheme 35). In the first step, substrate **45** reacted with *N,N*-dimethylacetamide in the presence of a base at -78°C to yield 2-acetyl-6-(3,5-dimethylpyrazol-1-yl)pyridine (**46**). This product was treated with *N,N*-dimethylformamide dimethyl acetal on heating; this resulted in the formation of β -amino-substituted enone **47**, which reacted with hydrazine hydrate to give the target ligand.

Scheme 35



Ruthenium(II) complex **48** with ligand **L29** is an efficient catalyst for the hydrogenation of ketones the mechanism of which includes a hydrogen atom transfer (Scheme 36).¹⁰⁵

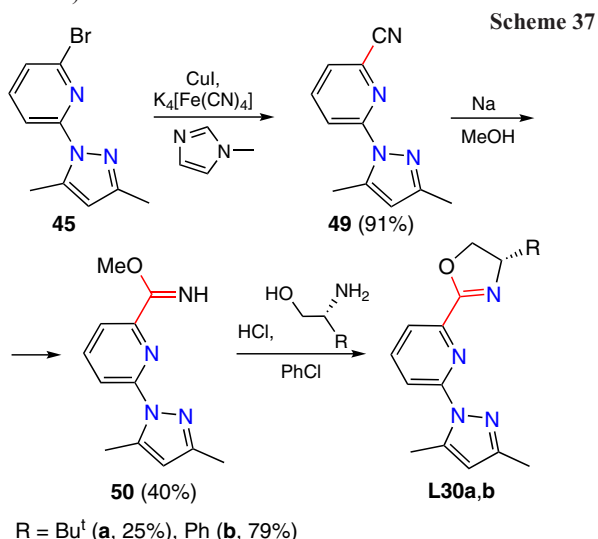
Scheme 36



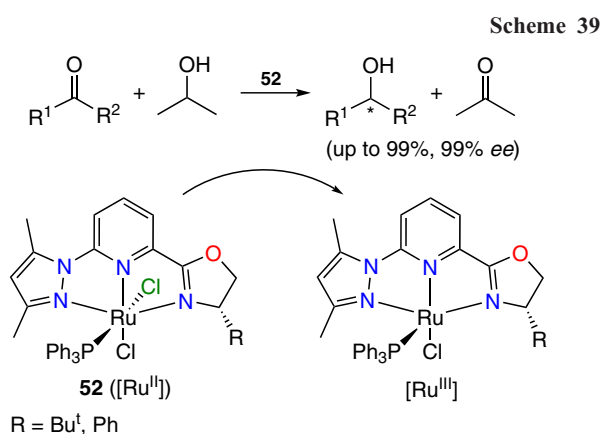
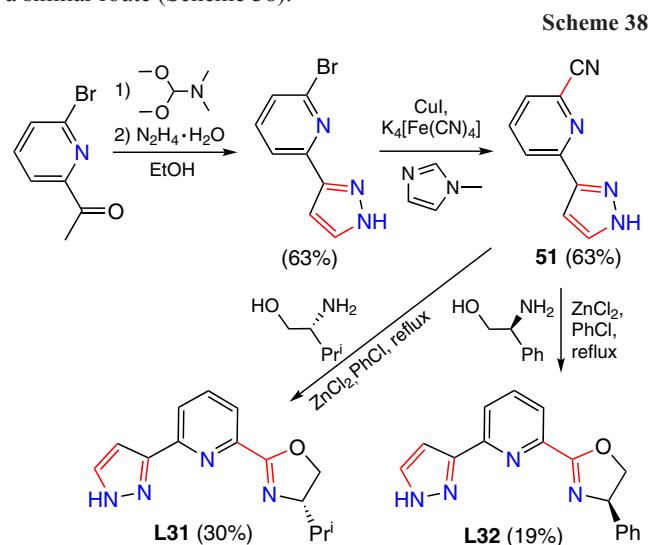
5.4. Unsymmetrical NNN ligands with oxazoline ring

Ye *et al.*¹⁰⁶ reported 2-(1*H*-pyrazolyl)pyridines **L30–L32** containing chiral oxazoline moieties in position 6. Ligands

L30a,b were synthesized by a three-step sequence of reactions. In the first step, 2-bromo-6-(pyrazol-1-yl)pyridine **45** was subjected to the copper complex-catalyzed reaction with potassium ferrocyanide, which resulted in the formation of a new C–C bond. The subsequent reaction of cyanide **49** with methanol in the presence of sodium gave imidate **50**, which reacted with chiral amino alcohols to give target ligands (Scheme 37).



Compounds **L31** and **L32** were prepared from cyanide **51** via a similar route (Scheme 38).

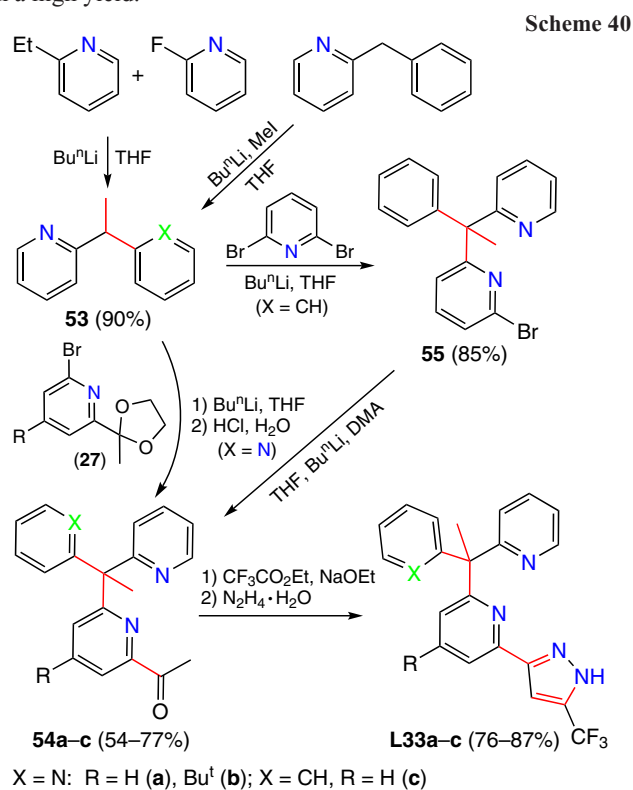


Ruthenium(II) complexes **52** based on ligands **L30a,b** are involved in the catalytic hydrogen atom transfer in the asymmetric hydrogenation of ketones (Scheme 39).¹⁰⁶

6. Polydentate ligands containing different types of coordination sites

6.1. Tetradentate CNNN and NNNN ligands

An increase in the number of coordination sites in the ligand additionally stabilizes the metal complex structure. Lee and co-workers^{107,108} synthesized non-planar tetradentate pyrazolylpyridines **L33a–c** containing an additional nitrogen atom by introducing a sterically crowded 1,1-bis(2-pyridyl)ethyl moiety at position 6 of the pyridine ring (Scheme 40). The starting 1,1-bis(2-pyridyl)ethane (**53**) was prepared by coupling of 2-ethyl- and 2-fluoropyridines. One bromine atom in 2,6-dibromopyridine was substituted by a 1,1-bis(2-pyridyl)ethane moiety, while the other one was replaced by an acetyl group; this gave ketone **54a** (R = H). Similar ketone **54b** with a *tert*-butyl substituent was synthesized by the reaction of 1,1-bis(2-pyridyl)ethane (**53**) with 1,3-dioxolane, with the dioxolane protecting group being subsequently removed. Intermediates **54** were treated successively with ethyl trifluoroacetate in the presence of a base and then with hydrazine hydrate.⁷⁸ Tetradentate pyrazolylpyridine **L33c** containing a phenyl group instead of one of the pyridine rings was synthesized from commercially available 2-benzylpyridine by a similar route.⁷⁹ In this case, intermediate **55** was isolated in a pure state in a high yield.



Depending on the reaction conditions and the starting reactants, compounds **L33** can be complexed with iridium(III) as either tridentate (see the structure of [Ir(κ^3 -**L33c**)Cl₂]₂ in Fig. 3) or tetradentate ligands (see, for example, [Ir(κ^4 -**L33a**)Cl₂] and [Ir(κ^4 -**L33a**)Cl·Py]). The complexes show blue to green emission, depending on substituents and structure, with a good electroluminescence quantum efficiency.^{107,108}

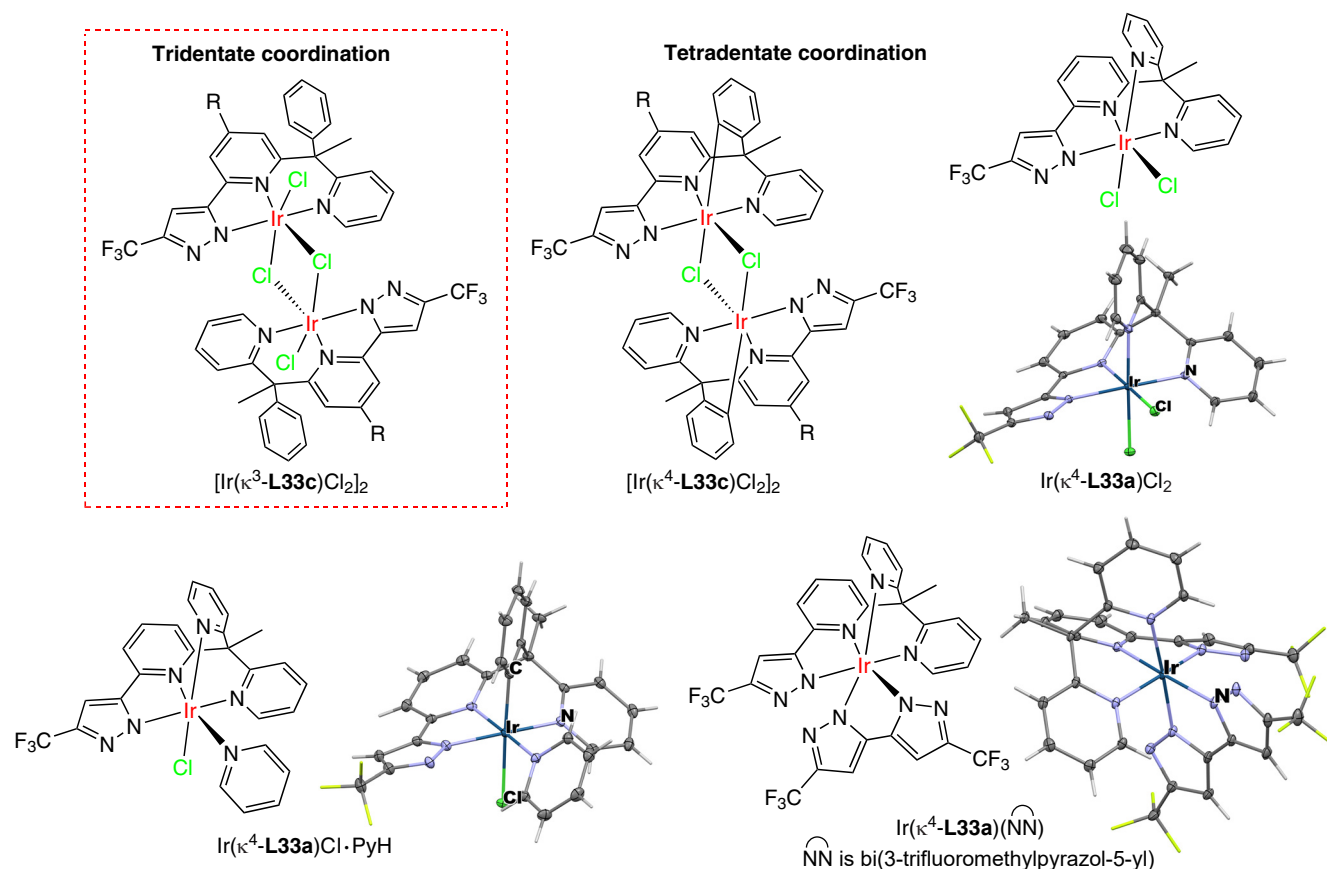


Figure 3. Examples of iridium(III) complexes with ligands **L33** demonstrating various types of coordination.^{107,108}

6.2. Ligands containing two pyrazolypyridine moieties

Tetradentate ligands able to form complexes with either square planar or distorted tetrahedral metal ion environment are of considerable interest. A change in the ligand structure may markedly stabilize the metal oxidation state upon complexation. Conformationally flexible ligands consisting of two

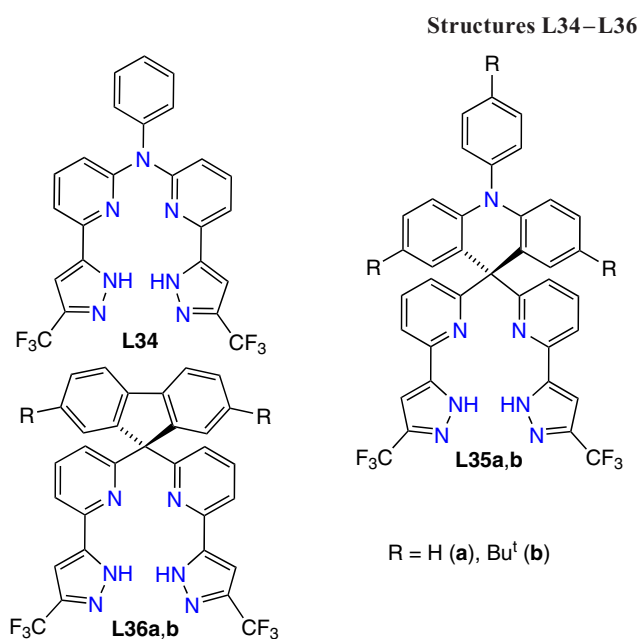
2-(1*H*-pyrazol-3(5)-yl)pyridine moieties linked to each other by an amine nitrogen atom (**L34**) or spiroacridine (**L35**) or spirofluorene (**L36**) carbon atom were prepared.

Compound **L34** was obtained in three steps from aniline and protected 6-acetyl-2-bromopyridine **27** (R = H).¹⁰⁹ The first step was palladium-catalyzed coupling of reactants to give two C–N bonds. Chang *et al.*¹⁰⁹ referred to the original¹¹⁰ method for the synthesis of intermediate **56** and indicated the need to carry out successive reactions with one equivalent of bromo derivative **27** and isolation of intermediate compounds after each step. Then the 1,3-dioxolane moiety was hydrolyzed to the acetyl group, and the resulting diketone **57** was converted to target *N,N*-bis[2-(pyrazolyl)pyridyl]aniline *via* the Claisen condensation and the subsequent cyclization with hydrazine (Scheme 41).

Ligands **L35a,b** were prepared also using 6-bromo-2-(2-methyl-1,3-dioxolan-2-yl)pyridine **27** as the starting compound. First, it was converted to ketone **58**, which was allowed to react with 2-iodobiphenyl to afford tertiary alcohol **59**. The subsequent dehydration and acyl deprotection in an acid medium resulted in the simultaneous formation of the spirofluorene bridge and two acetyl groups. Spiroacridine chelating ligands **L36a,b** were synthesized according to the same route (Scheme 42).¹¹¹

Ligands **L34–L36** were utilized for the synthesis of phosphorescent osmium(II) and platinum(II) complexes **60a,b–62a,b** (Fig. 4), which served for the fabrication of red,¹⁰⁹ blue and white¹¹¹ OLED devices.

Bis-amide ligand *N*¹,*N*³-bis[5(3)-(2-pyridyl)-1*H*-pyrazol-3(5)-yl]isophthalamide (**L37**), containing two pyrazolypyridine moieties, was employed to prepare nano-sized metalogels based



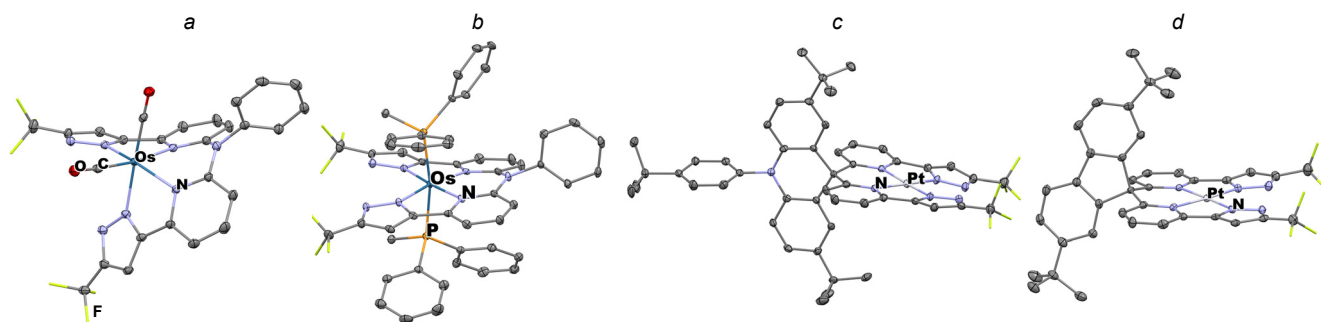
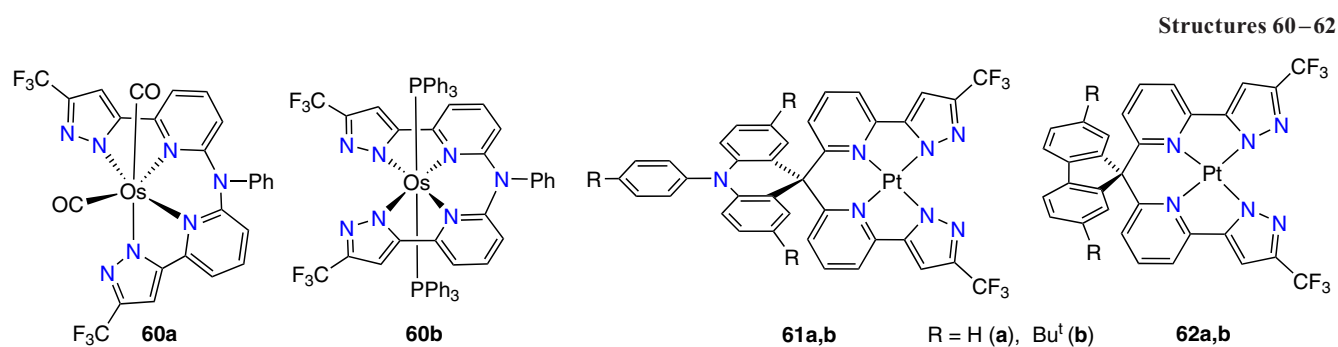
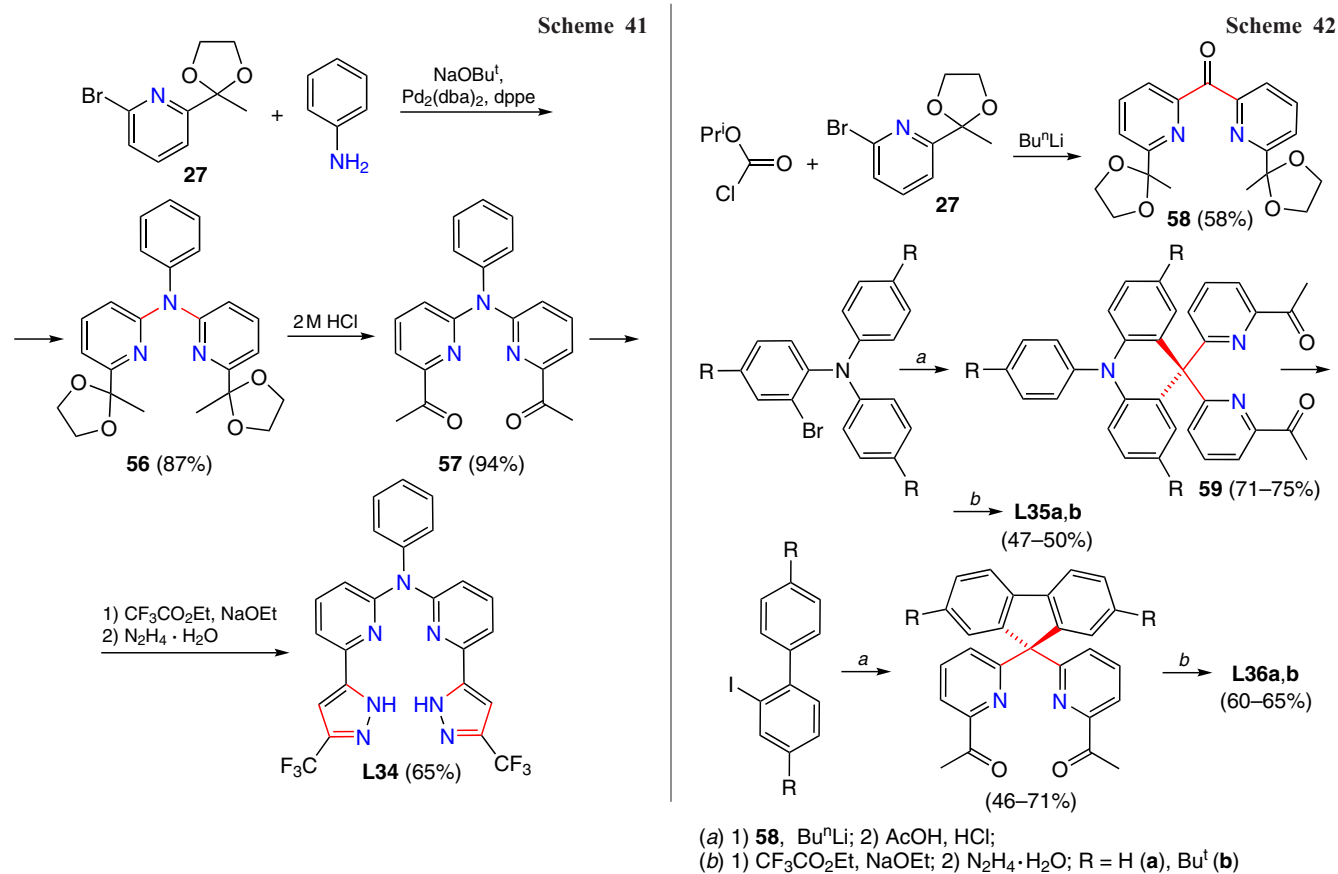
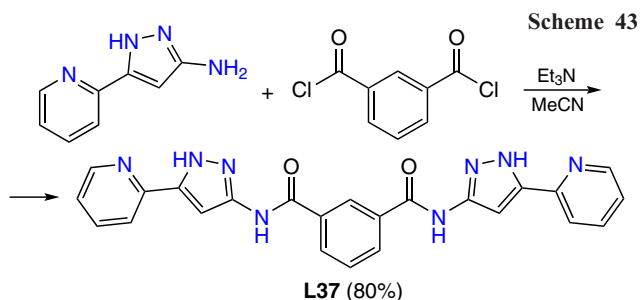


Figure 4. Molecular structures of osmium complexes **60a,b** (Ref. 109) and platinum complexes **61b**, **62b** (Ref. 111) according to X-ray diffraction data (*a–d*, respectively).

on copper salts. This compound is formed in the reaction of 3(5)-amino-5(3)-(2-pyridyl)-1*H*-pyrazole¹¹² and isophthaloyl chloride in the presence of triethylamine in acetonitrile (Scheme 43).¹¹³

6.3. Ligands with two pyridine and one pyrazole rings

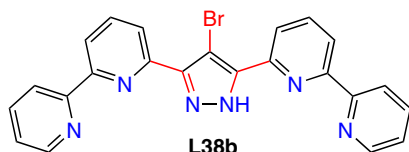
Schneider *et al.*¹¹⁴ described the synthesis of 3,5-bis(2,2'-bipyridin-6-yl)-4-methyl-1*H*-pyrazole (**L38a**), a ligand present in a cyclic tetranuclear Fe^{II} complex, which was found to be



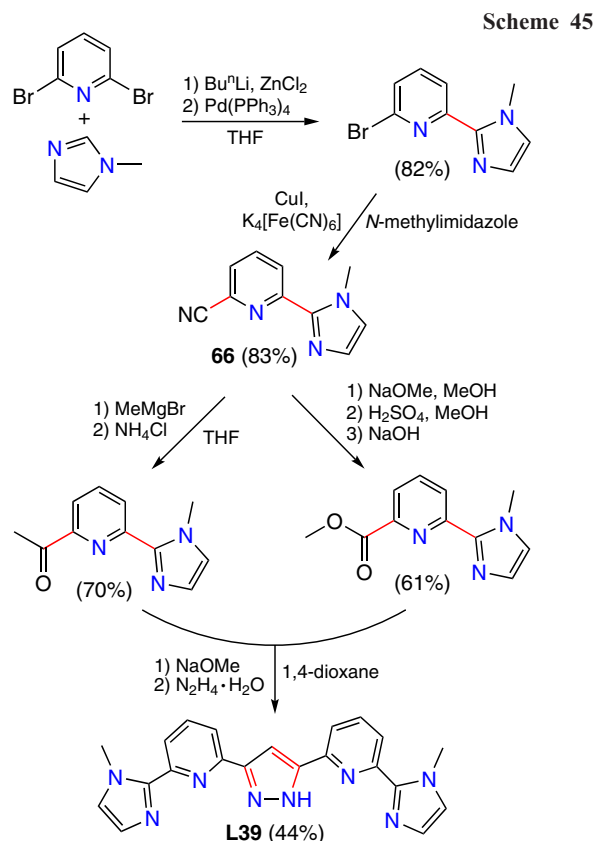
applicable as a molecular component for quantum logic devices. This ligand can be prepared from 6-cyano-2,2'-bipyridine in two ways (Scheme 44). The standard treatment of this reactant with sodium methoxide led to ester **63**, while addition of the Grignard reagent followed by hydrolysis gave ketone **64**. The Claisen pseudo-condensation involving intermediates **63** and **64** and the subsequent treatment with hydrazine furnished the target product in a moderate yield. Alternatively, ester **63** reacts with 6-acetyl-2,2'-bipyridine to give 1,3-diketone **65**, which is methylated in the presence of a strong base, potassium bis(trimethylsilyl) amide (KHMDS). The final cyclization with hydrazine results in the formation of ligand **L38a**.

Analogous ligand **L38b** with a bromine atom in position 4 of the pyrazole moiety is formed upon the bromination of 3,5-bis(2,2'-bipyridin-6-yl)-1*H*-pyrazole.¹¹⁵

Structure L38b



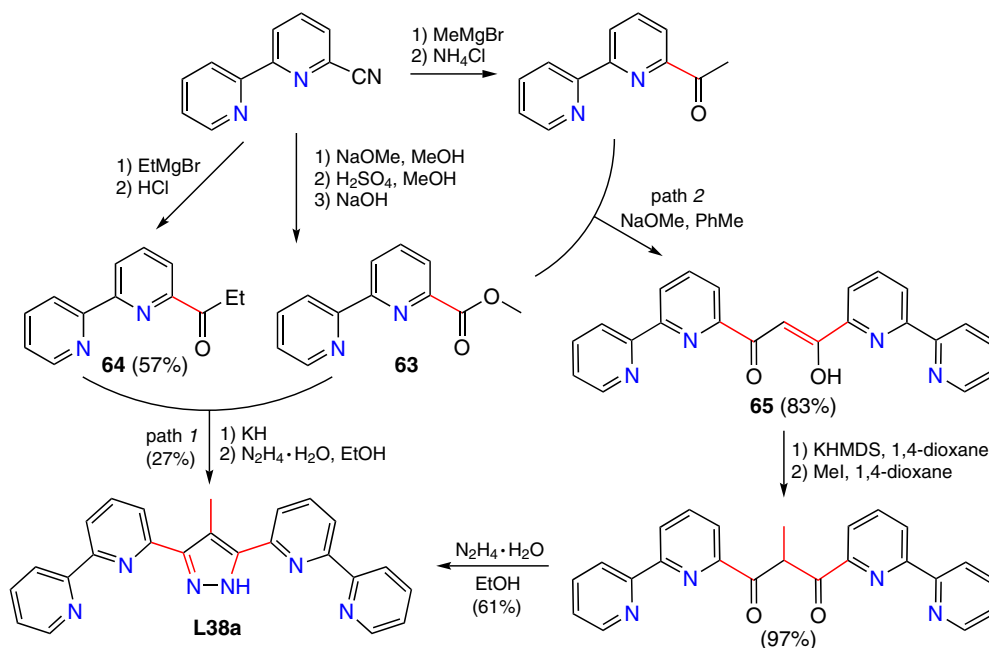
3,5-Bis[6-(1-methyl-1*H*-imidazol-2-yl)pyridin-2-yl]pyrazole (**L39**) was prepared from 2,6-dibromopyridine and 1-methyl-1*H*-imidazole. This ligand has a central pyrazole ring, positions 3 and 5 of which are substituted with pyridine moieties, which are both substituted with 1-methyl-1*H*-imidazole moieties (Scheme 45). The key intermediate compound, 6-cyano-2-(1-methyl-1*H*-imidazol-2-yl)pyridine (**66**), was modified by two



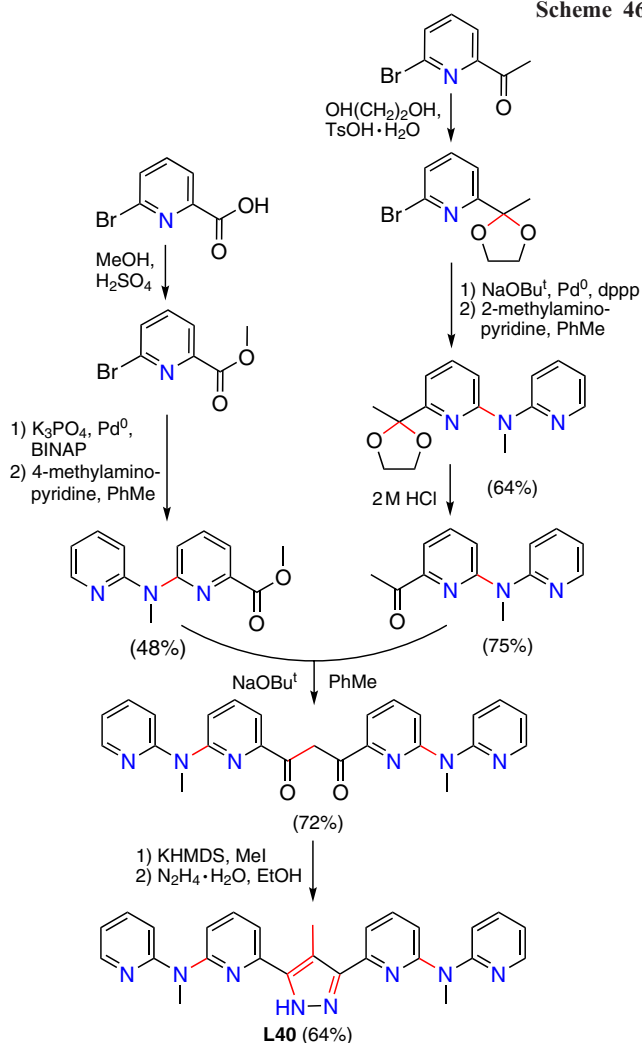
routes involving the intermediate formation of 6-acetyl- and 6-methoxycarbonyl-2-(1-methyl-1*H*-imidazol-2-yl)pyridines, respectively. The Claisen condensation of these intermediates followed by hydrazine-induced condensation furnished ligand **L39** (see Scheme 45).¹¹⁶

As a continuation of studies of the magnetic properties of iron complexes, Professor Meyer and co-workers¹¹⁷ synthesized a polydentate ligand containing four pyridine rings and one pyrazole ring: 3,5-bis[2-[*N*-methyl-*N*-(2-pyridyl)]aminopyridin-6-yl]-4-methyl-1*H*-pyrazole (**L40**). Bromosubstituted

Scheme 44



Scheme 46



7. Conclusion

This review systematizes published data on the methods of synthesis and functionalization of 1*H*-pyrazolopyridines and gives the structures and properties of coordination compounds of various metals with these ligands. One of the goals of this publication is to demonstrate the possibilities of the title ligands to directly affect the properties of metal complexes. The presented data are meant to contribute to establishing the ‘functional ligand–metal complex structure–property of the complex’ relationships. The currently available studies on 1*H*-pyrazolopyridine ligands mainly address the luminescent properties of the complexes. Among them, the greater part of papers are devoted to phosphorescent noble metal complexes,

which are applicable for the design of OLED devices and solar cells. Data on group 11 metal complexes with 1*H*-pyrazolopyridine ligands are limited to three dozens of examples. The possibility of preparing these ligands in the deprotonated form makes it possible to obtain neutral complexes, which simplifies the fabrication of thin films for OLED devices. Meanwhile, metal complexes with pyridine-pyrazole derivatives in the NH form are efficiently used in catalytic reactions owing to their ability to proton transfer or to additional stabilization of intermediates upon coordination. For this reason, the preparation of new ligands containing various functional groups and coordination compounds based on them remains relevant.

One more goal of this work is to demonstrate the advantages of 1*H*-pyrazolopyridine ligands over 2,2'-bipyridine derivatives. The data presented in the review demonstrate the ease of preparation of 1*H*-pyrazolopyridines and the ways to modify them according to the selected goal. The presence of two linked rings, pyridine and pyrazole ones, accounts for the wide choice of synthetic pathways. The key method of combining these heterocyclic moieties is the condensation of an ester and a ketone. Modification of both reactants before this step allows relatively easy synthesis of the target products with desired properties. This review should help scientists specializing in various fields of chemistry, including those unrelated to organic synthesis, to obtain a sufficient amount of information about 1*H*-pyrazolopyridines as multifunctional building blocks for metal complexes.

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8. List of abbreviations and symbols

The following abbreviations and symbols were used in the review.

BINAP — 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl,
 B2Pin2 — bis(pinacolato)diboron,
 DACH — diaminocyclohexane,
 dba — dibenzylideneacetone,
 DMA — *N,N*-dimethylacetamide,
 dpephos — bis(2-diphenylphosphinophenyl) ether,
 dppbz — 1,2-bis(diphenylphosphino)benzene,
 dppe — 1,2-bis(diphenylphosphino)ethane,
 dppf — 1,1'-bis(diphenylphosphino)ferrocene,
 dppm — bis(diphenylphosphino)methane,
 dppp — 1,3-bis(diphenylphosphino)propane,
 EDTA — ethylenediaminetetraacetic acid,
 HOMO — highest occupied molecular orbital,
 LEEC — light-emitting electrochemical cell,
 LG — leaving group,
 OLED — organic light-emitting diode,
 KHMDS — potassium bis(trimethylsilyl)amide,
 LUMO — lowest unoccupied molecular orbital,
 MW — microwave radiation,
 NBS — *N*-bromosuccinimide,
 NP — nanoparticles,
 PMP — *p*-methoxyphenyl,
 PTC — phase transfer catalyst,
 Py — 2-pyridyl,
 rt — room temperature,
 Ts — *p*-toluenesulfonyl (tosyl),

TBAB — tetra-*n*-butylammonium bromide,
Xantphos — 9,9-dimethyl-4,5-bis(diphenylphosphino)-
xanthene.

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