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Review

Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: Synthesis, functional materials properties, and applications to catalysis

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Dedicated to our distinguished colleague and friend Prof. Jean-Yves Saillard on the occasion of his 70th birthday.

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Unsymmetrically-substituted Schiff base complexes
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ABSTRACT

This review focuses on the recent developments of unsymmetrically-substituted multidentate Schiff bases whose steric and electronic characteristics are easily manipulated by selecting suitable condensing aldehydes or ketones and primary amines, and on their metal complexes. After a brief historical introduction, this manuscript is divided in three main sections. In the two first parts, the synthesis, reactivity, functions, and properties of tridentate Schiff base precursors and of quadridentate Schiff base metal complexes, respectively, are discussed through a literature survey including examples of research from the authors' groups. More specifically, the second section is formed of seven subsections with the synthesis of unsymmetrically-substituted tetradentate Schiff bases and their transition metal (V, Mn, Fe, Co, Ni, Cu, Zn, Ru, Pd, Pt) and uranyl complexes. Emphasis is given to our research work based on ferrocenyl-containing tri- and tetradentate unsymmetrically-substituted Schiff base complexes of Ni(II) and Cu(II) starting from variously substituted ferrocenyl-β-diketones. The unsymmetrically-substituted Schiff base complexes present a wide range of remarkable properties that are also summarized in this section, including structural, biocidal, magnetic, and second-order nonlinear optical properties. The third section is devoted to the catalytic activity of Schiff base metal complexes that is discussed through thirteen major organic reactions, including copper-catalyzed azide–alkyne cycloaddition (CuAAC), Henry and nitro-Mannich reactions, hydrosilylation of ketones, aldol, cyclopropanation and epoxidation reactions, among others.

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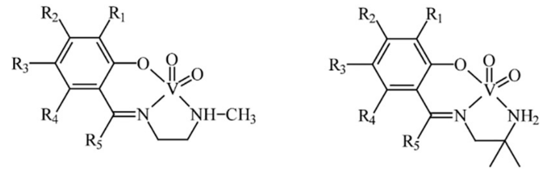
1. Introduction

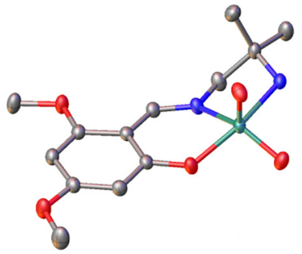
The term ≪Schiff base≫ comes from the name of Hugo Schiff (1834–1915) [1,2], an Italian-naturalized chemist, German by nationality, who synthesized the first so-called Schiff base (SB) in 1864 [3,4]. Schiff bases (SBs), characterized by an imine (>C=N—) or azomethine (—HC=N—) group, are generally synthesized by condensation reactions of carbonyl functionalities (ketone or aldehyde) with primary amines. SBs have gained considerable attention due to their remarkable biological activities (such as antiapoptotic, antifungal, antibacterial, anti-inflammatory and antiviral activities) [5–7], catalytic activities [8–13], electroluminescent properties [14–16], fluorescence properties [17–19], nonlinear optical (NLO) properties [20], and applications in sensors [21] and organic photovoltaic materials [22]. Owing to the easy tunability of their stereo-electronic structures, most SBs are fascinating ligands, because they readily form stable complexes with most of the transition metals [23,24]. Consequently, during the last decades the symmetrically-substituted SB metal complexes have been intensively studied because of their specific eminent catalytic activities, and this field has been the subject of numerous reviews [25–31]. For instance, Katsuki summarized the generation of *cis-β* metallosalen and its related complexes (the term salen represents the SB obtained through the condensation of two (identical or not) salicylaldehydes with a primary diamine), and reported their structural features and their applications in asymmetric synthesis [27]. On the other hand, Soloshonok and co-workers provided a good overview of using homologation of Ni(II) unsymmetrically-substituted SB complexes to obtain asymmetric α-amino acids [30,31]. Meanwhile, more than 500 new papers on unsymmetrically-substituted SB catalysts and unsymmetrically-substituted SB metal complex systems have been reported in the last three years. Many new features have also been discovered; for instance unsymmetrically-substituted SB metal complexes are more efficient catalysts than symmetrically-substituted SB complexes for the olefin polymerization [32]. The main factors contributing to the process of unsymmetrically-substituted SB complexes are the control of their specific structures with more than two different functional SB groups [33] and their excellent electronic and steric properties that are critical in catalytic systems [34].

Since their discovery, SBs are one of the most widely used ligands due to their easy preparation and remarkable versatility, and, therefore they played a pivotal role in the development of coordination chemistry of main group elements, transition metals and lanthanides. As a consequence, this very broad research field dealing with macrocyclic and acyclic SBs and their metal complexes has led to an extensive number of publications, and has been comprehensively reviewed in 1987 [35] and 2004 [36]. In 2016, Li and co-workers [37] also summarized some classical synthetic strategy of asymmetric SBs derived from diaminomaleonitrile and their Zn, Cd and Cu complexes. In this review, divided in three main parts, we will focus on the synthesis, reactivity, functions, and properties of multidentate SBs and their metal complexes, based on selected recent works. The two first part considers tridentate and unsymmetrically-substituted tetradentate SBs and their respective transition metal (V, Mn, Fe, Co, Ni, Cu, Zn, Ru, Pd, Pt) and uranyl complexes, and emphasizes our research work based on ferrocenyl-containing tri- and tetradentate unsymmetrically-substituted SB complexes of Ni(II) and Cu(II) starting from variously substituted ferrocenyl-*β*-diketones. Some aspects of the structural, biocidal, magnetic, and second-order nonlinear optical properties of both the multidentate SBs and complexes are also outlined in this section. The third part of the review highlights the application to catalysis of various multidentate SB complexes in a panoramic view of thirteen major organic reactions, including copper-catalyzed azide–alkyne cycloaddition (CuAAC), Henry and nitro-Mannich reactions, hydrosilylation of ketones, aldol, cyclopropanation and epoxidation reactions, among others.

2. Tridentate Schiff base ligands and their metal complexes

In general, ONN-tridentate SB ligands are formed upon mono-condensation reactions of a *β*-diketone with one end of a primary diamine [38–58]. Such singly condensed compounds having a free amino group are commonly referred as “half units” [38–40] as they are potential precursors in the preparation of unsymmetrically-substituted tetradentate SBs (see Section 3). The tridentate SBs can exist in solution as a tautomeric mixture of keto-amine (enaminone, —(O=)C(R)—CH=C(R′)—NH—), and keto-imine (iminone, —(O=)C(R)—CH_2—C(R′)=N—), forms [59]. In some instances, depending on the nature of the substituents of the *β*-diketone and/or the presence of transition metal ions in solution, either deacetylation of the starting *β*-diketone [60] or formation of 1,4-and/or 1,5-diazepine can occur [61,62]. In some instances, tridentate SBs can be isolated from condensation of salicylaldehyde and diamines such as 1,2-phenylenediamine or 1,2-diaminocyclohexane [63–66], but in the cases of 1,2-ethanediamine and 1,3-propanediamine, the half-units must be trapped as metal(II) half-unit complexes (M = Ni, Cu) in order to avoid the formation of the double-condensation products [67–70].





	R_1	R_2	R_3	R_4	R_5
1	H	H	H	H	H
2	H	H	OCH_3	H	H
3	H	H	CH_3	H	H
4	H	H	Br	H	H
5	H	H	NO_2	H	H
6	H	H	H	H	CH_3
7	H	H	H	H	C_6H_5
8	H	H	$-(CH)_4-$		H
9	$-(CH)_4-$		H	H	CH_3
10	H	OCH_3	H	OCH_3	H

	R_1	R_2	R_3	R_4	R_5
11	H	H	H	H	H
12	H	H	OCH_3	H	H
13	H	H	CH_3	H	H
14	H	H	Br	H	H
15	H	H	NO_2	H	H
16	H	H	H	H	CH_3
17	H	H	H	H	C_6H_5
18	H	H	$-(CH)_4-$		H
19	$-(CH)_4-$		H	H	CH_3
20	H	OCH_3	H	OCH_3	H

Fig. 1. Schematic representations of dioxovanadium(V) Schiff base complexes **1**–**20** (left), and the molecular structure of **20** (right) [71]. Hydrogen atoms have been omitted for clarity. Color code: V, emerald; O, red; N, blue. Partly reprinted from Ref. [71], copyright 2003, Elsevier B. V.

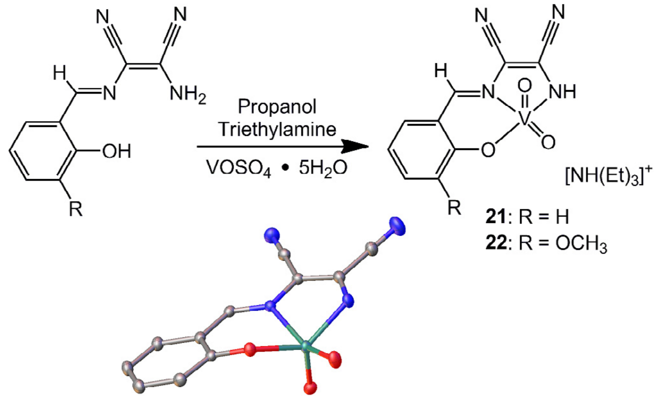


Fig. 2. Synthesis of the ionic vanadium(V) Schiff base complexes **21** and **22** (top), and the molecular structure of **21** (bottom) [72]. Hydrogen atoms and the counter cation have been omitted for clarity. Color code: V, emerald; O, red; N, blue.

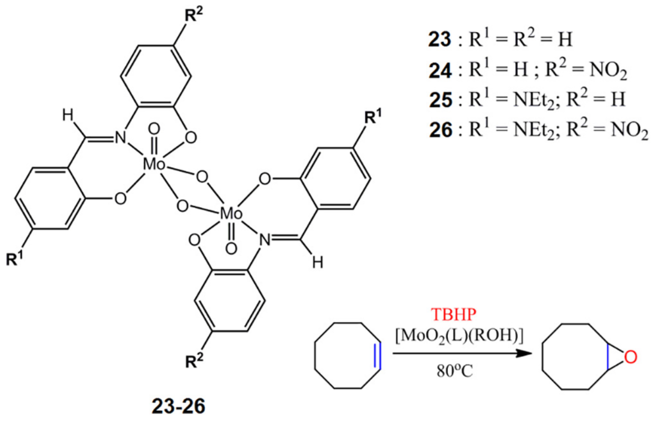


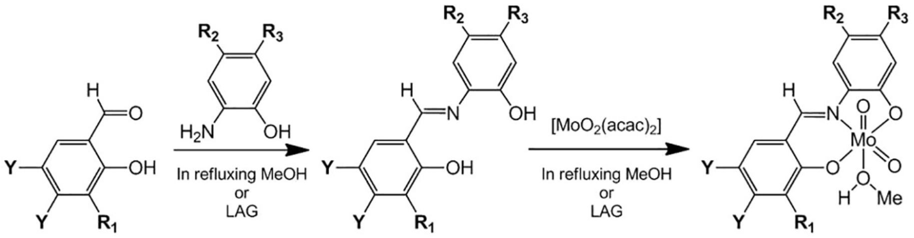
Fig. 3. Dioxomolybdenum(salicylidene-2-aminophenolate) complexes **23**–**26** derived of $[MoO_2(L)(EtOH)]$ compounds used for EFISH measurements [73] and catalytic epoxidation of cyclooctene [74].

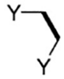
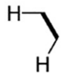
Kwiatkowski and co-workers synthesized a series of twenty new neutral dioxovanadium(V) complexes **1**–**20** (Fig. 1) with ONN-tridentate SB ligands through the condensation of salicylaldehyde or its derivatives, 2-hydroxybenzophenone, 2-hydroxyacetophenone, 2-hydroxy-1-naphthaldehyde and 1-hydroxy-2-acetonaphthone with 2-methyl-1,2-diaminopropane or N-methyl-1,2-diaminoethane [71]. The single-crystal X-ray structure of 2-(4-amino-4-methyl-2-aza-1-penten-1-yl)-3,5-dimethoxy-phenolato)dioxovanadium **2** revealed a distorted trigonal-bipyramidal coordination geometry (Fig. 1). The two 5-methoxyphenolato-vanadyl derivatives **2** and **12** catalyze the oxidation of thioanisole to the corresponding sulfoxide by cumene hydroperoxide.

On the other hand, Ebrahimipour and co-workers [72] prepared two ionic *cis* dioxido-vanadate(V) complexes, isolated as their triethylammonium salts **21** and **22** (Fig. 2), incorporating dimalononitrile-based dianionic O,N,N-tridentate SB ligands and showed, using single-crystal X-ray diffraction, that the vanadium (V) ions adopt a distorted square pyramidal geometry, as shown with derivative **21** containing the 3-((*E*)-(2-hydroxybenzylidene)) unit (Fig. 2). In addition, both compounds were found to possess significant antibacterial activity against Gram negative and Gram positive bacteria and antifungal activity against *Candida albicans*.

Dioxomolybdenum(VI) coordination compounds supported by ONO-tridentate SB ligands (L), based on the salicylidene-2-aminophenolato structure $[MoO_2(L)(EtOH)]$ (**23**–**26**, Fig. 3), showed both NLO properties and catalytic activity. Farfán *et al.* evaluated the second-order NLO responses of the monomeric complexes by means of electric field-induced second harmonic (EFISH) technique in ethanol phase, with values in the interesting range of $20–600 \times 10^{-30}$ esu (CGS unit, charge in electrostatic units). As expected, the push–pull derivative **26**, containing the strongest donor NEt_2 and acceptor NO_2 substituents, exhibited the largest $\mu\beta$ value owing to improved intramolecular charge transfer properties between the donor–acceptor groups and the central Mo-core [73]. Due to their easy one-pot preparation, air stability and excellent thermal resistance, such $[MoO_2(L)]$-type systems appear as good candidates for molecular materials with enhanced NLO properties.

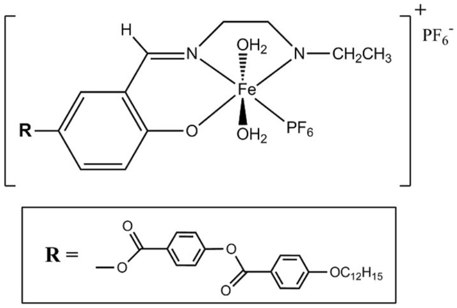
In parallel with this work, Poli and co-workers explored the electronic effect of the substituents in the ligand backbone on the catalytic activity of these dioxomolybdenum(VI) complexes **23**–**26** under solvent-free epoxidation conditions using aqueous *tert*-butyl peroxide (TBHP) as oxidant and cyclooctene as substrate (Fig. 3) [74]. The best cyclooctene conversion is achieved with complex **24** bearing the electron withdrawing NO_2 group, but in all the cases the selectivity is greater than 90%. Very recently, Agustin *et al.* reported a series of nine new complexes **27**–**35** of



	R_1	R_2	R_3	Complexes, **27-35**	
	H	H	H	$[MoO_2L^1(CH_3OH)]$	**27**
	H	Me	H	$[MoO_2L^2(CH_3OH)]$	**28**
	H	H	Me	$[MoO_2L^3(CH_3OH)]\cdot CH_3OH$	**29**^{a}
	OMe	H	H	$[MoO_2L^4CH_3OH]$	**30**
	OMe	Me	H	$[MoO_2L^5(CH_3OH)]$	**31**
	OMe	H	Me	$[MoO_2L^6(CH_3OH)]\cdot CH_3OH$	**32**^{a}
	H	H	H	$[MoO_2L^7(CH_3OH)]$	**33**
	H	Me	H	$[MoO_2L^8]_2$	**34**^{b}
	H	H	Me	$[MoO_2L^9(CH_3OH)]\cdot CH_3OH$	**35**^{a}

^{a} CH_3OH solvate, ^{b} dimeric species

Fig. 4. Schematic representations of *cis*-dioxo molybdenum(VI) ONO-tridentate Schiff base complexes **27**–**35** [75].



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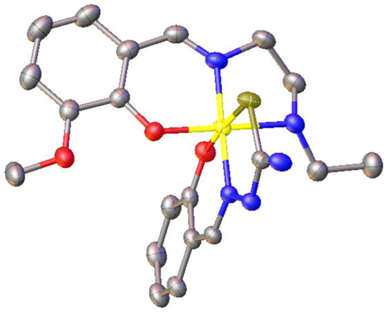
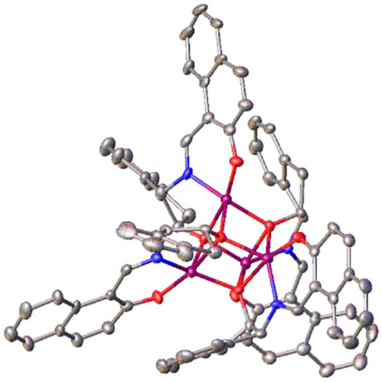


39

Fig. 5. Schematic representation of the structure of the liquid crystalline Schiff base complex $[Fe(L)(H_2O)_2PF_6]^+PF_6^-$ (**36**, left) [76], and molecular structure of the heteroleptic bis-tridentate [Fe(3-OMe-SalEen)(thsa)] SCO complex (**39**, right) [77]. Color code: Fe, yellow; N, blue; O, red; S, brown.



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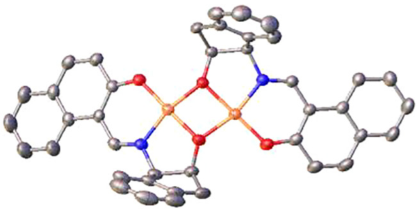


41

Fig. 6. Molecular structures of **40** (left) and **41** (right) [78]; hydrogen atoms have been omitted for clarity. Color code: Co, purple; Cu, orange; O, red; N, blue.

$[MoO_2(L)(ROH)]$ structure prepared by liquid-assisted mechanosynthesis, from $MoO_2(acac)_2$ and SBs derived from appropriately substituted *o*-hydroxyaldehydes and 2-aminophenol or its 4- and 5-methyl derivatives, that were also tested in the catalytic epoxidation of *cis*-cyclooctene, cyclohexene and (*R*)-limonene using aqueous TBHP and in the absence of an organic solvent (Fig. 4) [75].

Six-coordinate d^5 iron(III) complexes with SB ligands are known to display a variety of magnetic behaviors. Domracheva and coworkers synthesized a series of three liquid crystalline Fe(III) SB complexes $[Fe(L)(H_2O)_2X]^+X^-$, in which the iron center is coordinated by the O,N,N-atom donor set of the tridentate ligand L, the water molecules and the various counteranions (PF_6^- (**36**), NO_3^- (**37**), Cl^- (**38**)) [76]. Their magnetic, dynamic and structure properties were measured by EPR and Mössbauer spectroscopies. The results indicated that the low-spin (LS) iron complexes have a $(d_{xz},d_{yz})^4(d_{xy})^1$ ground state when the temperature ranges from 4.2 to 250 K. More fascinatingly, the PF_6^- derivative **36** (Fig. 5) exhibited a dynamic process caused by re-orientation of the PF_6^- counterion ($\Delta H = 27.9$ kJ·mol^{-1}), leading to a second-type of LS iron center observed by EPR spectroscopy in the liquid crystalline phase (387–405 K). Theoretical analysis of the observed *g* values of this second-type of LS complex indicated a stabilized $(d_{xy})^2(d_{xz}, d_{yz})^3$ ground state. The conversion between the two electronic configurations was found to be reversible and temperature dependent. In 2016, Murray *et al.* described the first example of a bis-tridentate heteroleptic iron(III) spin crossover (SCO) complex [Fe(3-OMe-SalEen)(thsa)] **39** (Fig. 5), which showed a gradual-abrupt spin transition at 344 K [77]. In this neutral species, the iron(III) center coordinates in a meridional fashion to the tridentate mono-anionic ONN- (3-OMe-SalEen)$^-$ and di-anionic ONS-(thsa)$^{2-}$ ligands derived from (*E*)-2-(((2-(ethylamino)-ethyl)imino)methyl)-6-methoxyphenol and thiosemicarbazone–salicylaldimine, respectively. The authors also revealed a clear correlation between π–π interactions and the $T_{1/2}$ value.

The use of tridentate SB ligands has received continuous attention for studying structure/magnetic property relationships in the chemistry of polynuclear transition metal compounds. The cubane-like cluster $[Co_4L_4]\cdot CH_3OH$ **40** and the dimeric complex $[Cu_2L_2]$ **41** (Fig. 6) were prepared by Li and co-workers by reacting 1-(((2-hydroxy-2,3-dihydro-1H-inden-1-yl)imino)methyl)naphthalen-2-ol, a H_2L SB ligand possessing an ONO chelating pocket, with hydrated cobalt(II) and copper(II) acetate salts, respectively, under solvothermal conditions [78]. Single-crystal X-ray diffraction studies showed that in both cases the metal(II) centers are bridged by alkoxo oxygen atoms to form a cubane-like $\{Co_4O_4\}$ core in **40** and a rhombic $\{Cu_2O_2\}$ core in **41**. For $[Co_4L_4]\cdot CH_3OH$, the variable-temperature dc magnetic susceptibility studies indicate ferromagnetic Co(II)···Co(II) exchange interactions (Curie constant = 9.66 cm^3 K·mol^{-1}, Weiss constant = 4.01 K), while the ac magnetic susceptibility measurements reveal slow magnetic relaxation (SMM) behavior. $[Cu_2L_2]$ exhibited antiferromagnetic Cu(II)···Cu(II) couplings ($J = -93$ cm^{-1}).

On the other hand, much interest has also been devoted to ferrocenyl-containing SBs because substitution of the β-diketone starting materials by the three-dimensional ferrocenyl (Fc) fragment brought about not only an expansion of the organic moiety into the third dimension, but also the very useful redox properties and the extremely rich chemistry of ferrocenyl (Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$) [79]. As such, Fc–containing chromophores are of continuous interest for fine-tuning and switching of the second-order NLO response, as illustrated in a very recent comprehensive review by Singh *et al.* who discussed structure-dependent linear and nonlinear optical properties along with electrochemical behavior of a wide variety (more than 200 species collected) of ferrocene-based donor–acceptor systems [80].

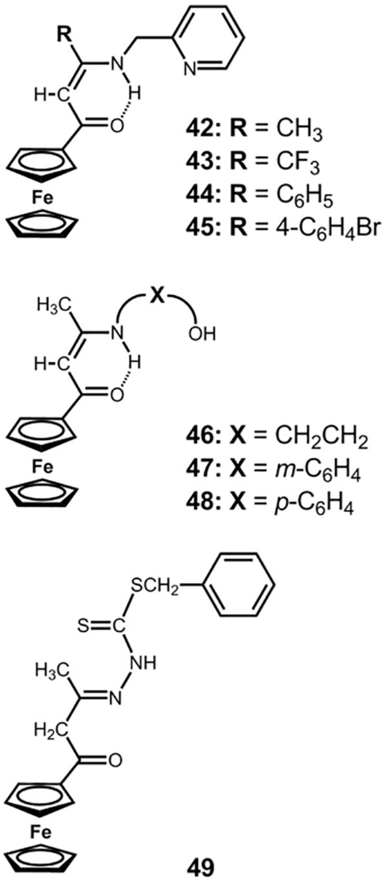
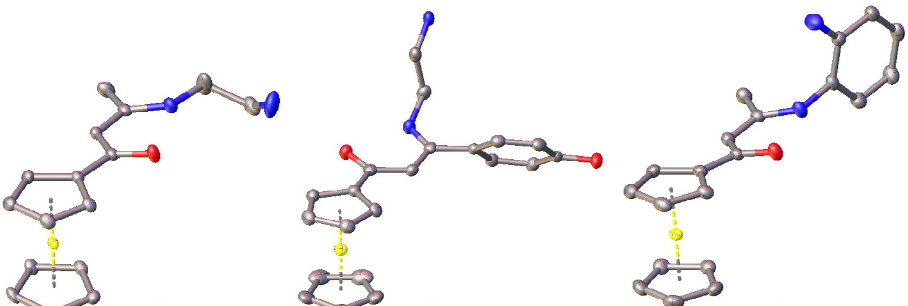


Fig. 7. Ferrocenyl-containing ONN-, ONO- and ONS-tridentate Schiff bases [81–85].

In the 2000s, Shi *et al.* reported on the synthesis and structural characterization of ferrocene-based tridentate metalloligand exhibiting ONN [81], ONO [82,83], and ONS-donor sets [84]; they were obtained by monocondensation of ferrocenoylacetone with 2-(aminomethyl)pyridine **42**, 2-aminoethanol or aminophenols **46**–**48**, and S-benzyldithiocarbazate **49**, respectively (Fig. 7). Very recently, the group of Fuentealba prepared and structurally characterized a series of four organometallic ONN-tridentate SBs upon reaction of variously substituted ferrocenyl β-diketones Fc-C(O)$CH_2C(O)R$ ($R = CH_3$ **42** (previously reported by Shi *et al.* [81]), CF_3 **43**, C_6H_5 **44**, 4-C_6H_4Br **45**) with 2-picolylamine (Fig. 7) [85]. Compounds **42**–**45** and **46**–**48** exist as their enaminone form in solution and in solid phases, whereas **49** exists as two tautomers in a 3:2 iminone:enaminone ratio in solution at room temperature. In the solid-state, only the tautomeric iminone form is present with characteristic C═O (1.221(4) Å) and C═N (1.271(5) Å) double bonds [85].

Our research groups have a long term interest in the synthesis of ONO- and ONN-tridentate SB ligands and half-units, respectively, and their metal complexes [86–92]. The parent ferrocenyl-containing ONN-tridentate SB half-unit **50** (Fig. 8) was first obtained by Hu and co-workers upon monocondensation of ferrocenoylacetone with 1,2-diaminoethane [93]. Compound **50** exists exclusively as its ferrocenyl-enaminone tautomeric form both in solution (methanol) and in the solid-state, showing a strong intramolecular N—H···O═C hydrogen bond ($d_{N\text{—}O} = 2.679$ Å), closing a pseudo six-membered ring [86]. Like **42**, its ONN-tridentate half-unit counterpart **51**, functionalized with the 4-hydroxyphenyl at the imine carbon (Fig. 8), does also exist exclusively as its ferrocenyl-enaminone tautomer in solution (DMSO, $\delta_{NH} = 10.83$ ppm) and in the solid-state ($d_{N\text{—}O} = 2.674(2)$ Å) [87].



50 **51** **52**

Fig. 8. ORTEP views of Fc-containing Schiff base half-units **50** (left) [86], **51** (middle) [87], and **52** (right) [88]. Color code: Fe, yellow; N, blue; O, red.

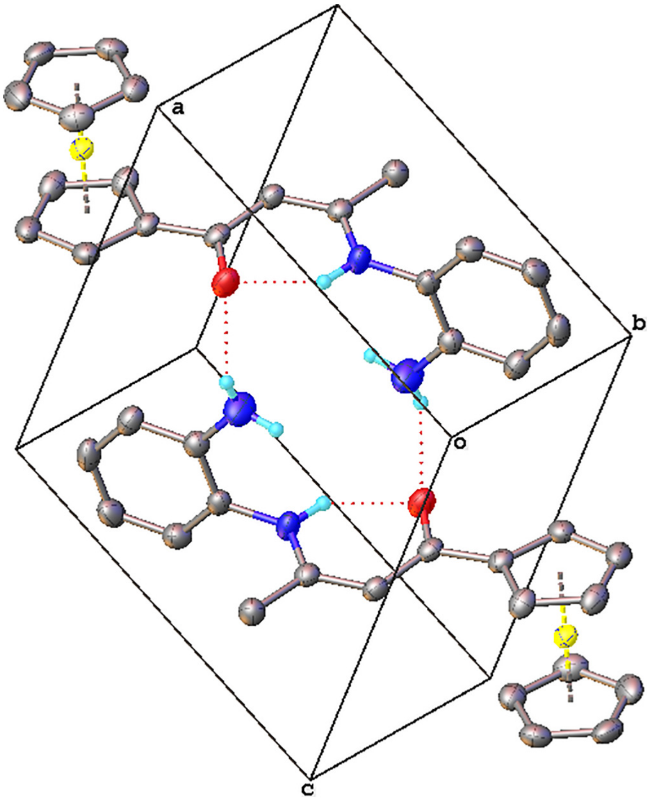


Fig. 9. Packing diagram of the half-unit **52** showing the molecular arrangement and hydrogen-bonding interactions [88]. Non-relevant hydrogen atoms have been omitted for clarity. Color code: Fe, yellow; N, blue; O, red; H, sky-blue.

By contrast, the ONN-tridentate half-unit **52** (Fig. 8), synthetized *via* monocondensation of 1,2-phenylenediamine with ferrocenoylacetone in refluxing toluene, exists in acetone solution as a mixture of two tautomeric isomers in the 3:2 keto-amine: keto-imine ratio as shown by ^{1}H NMR spectroscopy [88]. In the enaminone tautomer, the vinylic and amino protons appear at 5.67 and 12.18 ppm, respectively, whereas in the iminone form the methylene protons show up at 3.16 ppm. In the ^{13}C NMR spectra, their corresponding methine and methylene carbons resonate at 94.53 and 39.71 ppm, respectively. However, only the ferrocenyl-enaminone is found in the solid-state as ascertained by single-crystal X-ray crystallography, with C═O and vinylic C═C bond lengths of 1.259(3) and 1.371(4) Å, respectively [88]. The structure of this tridentate organometallic half-unit **52** is stabilized by two intra- and two inter-molecular hydrogen bond interactions, involving N—H, NH_2 and C = O groups and forming a twelve-membered ring in a self-assembled dimeric species *via* hydrogen bonding (Fig. 9).

Then, we synthesized the orange ferrocenyl- and colorless anisyl-containing ONO-tridentate SBs **53** and **54** by condensation of (1-ferrocenyl)- and (1-anisyl)-1,3-butanedione with 2-aminophenol, respectively (Figs. 10 and 11) [89]. The ternary Ni(II) and Cu(II) SB complexes **55**–**58** (Fig. 10) were readily obtained in a two-step procedure involving the double deprotonation of the diprotic enaminone precursors **53** and **54**, followed by addition of pyridine (or 4-^{t}Bu-pyridine) and the appropriate hydrated metal(II) nitrate salt in tetrahydrofuran (THF) at room temperature. In the absence of ^{t}Bu-pyridine, the doubly phenoxo bridged homobimetallic Cu(II) dimer **59** was invariably obtained (Fig. 10). X-ray crystallography indicated that in the Schiff base complexes **55**–**58**, the nickel(II) and copper(II) ions adopt a four-coordinate square-planar geometry (Fig. 11). The second-order NLO responses of **53**–**58** were studied by harmonic light scattering (HLS) measurements at 1.91 μm incident wavelength. The highest quadratic hyperpolarizabilities $\beta_{1.91}$ values of 350 and 290 × 10^{-30} esu were found for the mononuclear species **55** and **56**, respectively [89].

The dimeric complex **59** presents two tetracoordinated Cu(II) centers in a square planar environment and complex **58**, that is also a dimer in the solid-state due to a short apical Cu—O interaction ($d_{Cu—O}$ = 2.445(3) Å), exhibits two pentacoordinated Cu(II) centers with a square pyramidal coordination sphere (Fig. 12). A strong antiferromagnetic interaction ($J = -397\ cm^{-1}$) was determined for **59**, due to the coplanar disposition of the Cu(II) metal ions and acute Cu—O—Cu angle (102°). Both ΔMS = ±1 (g = 2.071) and ΔMS = ±2 (g = 4.181, triplet state (S = 1) signature) transitions were observed in the solid-state EPR spectrum of **58** [90].

A series of four new dimeric D—π—D double square planar SB Ni(II) and Cu(II) complexes **60**–**63** (Fig. 13) were readily obtained by reacting 1 equiv. of 4,4′-bipyridine with 2 equiv. of the desired *in situ* generated ONO-tridentate SB Ni(II) and Cu(II) building blocks [91]. In **60** and **62**, nickel(II) ions are coordinated in square planar geometry, whereas in **63** that forms a coordination polymer through apical Cu—O interactions ($d_{Cu—O}$ = 2.411(5) Å) between dimeric units, the five-coordinate Cu^{II} metal ion sits in a square pyramidal environment (Fig. 13). A weak antiferromagnetic couplings ($J = -0.83\ cm^{-1}$) was found for this latter compound.

Unexpectedly, the reaction of the diprotic precursor **53** with Co$(NO_3)_2 \cdot 6H_2O$ afforded the ionic Co(III) complex $[K(HOCH_2CH_3)_2]^+$ $[Co(Fc\text{-}C(O)CH{=}C(CH_3)N\text{—}o\text{-}C_6H_4O)_2]^-$ (**64**, Fig. 14). In this compound, the two dianionic ONO-tridentate SB ligands are meridionally coordinated to the cobalt ion that adopts a *pseudo*-octahedral geometry, and the doubly disolvated potassium counter-ion is disymmetrically located with respect to the two metalloligands (Fig. 14) [92]. Multidimensional ^{1}H and ^{13}C NMR spectral data suggest that the structure observed in the solid-state is retained in solution.

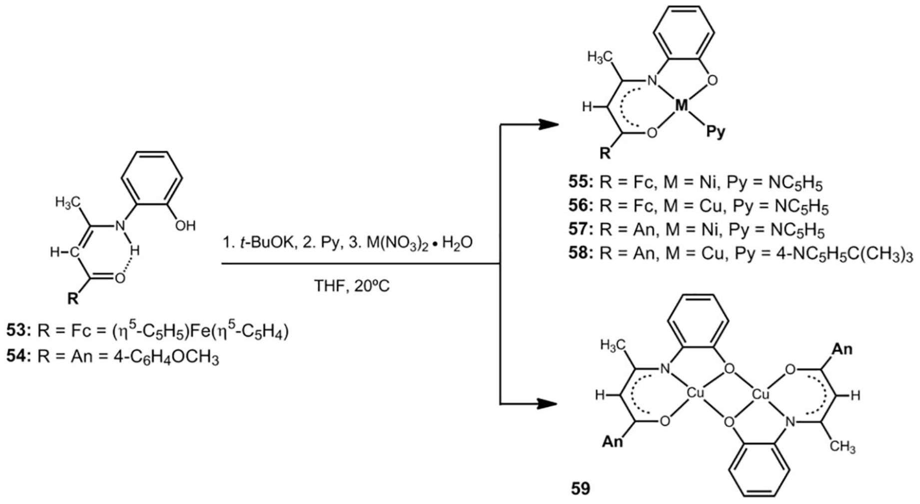


Fig. 10. Synthesis of ferrocenyl- and anisyl-containing ONO-tridentate Schiff base complexes of Ni(II) and Cu(II) [89].

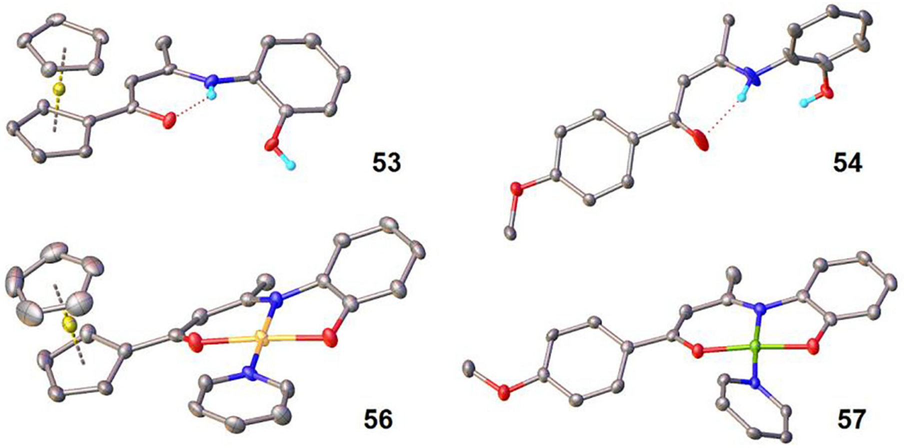


Fig. 11. ORTEP views of two pairs of half-unit/complex units: **53**/**56** (left column) and **54**/**57** (right column) [89]. Color code: Fe, yellow; Ni, light-green; Cu, orange; N, blue; O, red; H, sky-blue.

3. Unsymmetrically-substituted tetradentate Schiff base ligands and their metal complexes

Metal complexes with unsymmetrically-substituted tetradentate SBs are one of the most important classes of coordination compounds. They have been found in a lot of biologically active drugs [94], catalysts in both homogeneous [95] and heterogeneous chemical systems [96], and attractive applications in NLO materials [20,80,97,98]. They also attracted chemists' wide attention due to their structural variability, preparative accessibility, and tunable electronic properties (*via* modifications of ancillary functional group). In general, metal complexes with unsymmetrically-substituted tetradentate SB ligands are obtained *via* a multicomponent synthesis involving β-diketone, primary alkyl- or aryldiamine, salicylaldehyde or its derivatives and the metal salt in the 1:1:1:1 stoichiometric ratio [35,36,46]. Costes *et al.* reported the first non-template synthesis of N_2O_2 tetradentate unsymmetrically-substituted SB through the monocondensation of 2,4-pentanedione with 1,2-ethanediamine to generate the parent half-unit **A** (Fig. 15) that was then reacted with salicylaldehyde to yield the unsymmetrically-substituted diimine **B** (Fig. 15) [99]. Reaction of the diimines **B** with metal ions ultimately lead to the corresponding metal complexes **C** (Fig. 15) with N_2O_2 tetradentate unsymmetrically-substituted SB ligand. Applying this non-template procedure to ferrocenoylacetone leads to unsymmetrically-substituted SB metalloligand precursor **65** and **66** (Table 1) [100,101]. Hence, plenty of work was directed towards

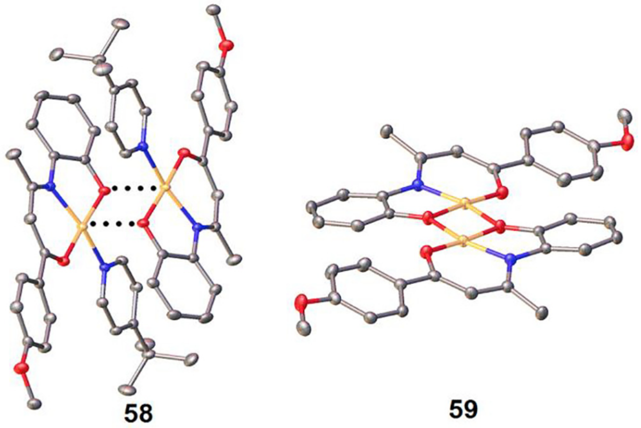
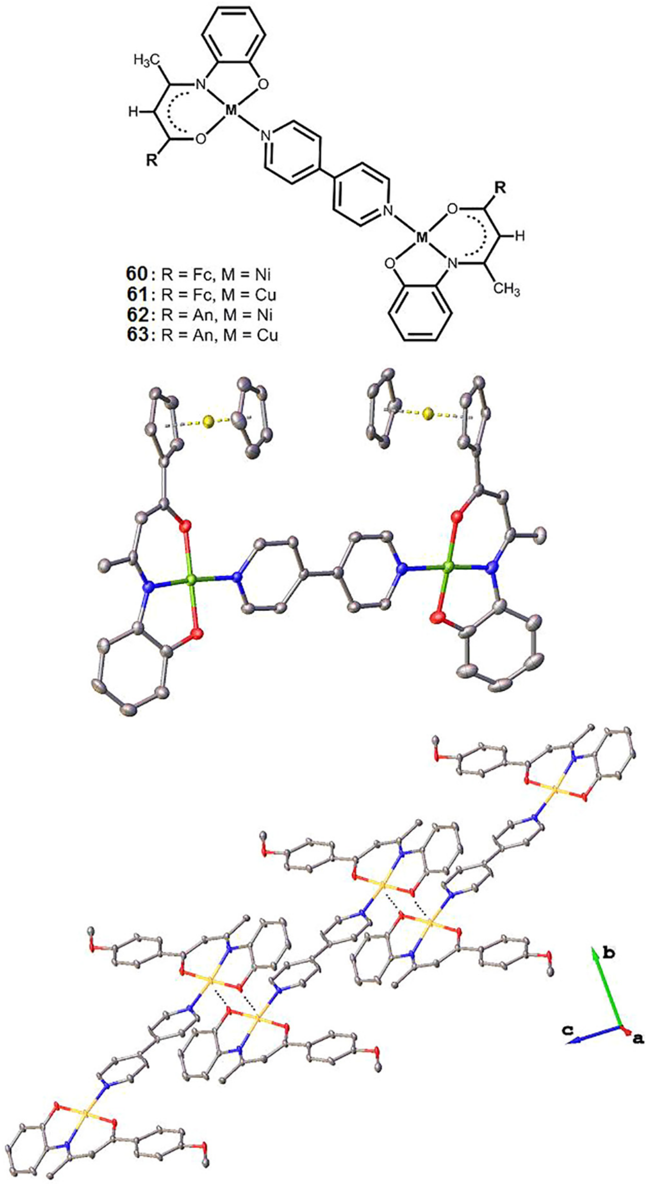


Fig. 12. ORTEP views of the dimeric species **58** (left) showing apical short contact Cu—O interactions in dotted-line and the doubly phenoxo bridged complex **59** (right) [90]. Color code: Cu, orange; N, blue; O, red.



60: R = Fc, M = Ni
61: R = Fc, M = Cu
62: R = An, M = Ni
63: R = An, M = Cu

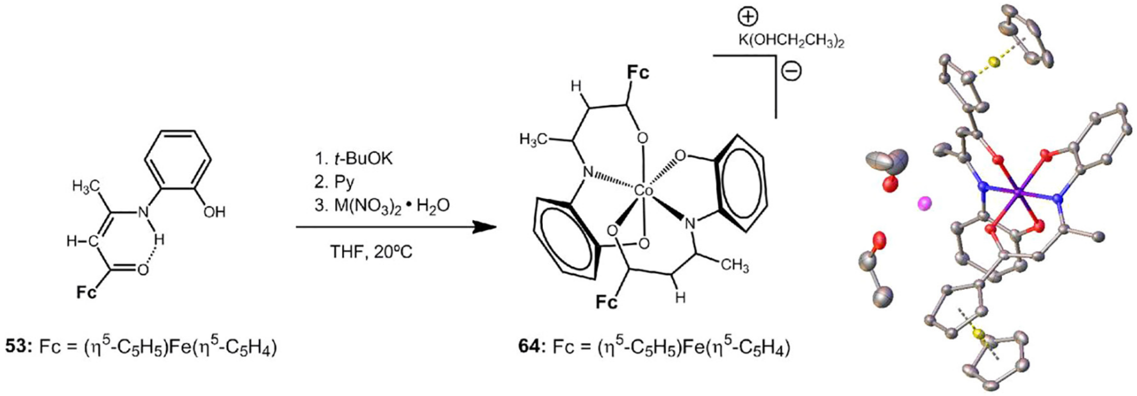
Fig. 13. Schematic representation of the dimeric species **60**–**63** (top), molecular structures of the heterotetrametallic complex **60** (middle) and of the coordination polymer **63** (bottom) showing an apical Cu—O short contact (dotted-line) with neighboring molecules [91]. Color code: Fe, yellow; Ni, light-green; Cu, orange; N, blue; O, red.

the study of their structural and spectroscopic properties. In fact, metal complexes possessing N_2O_2 tetradentate unsymmetrically-substituted SB ligand are the most important and widely used species of the non symmetrical SB metal family. Therefore, we will discuss herein various kinds of metal compounds of Ni, Cu, V, Mn, Fe, Co, Zn, Ru, Pd, Pt, and U with tetradentate unsymmetrically-substituted SB ligands.

3.1. Nickel(II) and copper(II) complexes

Our groups have also long term interest in the synthesis of heterobimetallic and heterotrimetallic Ni(II) and Cu(II) complexes with N_2O_2 tetradentate unsymmetrically-substituted SB ligands [86,100–110]. The various bimetallic species **67**–**88** (Table 2) were synthesized by condensation of half-units **50**–**52** and appropriately substituted salicylaldehydes in the presence of hydrated Ni(II) and Cu(II) acetate salts. The bimetallic species consist of a ferrocenyl donor moiety linked to a Ni(II)- or Cu(II)-centered N_2O_2 unsymmetrically-substituted macroacyclic SB complex, forming push–pull D—π—A systems when the salicylidene ring is substituted with electron withdrawing groups such as F, Br, NO_2, or CO_2H (Table 2). The central metal ion adopts a square planar geometry, being the focal point of three heterometallacycles (two six-membered and one five-membered ones) (Fig. 16). In the solid-state, the chelate SB scaffold forms an umbrella-type structure in the cases of complexes possessing the rigid *o*-phenylene bridge, with angles formed by the two central carbon atoms of the 6-membered chelate rings and the metal center of about 160–165° [100,104,107,109]. The same angles barely deviate from linearity in the case of the more flexible ethylene spacer [101–103,106]. In addition, suitably functionalized bimetallic SB complexes can be grafted onto organic polymers or self-condensed upon esterification reactions to form side-chain (**89**, **90**, **93**) and main-chain (**91**, **92**) metallopolymers, respectively (Table 2).

A series of nine molecular organometallic–inorganic hybrid materials **94**–**102** and a derivatized side-chin metallopolymer **103** were also designed and synthetized (Table 3). The trimetallic complexes possessing unsymmetrically-substituted N_2O_2 tetradentate SB ligands resulted from the hexa-hapto coordination of the cationic arenophile $[Cp^*Ru]^+$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) onto the salicylidene ring (Fig. 17). They were prepared either by reaction of the desired bimetallic precursor with the trisolvated arenophile source $[Cp^*Ru(NCCH_3)_3]^+$ [86,100,102,104], or by reaction of the preformed mixed sandwich salicylaldehyde ruthenium compound $[Cp^*Ru\{\eta^6\text{-}1,2\text{-}C_6H_4(CHO)OH)\}]^+$ with the free amino group of the appropriate half-unit (Fig. 17) [100,108]. These push–pull D—π—A chromophores contain a neutral electron-donating ferrocenyl group and a cationic electron-withdrawing mixed ruthenium



53: Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$

64: Fc = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$

Fig. 14. Synthesis of the ionic Co(III) complex **64** (left) and its molecular structure (right) [92]. Color code: Fe, yellow; Co, purple; K, magenta; N, blue; O, red.

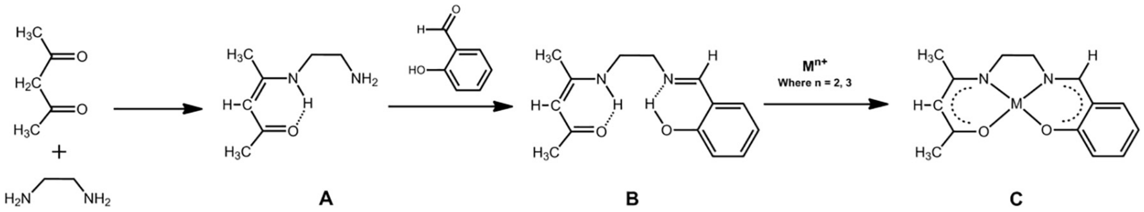
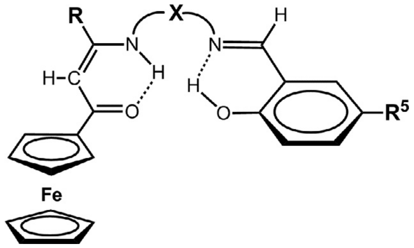


Fig. 15. Historical development of tetradentate unsymmetrically-substituted Schiff base ligands and their metal complexes.

Table 1
Substitution pattern of ferrocenyl-containing unsymmetrically-substituted Schiff base ligand precursors prepared in our groups, with their HLS β values determined at 1.91 μm.



Compd.	R	X	R^5	$\beta_{1.91}$ (10^{-30} esu)	Refs.
65	CH_3	CH_2CH_2	OH	155	[100]
66	p-C_6H_4OH	CH_2CH_2	NO_2	200	[101]

sandwich unit connected by a conjugated [$M(N_2O_2)$] macroacyclic entity. Both the *syn*- and *anti*-conformations were found in the solid-state (Fig. 18); the organometallic [$(\eta^5$-$C_5H_5)Fe$] and [$Cp^*Ru]^+$ moieties being located on the same and opposite face of the dinucleating inorganic ligand, respectively. As expected, due to the positive charge borne by its [$M(N_2O_2)$–$RuCp^*]^+$ substituent, the ferrocenyl moiety is oxidized at more anodic potentials ($20 < E_{1/2} < 170$ mV) than those of their corresponding bimetallic counterparts.

These series of mono-, bi-, and tri-metallic molecular systems in which a ferrocenyl donor is conjugated with various SB acceptors disclosed excellent NLO properties that were evaluated in solution phase using HLS techniques at 1.91 μm incident wavelength. Their structure-dependent optical (linear as well as nonlinear) properties along with their electrochemical behavior have recently been comprehensively reviewed and discussed [80]. A slight enhancement of the second-order NLO response was generally observed on passing from a metalloligand precursor to its neutral bimetallic SB complexes and to the corresponding trimetallic salt. For instance, in the sequence **65** → **71** → **98**, the NLO response of the Fe/Ni/Ru$^+$ derivative **98** is 1.5 times greater than that of the organometallic SB **65** [100].

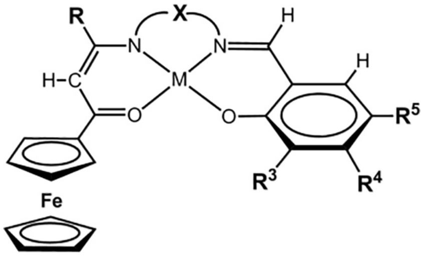
The reactivity of the bimetallic compounds were also investigated. For example, we synthesized the Ni(II) complex **72** *via* the Williamson coupling reaction of allyl chloride from the 5-substituted hydroxyl precursor **71** (Fig. 19) [103]. The structure of the orange Ni(II) complex of the allyloxo functionalized tetradentate unsymmetrically-substituted SB ligand **72** was confirmed by single-crystal X-ray diffraction study (Fig. 19). Owing to the presence of the allyloxo function or some of its own substituents as potential anchoring group, these Ni(II) and Cu(II) complexes with tetradentate unsymmetrically-substituted SB ligands might be covalently bound to oligomer and polymer backbones [111] or on surface [96,112] through a single point of attachment, and serve either as immobilized catalyst for organic transformations or to obtain oriented non-centrosymmetric materials exhibiting NLO responses.

Our group confirmed that these complexes can be linked to oligomer or polymer backbones *via* simple chemical reaction. In 2013, we reported the synthesis of a new polymethylmethacrylate (PMMA)-anchored ferrocenyl substituted nickel(II) SB complex **89** (Fig. 20) *via* the *trans*-esterification reaction of its bimetallic precursor **77** (Table 2), containing an aromatic free hydroxyl group, and PMMA under basic conditions [105]. Successful *trans*-esterification was established with the disappearance of the stretching vibration of the terminal hydroxyl group present in **77**, in the FT-IR spectrum of the formed metallopolymer **89**. The atomic force microscopy (AFM) images of the PMMA-supported film material containing the Ni(II) complex **89** showed a homogeneous film that presents a cauliflower-type morphology (Fig. 20).

In 2014, our group used the bimetallic precursors with a doubly functionalized ($R = p$-C_6H_4OH, $R^4 = CO_2H$) SB ligand **78** and **79** (Table 2) to synthesize their respective oligomeric main-chain Ni (II)- and Cu(II)-centered unsymmetrically-substituted N_2O_2 tetradentate SB compounds **91** and **92** upon esterification reactions (Fig. 21) [106]. Unexpectedly, the formation of **91** is accompanied by minute amounts of the purple crystalline by-product **80** in which the carboxylic group of **78** has been transformed into the (c-$C_6H_{11})_2NC(O)$ amide substituent. The main-chain oligomers **91** and **92** are composed of approximately six monomeric units, as confirmed by size exclusion chromatography (SEC). The results of thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses verified that they are thermally very stable with decomposition temperature higher than 230 °C, a useful property for practical applications.

More recently, we also used the esterification reaction under the same experimental conditions to link the unsymmetrically-substituted neutral bimetallic **85** and cationic trimetallic **102** Ni (II) SB complexes to polyacrylic acid (DP = 25) to synthetize their

Table 2
Substitution pattern of Ni(II) and Cu(II) complexes derived from ferrocenyl-containing unsymmetrically-substituted N_2O_2 tetradentate Schiff base ligands prepared in our groups, with some HLS β values determined at 1.91 µm.



Compd.	M	R	X	R^3	R^4	R^5	$\beta_{1.91}$ (10^{-30} esu)	Refs.
67	Ni	CH_3	CH_2CH_2	H	H	H	–	[102]
68	Cu	CH_3	CH_2CH_2	H	H	H	–	[102]
69	Ni	CH_3	CH_2CH_2	H	H	Br	230	[86]
70	Ni	CH_3	*o*-C_6H_4	H	H	Br	210	[86]
71	Ni	CH_3	CH_2CH_2	H	H	OH	–	[100]
72	Ni	CH_3	CH_2CH_2	H	H	$OCH_2CH{=}CH_2$	230	[103]
73	Ni	CH_3	*o*-C_6H_4	H	H	H	250	[100]
74	Cu	CH_3	*o*-C_6H_4	H	H	H	215	[100]
75	Cu	CH_3	CH_2CH_2	H	H	Br	–	[104]
76	Cu	CH_3	*o*-C_6H_4	H	H	Br	–	[104]
77	Ni	CH_3	*o*-C_6H_4	H	H	OH	–	[105]
78	Ni	*p*-C_6H_4OH	CH_2CH_2	H	CO_2H	H	220	[106]
79	Cu	*p*-C_6H_4OH	CH_2CH_2	H	CO_2H	H	240	[106]
80	Ni	*p*-C_6H_4OH	CH_2CH_2	H	C(O)NCy_2	H	–	[106]
81	Ni	CH_3	*o*-C_6H_4	H	H	NO_2	215	[107]
82	Cu	CH_3	*o*-C_6H_4	H	H	NO_2	270	[107]
83	Ni	CH_3	*o*-C_6H_4	F	H	F	215	[107]
84	Cu	CH_3	*o*-C_6H_4	F	H	F	200	[107]
85	Ni	*p*-C_6H_4OH	CH_2CH_2	H	H	NO_2	220	[101]
86	Ni	CH_3	*o*-C_6H_4	H	H	OCH_3	–	[109]
87	Cu	CH_3	*o*-C_6H_4	H	H	OCH_3	–	[109]
88	Cu	CH_3	*o*-C_6H_4	H	H	OH	–	[110]
89	Ni	CH_3	*o*-C_6H_4	H	H	O-PMMa	–	[105]
90	Cu	CH_3	*o*-C_6H_4	H	H	O-PMMA	–	[110]
91	Ni	*p*-C_6H_4O—	CH_2CH_2	H	CO_2—	H	400	[106]
92	Cu	*p*-C_6H_4O—	CH_2CH_2	H	CO_2—	H	330	[106]
93	Ni	*p*-C_6H_4O-PAA	CH_2CH_2	H	H	NO_2	650	[101]

PMMA = polymethylmethacrylate, PAA = polyacrylic acid.

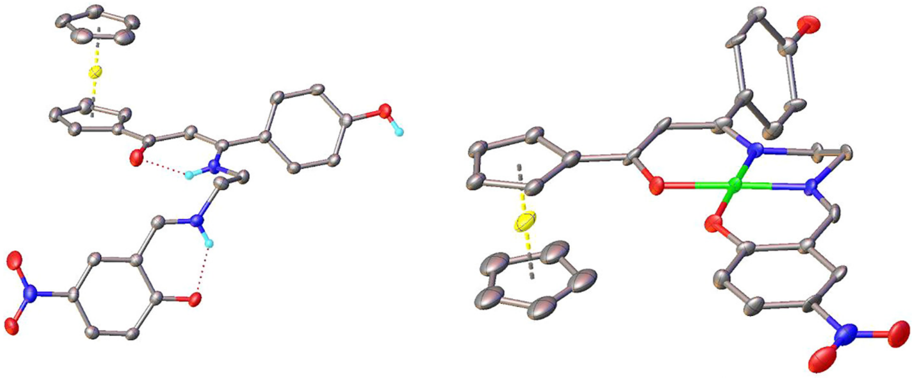
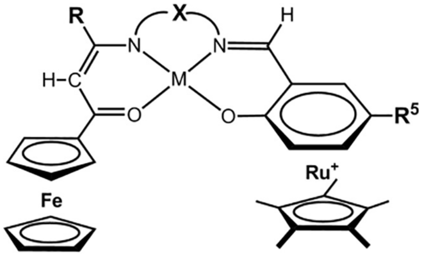

66 **85**

Fig. 16. Molecular structures of the unsymmetrically-substituted Schiff base metalloligand precursor **66** (left) and of its corresponding Ni(II) complex **85** (right) [101]. Non-relevant hydrogen atoms have been omitted for clarity. Color code: Fe, yellow; Ni, light-green; N, blue; O, red; H, Sky-blue.

corresponding side-chain polymers **93** and **103** (Fig. 22) [101,108]. SEC analysis revealed an average grafting degree of 40% for **93** and 12% for **103**, that is, on average, ten bimetallic and three trimetallic units attached per molecule of organic polymer, respectively. This great difference in the degree of substitution was accounted for by the steric constraints and charge repulsion caused by the ionic nature of **102**. Both metallopolymers **93** and **103** are thermostable up to 250 °C.

The second-order NLO responses of the main-chain oligomers **91** and **92**, and side-chain polymers **93** and **103** were also determined in solution using the HLS method. Hyperpolarizability $\beta_{1.91}$ values of **91** and **92** are of 400 and 330 × 10^{-30} esu,

Table 3
Substitution pattern of trimetallic Ni(II) and Cu(II) complexes derived from unsymmetrically-substituted N_2O_2 tetradentate Schiff base ligands prepared in our groups, with some HLS β values determined at 1.91 μm.



Compd.	M	R	X	R^5	$\beta_{1.91}$ (10^{-30} esu)	Refs.
94	Ni	CH_3	CH_2CH_2	H	–	[102]
95	Cu	CH_3	CH_2CH_2	H	–	[102]
96	Ni	CH_3	CH_2CH_2	Br	240	[86]
97	Ni	CH_3	o-C_6H_4	Br	–	[86]
98	Ni	CH_3	CH_2CH_2	OH	250	[100]
99	Ni	CH_3	o-C_6H_4	H	235	[100]
100	Cu	CH_3	o-C_6H_4	H	240	[100]
101	Cu	CH_3	CH_2CH_2	Br	215	[104]
102	Ni	p-C_6H_4OH	CH_2CH_2	H	120	[108]
103	Ni	p-C_6H_4O-PAA	CH_2CH_2	H	360	[108]

PAA = polyacrylic acid.

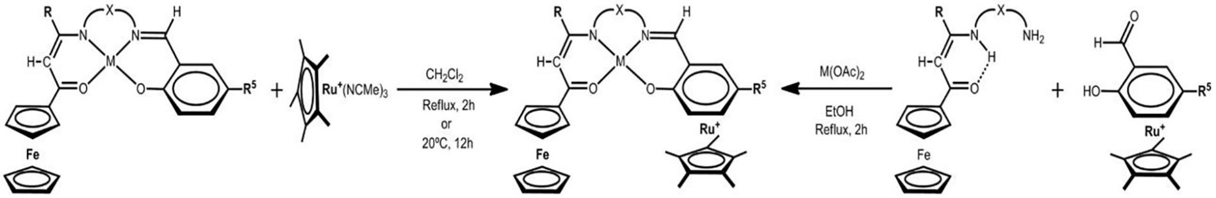


Fig. 17. Two synthetic pathways to prepare the trimetallic complexes with unsymmetrically-substituted tetradentate Schiff base ligands **94**–**102** (for the values of M, R, R^5 and X, see Table 3). The PF_6^- counter-ions are omitted for clarity.

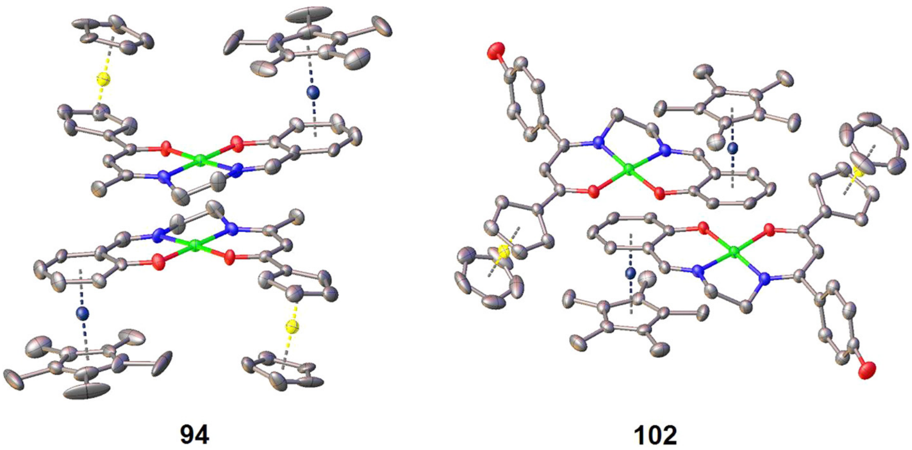


Fig. 18. Molecular structures of the heterotrimetallic Schiff base complexes **94** (left, *anti*-conformation) [102], and of **102** (right, *syn*-conformation) [108]. Color code: Fe, yellow; Ni, light-green; Ru, dark blue; N, blue; O, red.

respectively, much greater than those of their respective monomeric precursors **78** and **79** [106]. Indeed, the $\beta_{1.91}$ value found for **91** is almost twice that determined for **78**. However, the cumulative effect of the NLO response of the constituting monomers was not observed, suggesting that the monomers are not organized in an acentric order within the oligomer chain. The quite large $\beta_{1.91}$ value of 650×10^{-30} esu determined for the side-chain polymer **93** is almost three times greater than that found for the bimetallic subunit **85** (Table 2). This value is weaker than expected from the grafting degree, however, due to the statistical orientation of the SB chromophores along the polyacrylic acid chain [101]. Interestingly, a proportional increase of the NLO response was observed with **103** whose $\beta_{1.91}$ value was found to be three times greater than that of its trimetallic component **102**.

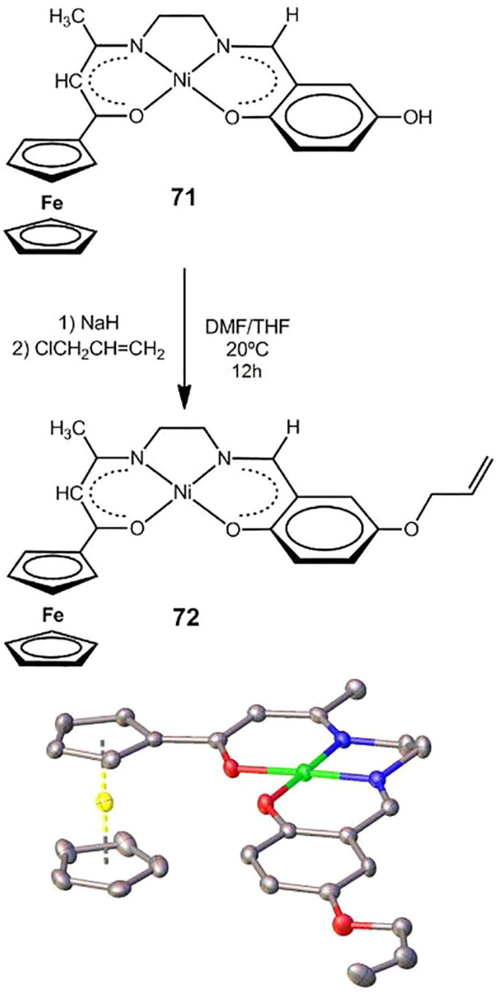


Fig. 19. Synthesis of the Ni(II) complex of the allyloxo functionalized Schiff base ligand **72** and its molecular structure [103]. Color code: Fe, yellow; Ni, light-green; N, blue; O, red.

This was accounted for by the steric demand and charge repulsion of the grafted cationic NLO-active units [108]. These molecular-based functional materials that combine high optical nonlinearity, chemical flexibility properties with good air and thermal stability, do certainly feature relevant materials having possible applications in the fields of optical devices.

A lot of work has continuously been devoted to Ni(II) and Cu(II) N_2O_2 complexes supported by unsymmetrically-substituted tetradentate SB ligands. For instance, in 2006 Demartin, Forni, Pasini and co-workers reported a series of eleven copper(II) complexes of unsymmetrically-substituted salen analogs **104**–**114**, in which the two salicylaldehyde moieties carry at the 5-position different electron donor and acceptor groups, producing a push–pull charge asymmetry (Fig. 23) [113]. Their NLO responses have been determined by the solution-phase direct-current EFISH measurements, with noticeable $\mu_g\beta_{vec}$ values in the range 180–67 2×10^{-30} D cm^5 esu^{-1}. As seen above [73] and for the same reasons, the highest NLO response is obtained with the push–pull derivative **110** containing the strongest donor $N(CH_3)_2$ and acceptor NO_2 substituents. One year later, Forni and co-workers synthesized the isostructural Ni(II) and Cu(II) complexes **115** and **116** by template condensation of 1-phenylbutane-1,3-dione mono-S-methylisothiosemicarbazone and 5-phenylazo-salicylaldehyde under basic conditions and in the presence of the metal salts (Fig. 23) [114]. The coordination to the metal ions of the unsymmetrically-substituted quadridentate N_2O_2 SB ligand is realized through the nitrogen atoms of the isothiosemicarbazide fragment and the oxygen atoms of the benzoylacetonic and salicylidene units. The second-order NLO properties were also investigated by the solution-phase direct-current EFISH methods, giving $\mu\beta\lambda$ product of -176×10^{-48} esu for the closed-shell Ni-SB derivative **115** and a threefold greater value of -538×10^{-48} esu for its open-shell Cu-SB counterpart **116**.

On the other hand, Meghdadi *et al.* reported the synthesis of four new unsymmetrically-substituted N_2O_2 SB Ni(II) and Cu(II) complexes **117**–**120** (Fig. 24), being derived from 3-(2-aminobenzylimino)-1-phenylbutan-1-one [115]. X-ray crystallography confirmed that [Ni(N_2O_2)] and [Cu(N_2O_2)] cores are distorted puckered squares in the four complexes because of the rigidity brought about by the —C_{phenyl}—C_{phenyl}—methylene–spacer. Electrochemical studies were found to show good agreement between the structural distortion and the redox potentials of the metal centers. Asadi *et al.* synthesized and characterized twelve new unsymmetrically-substituted N_2O_2 SB Ni(II) and Cu(II) complexes **121**–**132** (Fig. 24). In addition, the thermodynamic formation constant (K_f) of the complexes were determined spectrophotometrically at 25 °C, in methanol containing 0.1 M $NaClO_4$, and their free energies of formation (ΔG^0) were calculated at 25 °C [116]. In a subsequent paper, the authors determined the same thermodynamic parameters K_f (in DMF, 0.1 M $NaClO_4$ and ΔG^0) at 25 °C of complexes **135**–**142**, that were synthesized from salicylaldehyde derivatives and hindered aromatic diamine (3,4-diaminobenzo-phenone) (Fig. 24) [117]. In both cases, the results show that K_f and the free energy of formation of Ni(II) complexes are lower than those of their Cu(II) counterparts. Moreover, Meghdadi *et al.* reported the synthesis and characterization of unsymmetrically-substituted

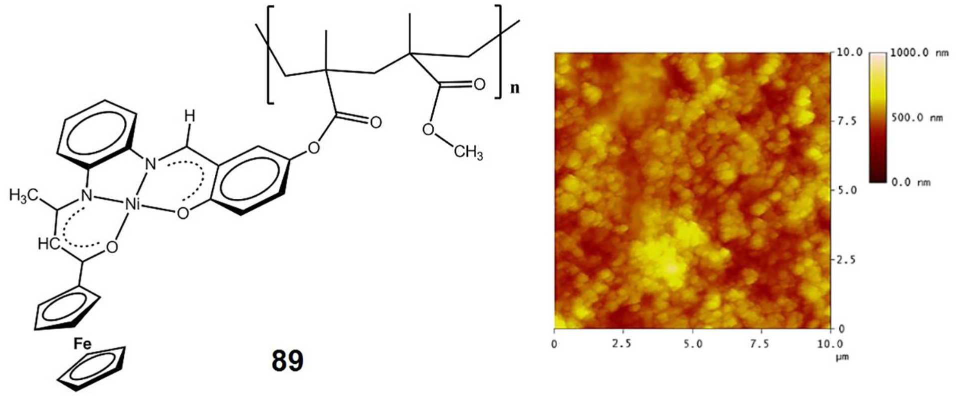
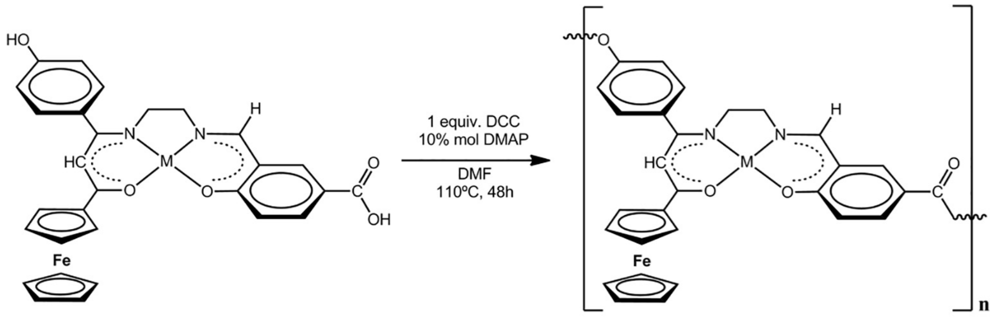
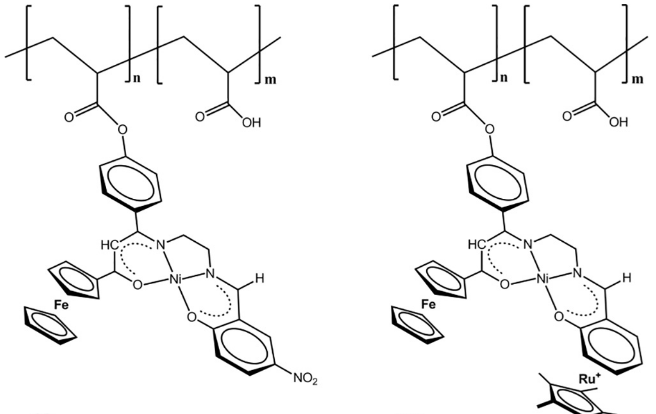


Fig. 20. Schematic representation of the metallopolymer **89** (left), and an AFM image of the corresponding PMMA-supported film material (right). Image reproduced with permission from Ref. [105]. Copyright 2013, Springer.



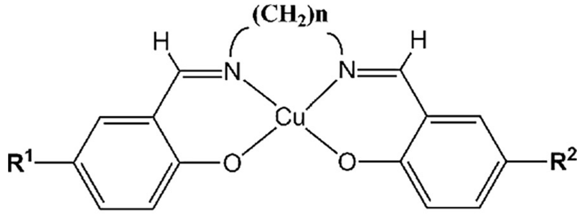
91: M = Ni
92: M = Cu

Fig. 21. Synthesis of the oligomeric main-chain Schiff base compounds **91** (M = Ni) and **92** (M = Cu), DMF = *N,N′*-dimethylformamide, DCC = *N,N′*-dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine.

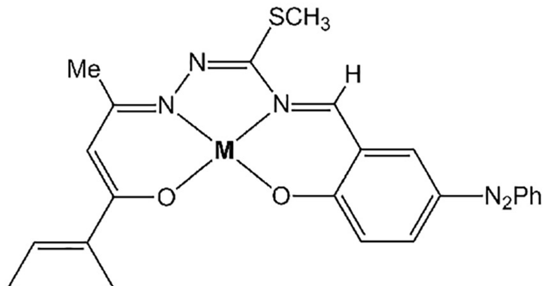


93 **103**

Fig. 22. Schematic representations of the neutral side-chain metallopolymer **93** (left) and of the ionic side-chain metallopolymer **103** (right).



Compd.	R^1/R^2	n	Compd.	R^1/R^2	n
104	H/CH_3	2	**110**	$NO_2/N(CH_3)_2$	2
105	H/OCH_3	2	**111**	H/OCH_3	3
106	$H/N(CH_3)_2$	2	**112**	$H/N(CH_3)_2$	3
107	$(NO_2/H$	2	**113**	NO_2/H	3
108	NO_2/CH_3	2	**114**	$NO_2/N(CH_3)_2$	3
109	NO_2/OCH_3	2			



115: M = Ni
116: M = Cu

Fig. 23. Schematic representations of complexes **104**–**116** with unsymmetrically-substituted N_2O_2 tetradentate Schiff base ligands [113,114].

N_2O_2 SB complexes of Ni(II) and Cu(II) **133** and **134** (Fig. 24) that were screened for their *in vitro* antimicrobial activity. Antimicrobial results showed that [Cu(naphsal)] **133** has an excellent antibacterial activity against *Staphylococcus aureus* and *Bacillus cereus* comparable to that obtained with penicillin, while [Ni(salnaph)] **134** does not show any positive effect on these bacterial species [118].

Tetradentate unsymmetrically-substituted SBs containing ON_2S or N_2S_2 mixed donor set where sulfur is a soft donor atom in the backbone, and their transition metal complexes play an important role in the areas of the bioinorganic and medicinal chemistry in providing interesting synthetic models for the metal-containing sites in metallo-proteins and enzymes [119–122]. For example, Menati *et al.* synthesized ON_2S tetradentate unsymmetrically-substituted SB complexes of Ni(II) and Cu(II) **143** and **144** (Fig. 25), *via* the condensation of methyl-2-{N-(2′-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden), 3,5-di-*tert*-butyl-2-hydroxy-benzaldehyde and Ni(II) or Cu(II) salts in the ratio 1:1:1. Above all, complex **144** has a slightly distorted square-planar Cu(II) center where the metal ion is coordinated to two imine nitrogen atoms, a sulfur atom of the methyl dithiocarboxylate moiety and a phenolic oxygen atom [123].

In 2010, Asadi *et al.* reported the synthesis and characterization of two sets of eight Ni(II) **145**–**152** and eight Cu(II) **153**–**160** complexes with unsymmetrically-substituted ON_2S tetradentate SB ligands, obtained by condensation of methyl-2-(3-aminopropy lamino)cyclopentenedithiocarboxylate with several substituted salicylaldehydes, 2-hydroxy acetophenone, and 2-hydroxy benzophenone (Fig. 26) [124]. They had also confirmed that Cu(II) ON_2S SB complexes had higher K_f and free energy values than the Ni(II) ON_2S derivatives, which is supported by higher positive charge distribution and ligand deformation geometry. This trend is similar to that observed in the N_2O_2 series discussed above.

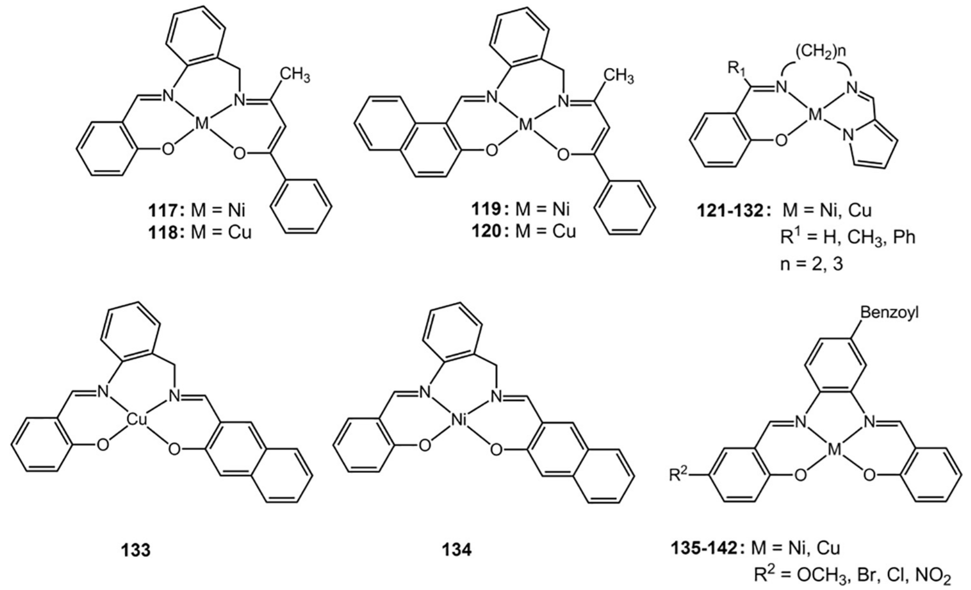


Fig. 24. Ni(II) and Cu(II) complexes **117**–**142** with unsymmetrically-substituted N_2O_2 tetradentate Schiff base ligands [115–118].

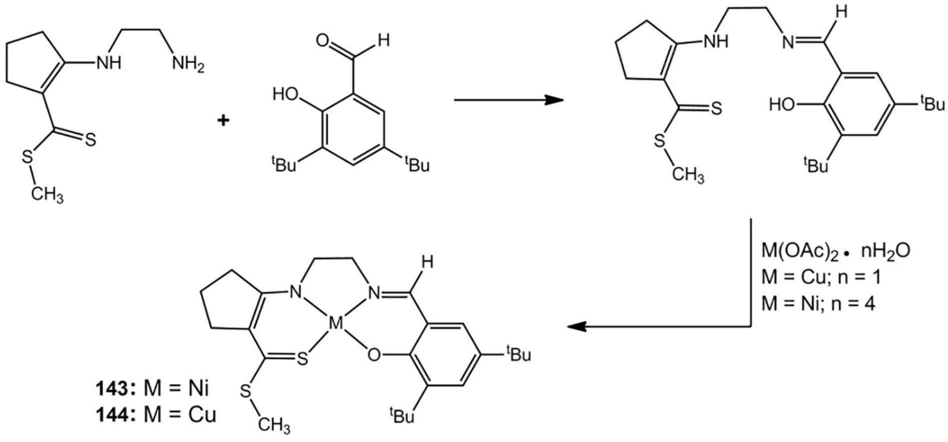
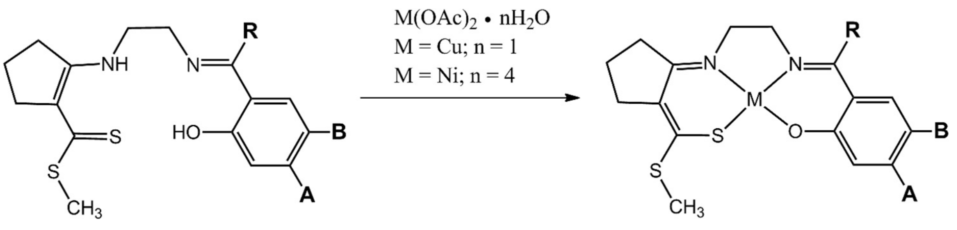
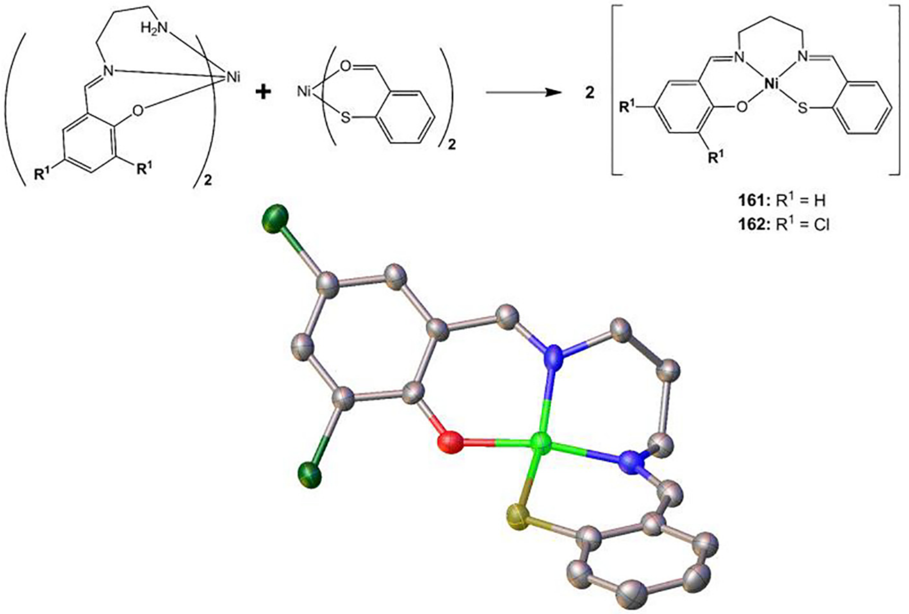


Fig. 25. Synthesis of Ni(II) and Cu(II) complexes with unsymmetrically-substituted ON_2S tetradentate Schiff base ligands **143** and **144** [123].



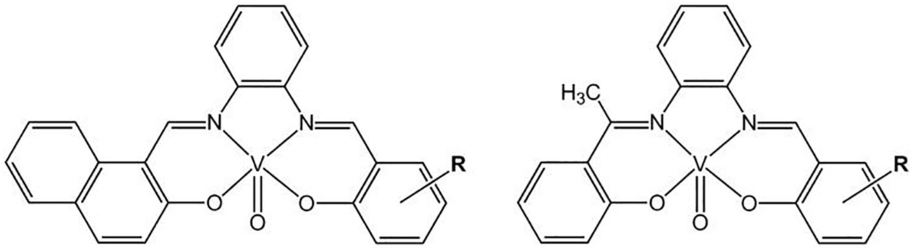
Ni(SB)	Cu(SB)	SB ligand	R	A	B
145	**153**	$C_{23}H_{26}N_2OS_2$	C_6H_5	H	H
146	**154**	$C_{18}H_{24}N_2O_2S_2$	H	OCH_3	H
147	**155**	$C_{18}H_{24}N_2O_2S_2$	H	H	OCH_3
148	**156**	$C_{17}H_{22}N_2O_2S_2$	H	OH	H
149	**157**	$C_{17}H_{21}N_2ClOS_2$	H	H	Cl
150	**158**	$C_{17}H_{21}N_2BrOS_2$	H	H	Br
151	**159**	$C_{17}H_{21}N_3O_3S_2$	H	H	NO_2
152	**160**	$C_{17}H_{21}N_2O_4S_3Na$	H	H	SO_3Na

Fig. 26. Synthesis of the two sets of Ni(II) and Cu(II) complexes with unsymmetrically-substituted ON_2S tetradentate Schiff base ligands reported by Asadi *et al.* [124].



161: R^1 = H
162: R^1 = Cl

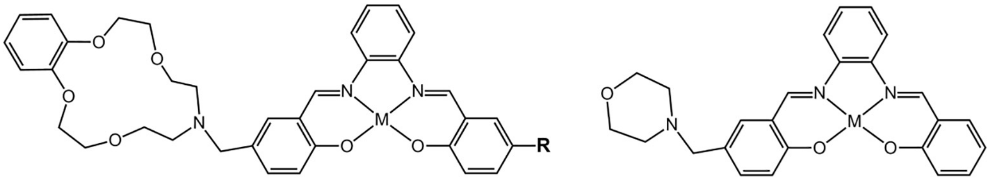
Fig. 27. Synthesis of Ni(II) complexes **161** and **162** featuring unsymmetrically-substituted ON$_2$S tetradentate Schiff base ligands (top), and molecular structure of the dichloro derivative **162** bottom) [125]. Hydrogens are omitted for clarity. Color code: Ni, light-green; N, blue; O, red; S, brown; Cl, dark-green.



163 : R = H
164 : R = 5-Cl
165 : R = 5-NO$_2$
166 : R = 3-OEt

167 : R = H
168 : R = 5-Br
169 : R = 5-NO$_2$
170 : R = 5-OMe
171 : R = 4-OMe
172 : R = 3-OMe

Fig. 28. Oxovanadium(IV) complexes supported by unsymmetrically-substituted N$_2$O$_2$ tetradentate Schiff base ligands **163**–**166** [133] and **167**–**172** [134].



173: M = MnCl, **R** = H
174: M = Co, **R** = H
175: M = Co, **R** = Cl

176: M = MnCl

Fig. 29. Synthesis of unsymmetrically-substituted Schiff base Mn(III) and Co(II) complexes **173**–**176** [137].

De Castro and co-workers synthesized and studied the Ni(II) complexes **161** and **162** with unsymmetrically-substituted ON$_2$S tetradentate Schiff base ligands obtained by condensation of 1,3-propanediamine with salicylaldehyde and thiosalicylaldehyde (Fig. 27) [125]. Single-crystal X-ray diffraction analysis of the [2-({3-[(3,5-dichloro-2-hydroxyphenyl)methyleneamino]-propyl}iminomethylene)benzenethiolato]nickel(II) derivative **162** showed a tetrahedrally distorted square-planar coordination geometry for the Ni(II) metal ion, with a dihedral angle between the NiNO and NiNS planes of 24.50(10)° (Fig. 27). Their Ni(I) counterparts were

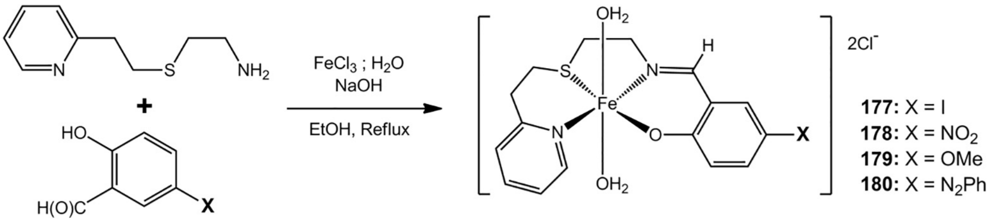


Fig. 30. Synthesis of Fe(III) complexes with ON_2S unsymmetrically-substituted Schiff base ligands **177–180** [142].

generated in solution, either chemically or electrochemically, and reduction potentials were found to be strongly dependent on the tetrahedral distortion of the Ni(II) complexes.

3.2. Vanadium complexes

Vanadium, a rare but essential element [126], has been found to play a key role in biological systems [127]. It has also been discovered that it exists in some organisms (amanita mushrooms and certain ascidians) of animals and humans [128,129]. Moreover, unsymmetrically-substituted tetradentate SB complexes of oxovanadium(IV) with the N_2O_2 chromophore have been used as therapeutic agents due to good insulin-enhancing properties [130–132]. For instance, Nejo *et al.* reported the synthesis of four new tetradentate unsymmetrically-substituted SB oxovanadium(IV) complexes **163–166** (Fig. 24), *via* the condensation of 2-hydroxy-1-naphthaldehyde, phenylenediamine, salicylaldehyde or substituted salicylaldehyde and oxovanadium(IV) sulfate in an ethanolic medium buffered with triethylamine at 50 °C for 3 h [133]. The results of room temperature magnetic susceptibility measurements showed that these monomeric square pyramidal shaped five-coordinate oxovanadium(IV) complexes, which have 1.6–1.8 BM magnetic moments, were of d^1 configuration. Interestingly, all the oxovanadium(IV) SB complexes exhibited significant stimulation of cell glucose utilization with 0.05 mg mL^{-1} negligible cytotoxicity by insulin-mimetic tests on C2C12 muscle cells using Biovision glucose assay. Kianfar *et al.* also synthesized six new tetradentate unsymmetrically-substituted N_2O_2 SB VO(IV) complexes **167–172** (Fig. 28) [134]. Cyclic voltammetry data indicated that the oxidation potentials of these complexes increased as a function of the electron withdrawing power of the substituents of the SB ligands: MeO < H < Br < NO_2.

3.3. Manganese(III) and cobalt(II) complexes

In recent years, the studies on the hydrolysis of phosphoric and carboxyl esters were developed in the field of environment and biological medicine [135,136]. A series of researchers have developed more efficient and selective catalysts in terms of environmentally-friendly and economical efficiency. Mn(III) and Co(II) based catalysts are two of the most efficient and cheapest catalysts species in hydrolysis of phosphoric and carboxyl esters. Along this line, Li and co-workers reported the synthesis and characterization of four new Mn(III) and Co(II) complexes with unsymmetrically-substituted tetradentate SB ligands **173–176** with either benzo-10-aza-crown ether pendants **173–175** or a morpholino pendant **176** (Fig. 29), as models for hydrolase enzymes by investigating the kinetics of their hydrolysis reactions with *p*-nitrophenyl picolinate (PNPP). The results indicated that these four complexes have efficient catalytic activity for hydrolysis reactions and that the reaction rate increased with the pH increment [137].

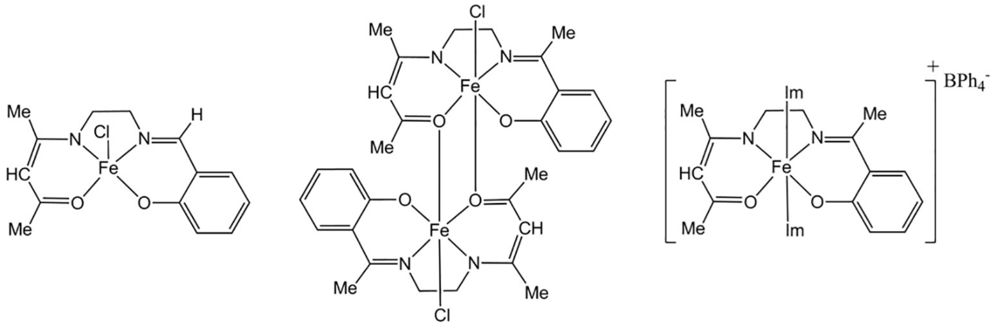
3.4. Iron(III) complexes

Iron(III) complexes supported by tetradentate unsymmetrically-substituted SB ligands have also attracted wide attention for the potential application as iron-containing enzymes. Importantly, coordinated salicylidene amine ligands (N_2O_2 or ON_2S) iron(III) complexes provide a useful electronic, synthetic and structural models for studying iron(III) coordination complex system in the heme iron enzymes [138–141]. Saghatforoush *et al.* reported the synthesis and characterization of four new Fe(III) complexes possessing ON_2S-tetradentate unsymmetrically-substituted SB ligands **177–180** derived from 5-X-N-(2-pyridylethylsulfanylethyl)salicylideneimine (X = I, NO_2, OMe, N_2Ph; Fig. 30) [142]. TGA and DSC analyses showed that both the free tetradentate unsymmetrical SBs and their iron complexes **177–180** had good thermal stabilities. In all these complexes, the geometry is octahedral around the ferric ion with the SB ligand coordinated through the imine and pyridine-type nitrogens, the thioether sulfur, and phenolic oxygen. Ironically, the free tetradentate SB ligand exhibited better positive antimicrobial activities than their Fe(III) complexes.

Besides their function as model compounds for biological systems, iron(III) complexes with SB ligands were found to be active NLO chromophores [143,144], and to possess interesting magnetic and spin-crossover properties [145]. For instance, Matsumoto *et al.* prepared two neutral five-coordinate chloro iron(III) complexes, **181** and **182**, with planar unsymmetrically-substituted N_2O_2 quadridentate SBs composed of 1:1:1 condensation products of pentan-1,3-dione, ethylenediamine, and either salicylaldehyde or 2-hydroxyacetophenone (Fig. 31) [146]. The magnetic moment of **181** is 5.96 BM at 302 K and remained unchanged down to 80 K, indicating that the complex is a monomeric species of high-spin configuration ($S = 5/2$). By contrast, the effective magnetic moment of **182** decreases gradually from 5.31 BM at 301 K to 3.46 BM at 80 K, and was interpreted by an intermolecular antiferromagnetic exchange ($J = -10\ cm^{-1}$) presumably originating from pairwise interactions. On the other hand, the ionic hexacoordinated iron(III) SB complex **183** (Fig. 31) exhibited striking thermochromic behavior in solution, changing from dark red to green when the temperature is lowered from 298 K to 80 K. Electronic, NMR and ESR spectra confirmed that the thermochromism is caused by spin-equilibrium between high-spin and low-spin states of the iron(III) center. Complex **183** is essentially of low-spin configuration ($S = ½$) in the solid-state.

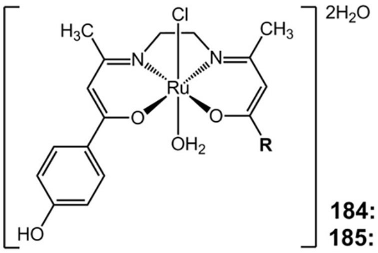
3.5. Ruthenium complexes

Ruthenium complexes with tetradentate SB ligands have been widely applied as analytical, biochemical, and antimicrobial reagents [147,148], and have shown a great interest in oxygenation and azomethination of Ru(III) complexes for the development of new therapeutic agents and DNA probes for disease defense. Ejidike and Ajibade reported the synthesis and characterization



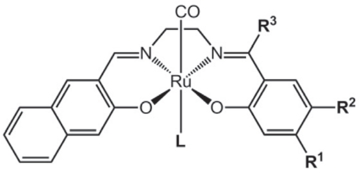
181 **182** **183**

Fig. 31. Schematic representations of the neutral five-coordinate chloro iron(III) complexes with unsymmetrically-substituted N_2O_2 tetradentate Schiff base ligands **181** and **182**, and of the ionic six-coordinate bis-imidazole iron(III) derivative **183** [146].



184: R = Me
185: R = Ph

Fig. 32. Schematic representations of unsymmetrically-substituted Schiff base complexes of Ru(III) **184** and **185** [149].



Compd	L	R^1	R^2	R^3	Compd	L	R^1	R^2	R^3
186	PPh_3	H	H	H	192	$AsPh_3$	OCH_3	H	H
187	PPh_3	H	Cl	H	193	$Asph_3$	H	H	CH_3
188	PPh_3	OCH_3	H	H	194	NC_5H_4	H	H	H
189	PPh3	H	H	CH_3	195	NC_5H_4	H	Cl	H
190	$AsPh_3$	H	H	H	196	NC_5H_4	OCH_3	H	H
191	$AsPh_3$	H	Cl	H	197	NC_5H_4	H	H	CH_3

Fig. 33. Schematic representations of unsymmetrically-substituted Schiff base complexes of Ru(II) **186**–**197** [150].

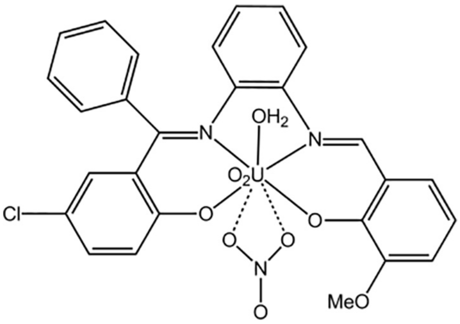
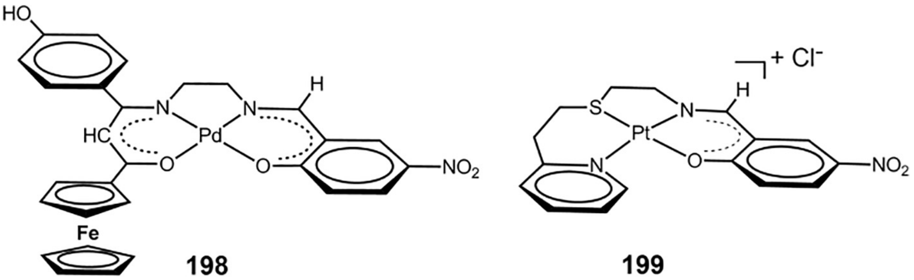


Fig. 35. Schematic representation of the unsymmetrically-substituted tetradentate Schiff base complex of uranyl(VI) **200** [152].

of two new six-coordinate octahedral ruthenium complexes **184** and **185** of the type $[RuL(Cl)(H_2O)]$ resulting from the reaction between $RuCl_3{\cdot}3H_2O$ and unsymmetrically-substituted N_2O_2 tetradentate SB H_2L, derived from ethylenediamine, 4-acetylresorcinol, pentane-1,3-dione, and 1-phenylbutane-1,3-dione (Fig. 32) [149]. The synthesized complexes exhibited strong scavenging activities against 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical but low biological activities as potential anticancer agents.

Ruthenium(II) complexes supported by unsymmetrically-substituted N_2O_2 tetradentate SB ligands have been used as catalysts. For instance, Gowri and co-workers reported the synthesis of a series of octahedral six-coordinate Ru(II) pre-catalysts [Ru(CO)(SB)(L)] **186**–**197** where SB is a salicylaldehyde ethylenediamine 2-hydroxy-1-naphthaldehyde type derivative and L is PPh_3, $AsPh_3$ or pyridine (Fig. 33) [150]. They have been found to be efficient catalysts for the transfer hydrogenation of ketones and showing moderate activity for carbon–carbon coupling reactions.



198 **199**

Fig. 34. Schematic representations of the unsymmetrically-substituted tetradentate Schiff base complexes of Pd(II) **198** (left) [101], and of Pt(II) **199** (right) [151].

3.6. Palladium(II) and platinum(II) complexes

The palladium(II) complex **198** with the ferrocenyl-containing unsymmetrically-substituted N_2O_2 tetradentate SB ligand was prepared in an one-pot template procedure using equimolar amounts of half-unit **51**, 2-hydroxy-5-nitrobenzaldehyde and Pd(II) acetate, under mild conditions (Fig. 34) [101]. In the solid-state, the Pd(II) metal ion adopts a square planar geometry, with the substituted cyclopentadienyl ring of the donor ferrocene and the electron-withdrawing nitro groups being coplanar with the three fused heterometallacycles. This peculiar push–pull system exhibited a remarkably large quadratic hyperpolarizability $\beta_{1.91}$ of $970 \times 10^{--30}$ esu, that is almost four times greater than that determined for its nickel(II) analog **85** (Table 2).

The ionic unsymmetrically-substituted ON_2S tetradentate SB complex of platinum(II) **199** (Fig. 34) has been synthesized by Akbari *et al. via* the condensation of 1-(2-pyridyl)-3-thia-s-amino pentane, 5-nitrosalicylaldehyde and $PtCl_2(SMe_2)_2$ in the molar ratio 1:1:1 [151]. The experimentally proposed cationic square planar structure of the complex was confirmed by DFT calculations (optimized geometry and vibration frequencies).

3.7. Uranium(VI) complexes

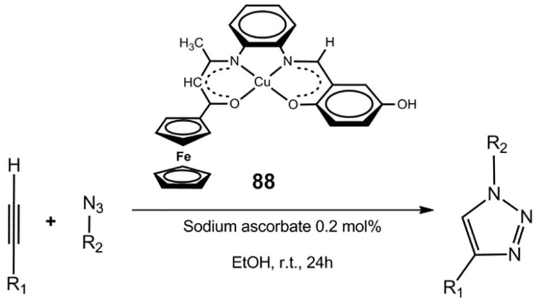
Feng *et al.* reported the synthesis of a new unsymmetrically-substituted tetradentate SB complex of uranium(VI) $[UO_2(HL)(NO_3)(H_2O)]\cdot H_2O$ **200** *via* the condensation of 5-chloro-2-hydroxybenzophenone, *o*-vanillin, *o*-phenylenediamine and uranyl nitrate (Fig. 35) [152]. The Schiff base HL acts as a mono-anionic $[HN_2O_2]^-$ ligand and the NO_3^- ion is coordinated to the metal center in a bidentate fashion. TG and DTG curves indicates that complex **200** decomposes in six steps. The kinetic parameters as well as the activation free-energy ($\Delta G^{\neq}$ = 120.6 kJ mol^{-1}) and the activation entropy ($\Delta S^{\neq}$ = −79.84 J mol^{-1} K^{-1}) of the third thermal decomposition stage (310–405 °C), corresponding to the loss of the *o*-vanillin-C=N fragment, were determined.

4. Organic transformations catalyzed by Schiff base metal complexes

SB ligand have been known since 1864 [1,2], and the first example of their metal complexes was investigated systematically by Pfeiffer and co-workers in the 1930s [153]. In parallel, the first chiral non-racemic unsymmetric SB metal complexes was discovered [154]. Since then, unsymmetrical SB metal complexes had been widely used as effective catalysts for the synthesis of organic semiconductors. Meanwhile, they were widely found in dyes, pigments [155], sensor [156], and materials science [157]. For example, Zou *et al.* reported a photochromic phenomenon initiated by tridentate unsymmetrical SB ligand coordinating Cu^{2+} ions in organic solvents. Further study indicated that the gated photochromic property resulted from the energy levels of frontier molecular orbitals that were altered by the interaction of the tridentate unsymmetrical SB ligand with Cu(II) ions according to theoretical simulations. It has been found that the gated photochromic material have great latent capacity as a switch between the photo-inactive and photo-active states by adding Cu^{2+} or not [155]. Aziz *et al.* reported the usage of a novel unsymmetrically-substituted tetradentate SB ligand (N-(2-hydroxyphenyl)-N′-(2-mercaptophenyl)-*o*-phthalylidene (HMP)) to detect Hg^{2+} ions with a detection limit of 9.57×10^{-12} mol/L. This system was applied successfully in hair and urine samples [156]. Luo *et al.* reported the synthesis of tetradentate unsymmetrical SBs Cu(II), Co(II) and Hg(II) complexes and their application as neutral carrier for thiocyanate-selective electrode. Their results showed that the nature of the coordinated metals directly affected the performances of the electrodes [157]. Herein, we will pay more attention to the catalysis by SB complexes, especially in organic chemistry where they have already been employed, as for instance for carbonylation of aniline to diphenyl urea, and coupling of cyclohexene oxide (CHO) and carbon disulfide (CS_2) [158]. In this section, we will discuss a panorama of important organic reactions catalyzed by metal complexes of different types of SB ligands, such as copper-catalyzed azide–alkyne cycloaddition (CuAAC), epoxidation of styrene, asymmetric trimethylsilylcyanation of aldehydes and asymmetric synthesis (including Henry reaction, addition reaction, cyclopropanation reaction, oxidation of sulfides, hetero-ene reactions, etc).

4.1. Copper-catalyzed azide–alkyne cycloaddition (CuAAC)

In 2016, our group first used the new tetradentate unsymmetrically-substituted SB heterobimetallic Fe(II)–Cu(II) complexes **88** and its PMMA-anchored derivative **90** (Fig. 36) as catalysts or catalyst precursors for the CuAAC reaction (Eq. (1)) [110]. We found that the bimetallic complex **88** exhibited an efficient catalytic activity with a 0.2 mol% of loading with various organic azides and terminal alkynes in the synthesis of 13 different triazoles under ambient conditions in ethanol, as shown in Eq. (1).

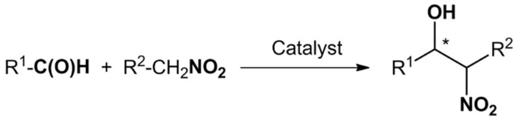


Eq. (**1**)

Then, we grafted complex **88** onto the PMMA polymer to generate the metallopolymer **90** with the purpose of recycling the catalyst. Compound **90** also exhibited a good catalytic activity in the CuAAC reaction and was reused at least three times without any lost of activity or copper leaching.

4.2. Henry reaction

The Henry reaction (or nitroaldol reaction), discovered in 1895 [159], is crucial in carbon–carbon bond coupling of carbonyl groups and nitro alkanes (Eq. (2)). The Henry reaction can be used to generate organic intermediates of various valuable natural products and biological drugs and dyes [160–162].



Eq. (**2**)

Since Shibasaki *et al.* first reported the asymmetric catalytic Henry reaction in 1992 [163], a large number of catalysts exhibiting high enantioselectivity had been developed for the synthesis of nitro alcohol [164–174]. Herein we will discuss some interesting unsymmetrical SB ligands and metal complexes **201**–**219** (Fig. 37) as catalysts for asymmetric Henry reaction. In the beginning, some unsymmetrical SB ligand, **201** [175], **202** [176], **203**

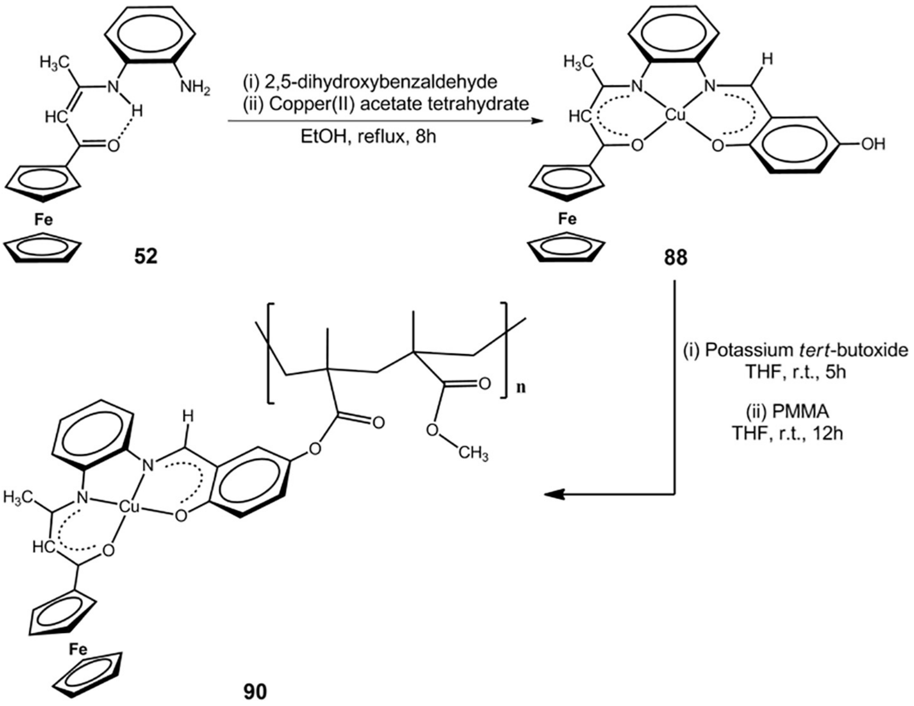


Fig. 36. Synthesis of the heterobimetallic complex **88** and of its PMMA-supported derivative **90**. Compound **90** is a mixture resulting from the random ordering of the monomer units and the bulk effect of the inorganometallic group in the polymer. The monomer ordering that is represented in the drawing of **90** is a simplification. Reproduced with permission of Ref. [110]. Copyright 2016, The Royal Society of Chemistry and the Centre National de la Recherche Scientifique.

[177], **204** [179], and **205** [180] have been designed and synthesized, However, most of them were found to be not efficient for the asymmetric Henry reaction. For example, the bisthiophene SB **204** only achieved 17% ee in this reaction [179]. The most efficient species was the phosphine SB ligand **205** that yielded 80% ee [180]. Their metal complexes were, indeed, found to be more efficient.

For instance, the related paracyclophane SB chiral Cu(II) complex **206** exhibited high enantioselectivity, but it was only applicable to 2-nitrobenzaldehyde [170]. By using Cu(II) chiral SBs iminopyridines complex **211**, Pedro's group obtained up to 85% chiral products for Henry reactions between nitromethane and a number of aliphatic and aromatic aldehydes, but it requires quite harsh reaction conditions like 11 mol% Cu(II) loading at 65 °C. The reactions were insensitive to air or moisture [178]. Compared to tridentate unsymmetrical SB ligands, Co, Cr and Cu complexes of salen ligands **212**–**215** improved the chiral induction of Henry reaction [181–187]. In this catalytic system, *m*- and *p*-substituted benzaldehydes only required an inert atmosphere and low temperature condition. Then, lots of efforts had been devoted to improve the enantioselectivity of Henry reactions. For example, Wang and co-workers reported the synthesis of a series of tridentate chiral SB type Cu(II) complexes and their applications in asymmetric Henry reactions with good yields and high enantioselectivities (up to 96% ee). They also investigated how substituents on the phenol ring of complex **207** affect the enantioselectivity and yield of the Henry reaction [188–190]. In 2014, Shen and co-workers have successfully anchored Cu(II) SB complex **207** onto polymer to obtain polymer supported Cu(II) SB complex **208**. They found that the Cu(II) metallopolymer **208** exhibited high yield (98%) and enantioselectivity (98% ee) for catalysis of Henry reaction under mild condition. In addition, the polymer-supported complex **208** could be reused at least 6 times with good catalytic activity and could be recycled by a simple filtration [111]. Chen and co-workers have developed a new aminoisoborneol SB ligand and its bifunctional copper complex **209** for asymmetric Henry reaction with high yields (up to 99%) with excellent enantioselectivities (up to 98% ee). This catalytic system only requires 1% mol Cu(II) complex. The manipulation process is easy with good tolerance to air and moisture, and a wide range of substrates of aldehydes and 1-nitropropane are suitable for this catalytic system [191]. Du and co-workers reported the synthesis of Cu(II) complex **210** *via in situ* three-component formation of oxazoline moieties and salicylaldehyde derivatives and Cu(OAc)$_2$ in EtOH. The catalytic activity of the Cu(II) complex **210** was tested in the model asymmetric Henry reaction, and the chiral nitroalcohols were obtained in moderate to good yields and enantioselectivities (up to 92% ee) [192]. In 2016, Bania and co-workers synthesized four new chiral Ni(II)–Schiff base complexes **216**–**219** and anchored them inside the cavity of zeolite-Y. They also tested them as heterogeneous chiral catalysts for asymmetric Henry reactions, and these heterogeneous catalysts exhibited high yield (up to 92%) and high enantioselectivity (up to 83% ee) [193].

For *anti*-selective Henry reactions, Handa *et al.* reported a new heterobimetallic Pd/La complex **220** (Fig. 38) with high yield (up to 97%) and high enantioselectivity (*anti*/*syn* = 22:1–3:1, and 92–72% ee). The authors also revealed the application of the reaction in the short synthesis of clinically important beta-adrenoceptor agonists [194].

4.3. Nitro-Mannich reaction

Over the past decades, the nitro-Manich reaction attracted chemists' extensive attention because its corresponding product β-nitroamines are common intermediates of α-aminocarbonyl complexes and 1,2-diamines. Hundreds of catalysts have been developed for the *anti*-selective catalytic asymmetric nitro-Manich reaction, as shown in Fig. 39 [195–198].

For the *syn*-selective catalytic asymmetric nitro-Manich reaction, Shibasaki and co-worker first reported the new heterobimetallic Cu–Sm–Schiff base complex **221** (Fig. 40) as catalyst to

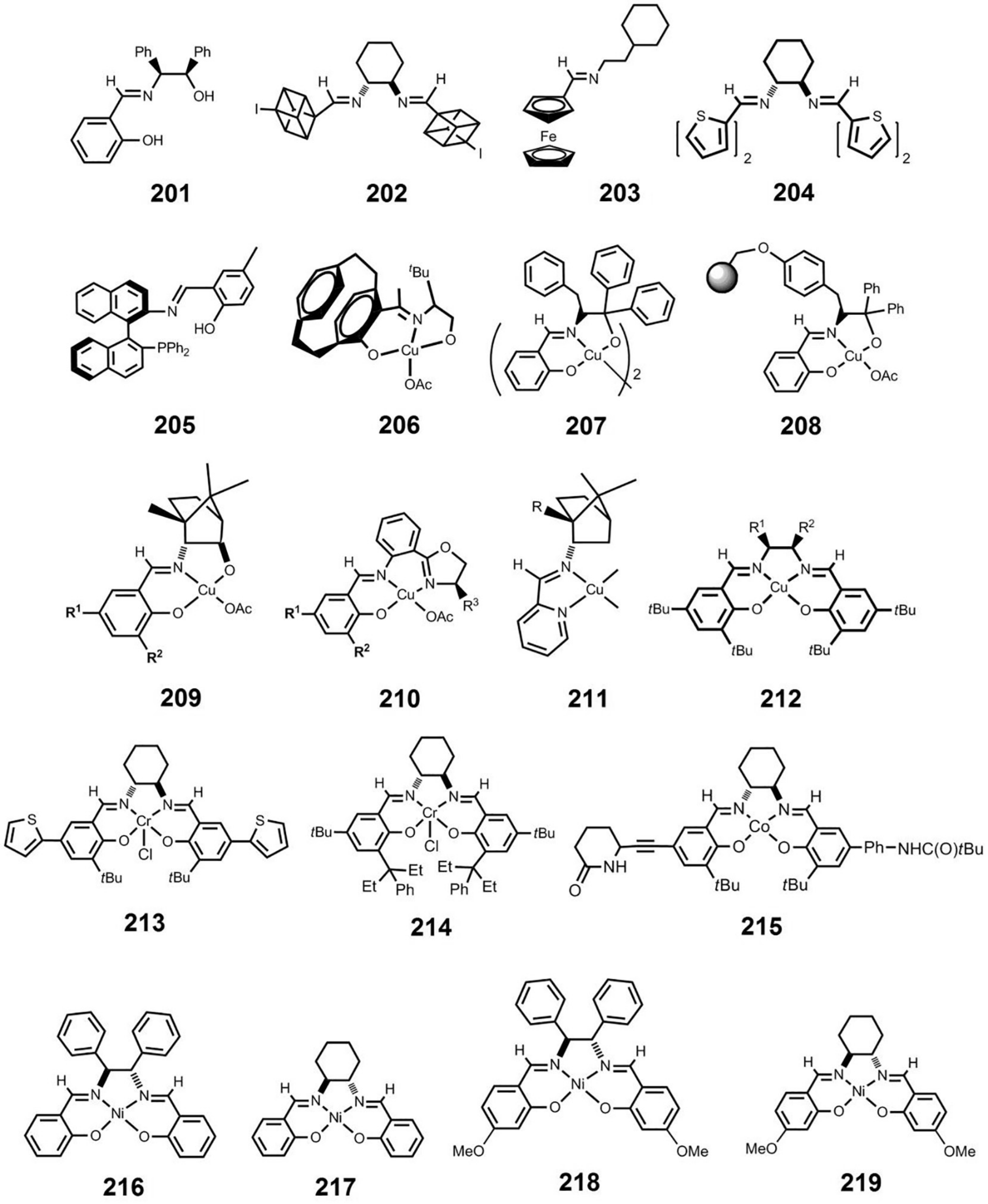


Fig. 37. Structure of various Schiff base ligands and metal complexes **201**–**219** used in the asymmetric catalytic Henry reaction.

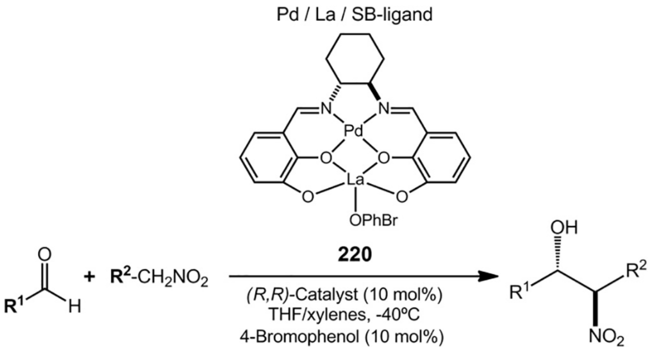


Fig. 38. *anti*-Selective nitroaldol reactions with various aldehydes and nitroalkanes using the heterobimetallic complex **220** [194].

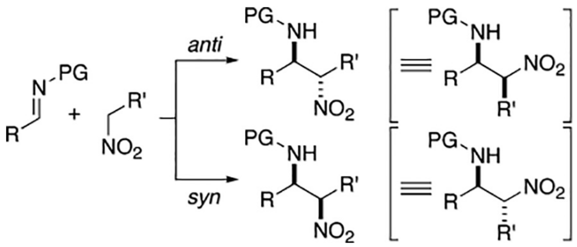


Fig. 39. The *anti* and *syn* selectivity of nitro-Manich reaction.

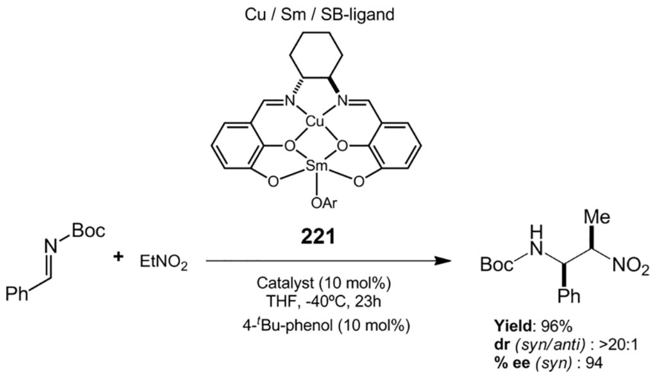


Fig. 40. Illustration of a highly *syn*-selective catalytic asymmetric nitro-Mannich reactions using the heterobimetallic Cu/Sm/SB complex **221** as catalyst [199].

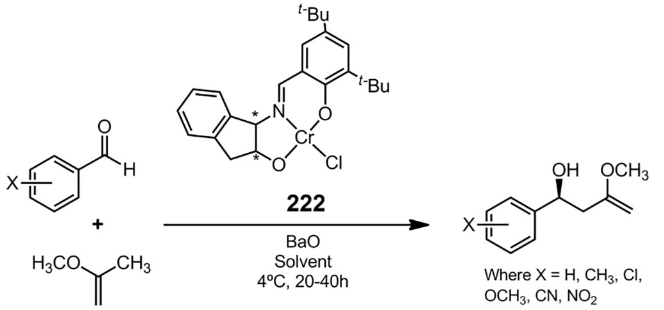


Fig. 41. Ene reaction of 2-methoxypropene with aldehydes using the chiral tridentate Schiff base chromium(III) catalyst **222** [201].

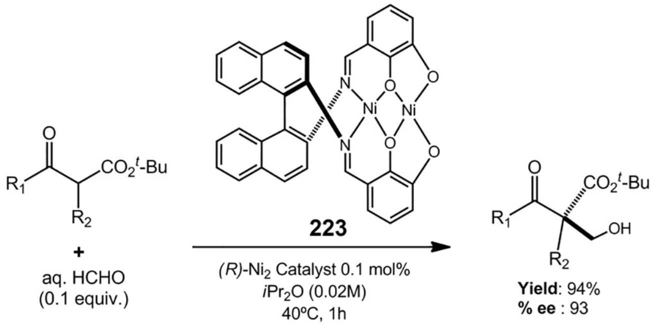


Fig. 42. Direct catalytic asymmetric aldol reaction of β-keto esters with formaldehyde using the homodinuclear Ni(II) unsymmetrical Schiff base catalyst **223** [208].

obtain the corresponding product [199]. This catalytic system showed high *syn*-selectivity (up to 99%) and high enantioselectivity (up to 98% ee). The authors also found that both Cu and Sm metals were essential for high *syn*-selectivity. Three years later, the same group reported their second-generation catalyst of $Sm_5O(O^iPr)_{13}$, replacing $Sm(O\text{-}^iPr)_3$, during the synthesis of catalyst. They found the second-generation catalyst showed broader substrate scope, as well as higher reactivity and stereoselectivity than the first-generation catalyst [200].

4.4. Hetero-ene reaction

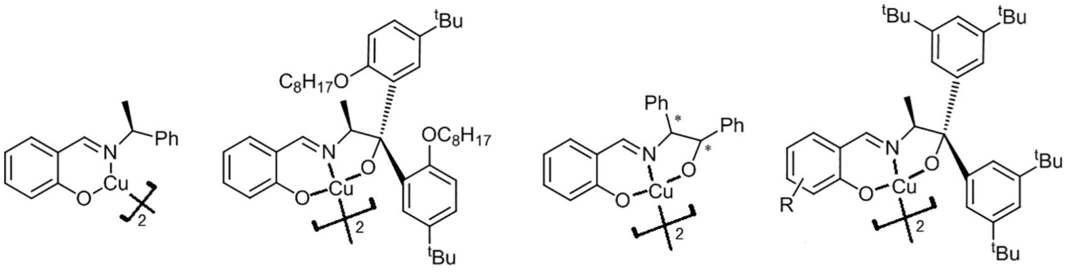
Asymmetric hetero-ene reaction is a C—C bond forming process of aldehydes and enol ethers. Its corresponding products had been comprehensively applied in the synthesis of various chiral β-hydroxycarbonyl derivatives. In recent years, chiral tridentate SB chromium(III) complexes had been found to be highly enantioselective and diastereoselective for asymmetric hetero-ene reactions. For instance, Jacobsen and co-workers synthesized the chiral tridentate SB chromium(III) complex **222** *via* the condensation of 3,5-di-*tert*-butylsalicylaldehyde with *cis*-1,2-aminoindanol and with $CrCl_2$, as shown in Fig. 41. The catalytic application in the hetero-ene reaction of aryl aldehydes and 2-methoxypropene or 2-trimethylsilyloxypropene showed highest enantioselectivities and fastest rates with acetone or ethyl acetate as solvent and BaO as desiccant [201]. One year later, the same research group expanded the application to a wide range of prochiral and chiral aliphatic aldehydes with highly enantioselectivity and diastereoselectivity [202].

4.5. Asymmetric aldol reaction

The direct catalytic asymmetric aldol reaction is the most efficient and economical method for the synthesis of chiral β-hydroxy carbonyl compounds [203–207]. To date, a great deal of unsymmetrical SB metal complexes had been found as catalysts for the asymmetric aldol reactions. Shibasaki and co-workers reported a novel homodinuclear Ni(II) complex **223** as chiral catalyst for direct asymmetric aldol reaction of β-keto esters with formaldehyde (Fig. 42). Only 0.1–1 mol% Ni(II) complex **223** was needed to obtain high yield (94%) and high enantioselectivity (93% ee) of hydroxymethylated products [208].

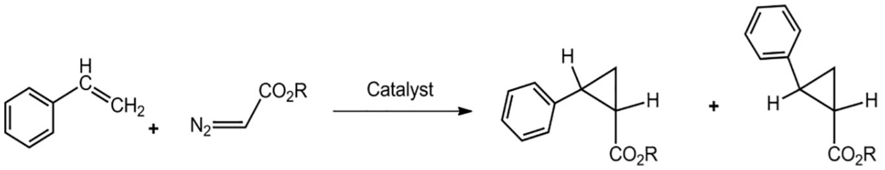
4.6. Asymmetric cyclopropanation reaction

Since Nozaki *et al.* first reported Cu(II) complex **224** (Fig. 43) as chiral catalyst for asymmetric cyclopropanation reaction (though only obtaining 6% ee) [209], this kind of reaction (Eq. (3)) of diazoacetates with ethers has mushroomed.



224 **225** **226** **227**

Fig. 43. Schiff base Cu(II) complexes **224–227** used as catalysts for the asymmetric cyclopropanation reaction.



Eq. (3)

Then, various SB metal complexes have been successfully used as catalysts for asymmetric cyclopropanation reaction to improve the optical yields. For example, based on Nozaki's catalyst, Aratani *et al.* synthesized a new Cu(II) complex **225** (Fig. 43), and disclosed its corresponding application in asymmetric cyclopropanation reaction with dramatic improvements in optical yields for selected intermolecular cyclopropanation reaction [210,211]. Some improved versions of Aratani's catalyst, with double chiral centers, such as **226** and **227** (Fig. 43), have been reported by Li *et al.* [212], Cai *et al.* [213], You *et al.* [214], and Li *et al.* [215]. In addition, Co(II) unsymmetrical SB complexes with a C_2 symmetry, derived from reaction of salicylaldehyde or diketone, and chiral 1,2-diaryl-1,2-ethanediamines and cobalt salts, were also revealed as efficient catalysts for asymmetric cyclopropanation reactions [216–220].

4.7. Asymmetric synthesis of α-amino acids

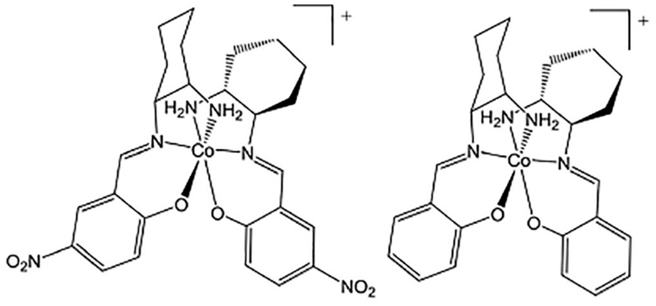
Enantiomerically enriched α-amino acids are widely applied for positron emission tomography (PET) diagnostics when they are labeled with short living isotopes [221–225]. SB Ni(II) complexes have been widely used as chiral auxiliaries and catalysts for the synthesis of α-amino acids. For instance, Saghiyan *et al.* reported a new Ni(II) complex **229** derived from ligand **228**, glycines and $Ni(NO_3)_2$ to synthesize the α-amino acid **231**, *via* nucleophilic substitution by HCHO or CH_3CHO to obtain the intermediate **230**, in coordination with the releasing of ligand **228**, as shown in Fig. 44 [226].

4.8. Hydrogen generation reaction

With the sharply increasing demand of chemical fuels, the development of clean and renewable energy is becoming more and more important. In recent years, conversion of solar energy into chemically stored fuel has caused multitudinous attentions [227,228]. This process is always defined as using electrocatalysts, with chromophores, splitting water into H_2 and O_2 *via* artificial photosynthesis. Lots of noble metal complexes (such as Pd) have been successfully applied as catalysts for hydrogen generation reactions. Interestingly, McNamara and co-workers found that octahedral cobalt complexes with unsymmetrical SB ligands could be used as efficient catalysts for hydrogen generation reactions [229]. Complexes **232** and **233** were obtained by condensation of 2-hydroxy-5-nitrobenzaldehyde or 2-hydroxybenzaldehyde, (1R,2R)-(−)-diaminocyclohexane, cobalt(II) tetrafluoroborate hexahydrate, and KPF_6 (Fig. 45). Complex **232** exhibited high activity (TOF = 420 s^{-1}) for hydrogen generation with a modest overpotential, whereas complex **233** was inert toward hydrogen generation. Nitro functionalities *para* to the phenolate of the ligand favored the reaction.

4.9. Epoxidation of styrene

Epoxides and their derivatives, an important class of O-containing heteroaromatic compounds, were found in a large number of pharmacologically active compounds and natural products [230–233]. Many methodologies have been developed for the synthesis of epoxides. Among them, the typical method is the oxidation of olefins using unsymmetrical SB metal (Mn, Cr, VO_2) complexes as catalyst (Eq. (4)). Jacobsen [234] and Katsuki [235] first independently reported the efficient optically active Mn (salen) catalysts for enantioselective epoxidation of olefins in



232 **233**

Fig. 45. Schematic representation of octahedral Co(III) complexes with unsymmetrical Schiff-base ligands **232** and **233** [229].

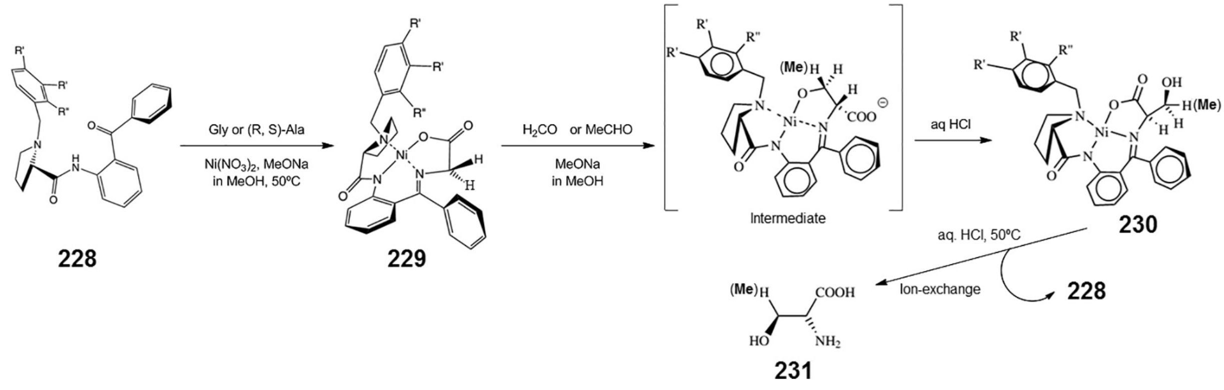
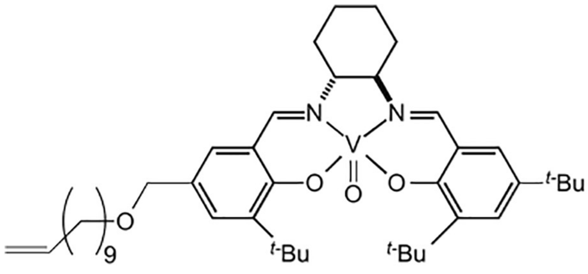


Fig. 44. Asymmetric synthesis of α-amino acid **231** [226].



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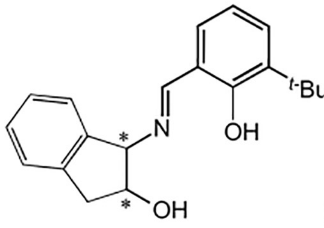
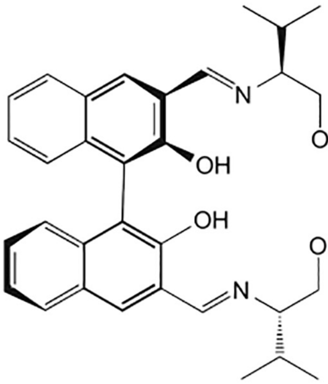


In presence of Ti(O-*i*-Pr)$_4$

235

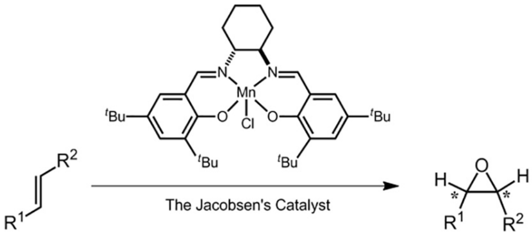


In presence of Ti(O-*i*-Pr)$_4$

236

Fig. 46. Unsymmetrical Schiff base vanadyl complex **234** (top) [283], and ligands **235** (middle) [284] and **236** (bottom) [285] utilized to prepare *in situ* Ti(IV) Schiff base complexes, used as catalysts in the trimethylsilylcyanation of aldehydes.

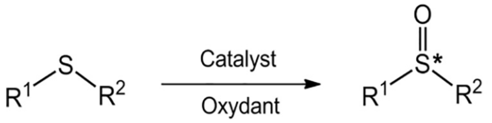
1990. Since then, plenty of unsymmetrical SB metal (Mn [236–240], Cr [241], V [242–244]) complexes have been developed, and high enantioselectivities have been achieved in the epoxidation of conjugated *cis*-di-, *cis*-tri-, and some tetra-substituted olefins.



Eq. (**4**)

4.10. Asymmetric oxidation of sulfides

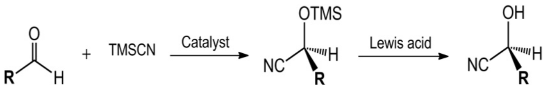
During the recent years, chiral sulfoxides have attracted a constant attention due to their wide applications in modern organic chemistry and pharmacologic drugs [245–254]. A lot of methods have been developed for the synthesis of optically active sulfoxides [255–258]. Among them, the most efficient method is the oxidation of prochiral sulfides (Eq. (5)) using unsymmetrical SB metal complexes as catalyst. In 1984, the first enantioselective oxidation of prochiral sulfides was independently discovered by Kagan [259] and Seraglia [260]. They used Ti(O^{i}Pr)$_4$-chiral tartrate systems for this purpose. Since then, a great number of unsymmetrical SB metal (Ti [261–263], Mn [264], Fe [265], V [266–276]) complexes have been developed, and high enantioselectivities have been achieved in the oxidation of prochiral sulfides.



Eq. (**5**)

4.11. Asymmetric trimethylsilylcyanation of aldehydes

Because their corresponding products (optically active cyanohydrins) of asymmetric trimethylsilylcyanation of aldehydes are very useful organic intermediates for the synthesis of α-hydroxy ketones, α-amino alcohols, chiral-hydroxy carboxylic acids and α-hydroxy aldehydes [277–282], the study of synthetic methods is a hot topic, especially the study with the homo- and hetero-metallic unsymmetrical SB metal complexes as chiral efficient catalysts. The transformation only require a bit addition of Lewis acid (Eq. (6)).



Eq. (**6**)

Plenty of efficient asymmetric methodologies approaching optically active cyanohydrins have been reported. A successful case is the asymmetric trimethylsilylcyanation of aldehydes, in the presence of Lewis acid, using unsymmetrical SB metal (Ti, V) complexes as catalysts. For example, Corma and co-workers synthesized a series of chiral vanadyl SB complexes **234** (Fig. 46) bearing a terminal C═C double bond pending alkyl chains of various lengths attached to the *para* position of the salen ligand, and anchored them on silicas to form solid enantioselective catalysts for the formation of cyanohydrins. The authors found that the optimized solid catalysts showed activity similar to that of the mononuclear precursor in solution under optimal conditions (CHCl$_3$ as solvent and 0 °C) [283]. Walsh and co-workers reported the bulky chiral SB ligand **235** derived from condensation of salicylaldehydes and amino alcohol. The catalyst was generated *in situ* by mixing the ligand with titanium tetraisopropoxide, and exhibited excellent enantioselectivity for the trimethylsilylcyanation of aldehydes [284]. Belokon *et al.* also reported a new chiral binuclear titanium complex of hexadentate SB ligand **236** for the asymmetric trimethylsilylcyanation of aldehydes and the ring opening of cyclohexene oxide [285].

4.12. Asymmetric hydrosilylation of ketones

Similar to asymmetric trimethylsilylcyanation of aldehydes, unsymmetrical SB metal complexes are also widely used as chiral catalysts for the asymmetric hydrosilylation of ketones (Eq. (7)).

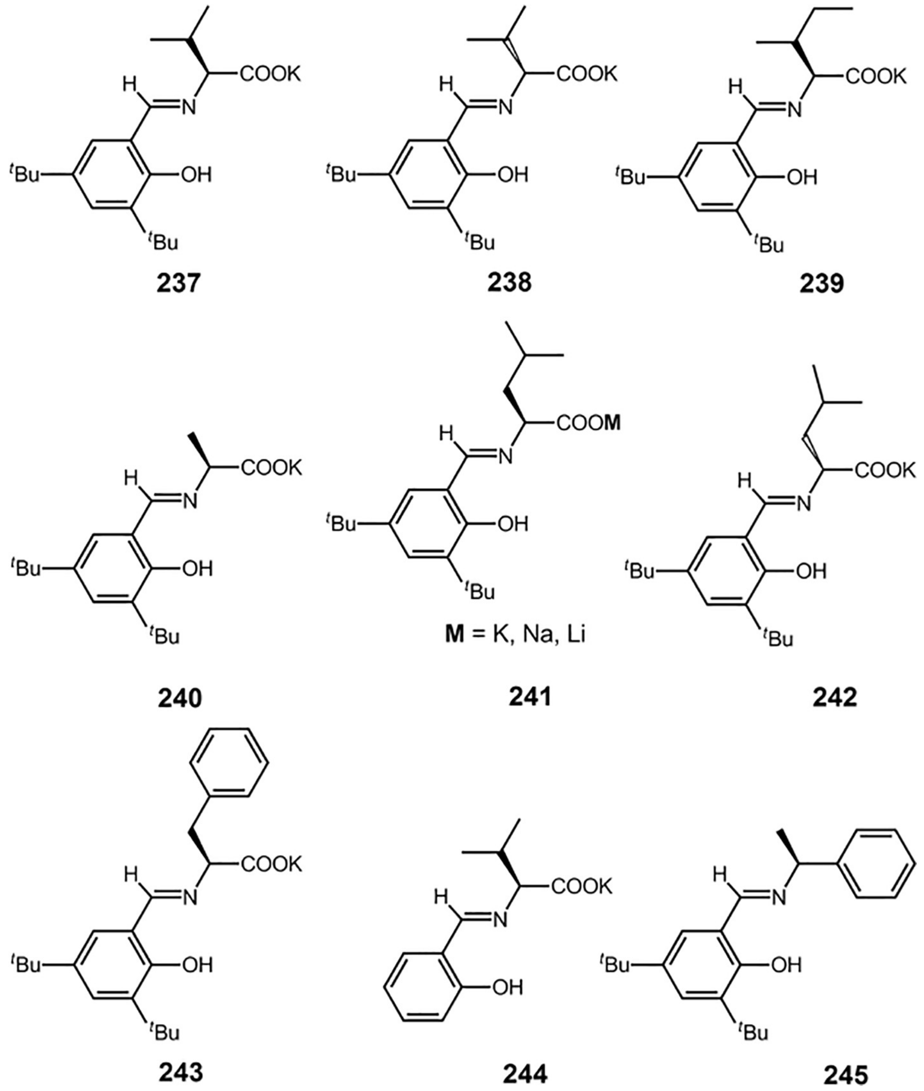
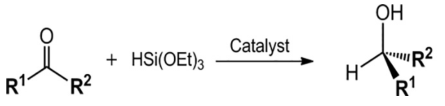
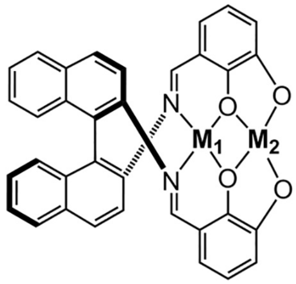


Fig. 47. Structures of the Schiff base ligands **237–245** used in the asymmetric hydrosilylation of ketones [291].



Eq. (**7**)

The asymmetric hydrosilylation of prochiral ketones was first discovered in the early 1970s. Since then, thousands of catalysts have been reported for the asymmetric hydrosilylation of ketones [286–290]. For instance, Liu *et al.* synthesized nine new types of chiral SB ligands **237**–**245** (Fig. 47) derived from α-amino acids and salicylaldehydes, and their zinc complexes exhibited excellent catalytic activity (up to 97% ee) for asymmetric hydrosilylation of ketones. They found that the nature of ligands had a very important influence on the catalytic activity. In addition, the substituents of salicylaldehyde showed a great impact on enantioselectivity of hydrosilylation of ketones [291].



246: $M_1 = M_2 = Co$

247: $M_1 = M_2 = Mn$

248: $M_1 = M_2 = Ni$

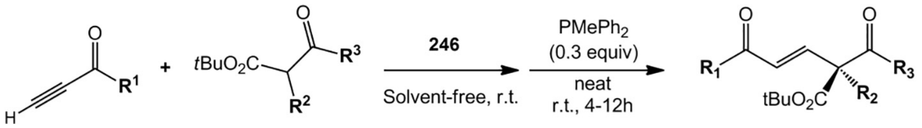
249: $M_1 = Ga$, $M_2 = Yb$

Fig. 48. Matsunaga and Shibasaki's chiral Schiff base metal complexes **246–249** used as catalysts for asymmetric addition reactions [295–299].

4.13. Asymmetric addition reaction

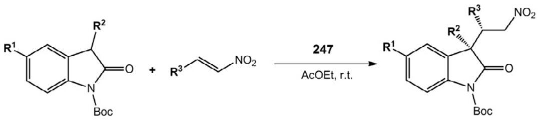
Recently, a handful of unsymmetrical SB metal complexes have been designed and used for asymmetric addition reaction, such as Bajaj's Cu(II) chiral amino alcohol based SB catalyst for asymmetric Friedel-Crafts addition of indoles to N-sulfonyl aldimines [292]. Wang *et al.* reported a new chiral SB Zn(II) complex that catalyzed asymmetric addition of 1-ethynylcyclohexene to ketones [293]. Belokon and co-workers synthesized a chiral octahedral SB Co(III) complex for asymmetric addition of a glycine-based SB ester to activated olefins [294]. Matsunaga and Shibasaki's research group reported a hexadentate SB ligand and its metal complexes for asymmetric addition reactions (Fig. 48). They found that only 2.5–0.25 mol% homodinuclear Co(III) complex **246** can be used as chiral catalyst for the 1,4-addition of β-keto esters to alkynones

(Eq. (8)) at room temperature with high enantioselectivity (up to 99% ee) [295].



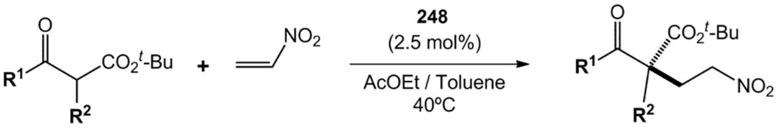
Eq. (**8**)

If the coordinated metal Co(III) was replaced by Mn(III), the resulting homodinuclear Mn(III) complex **247** (Fig. 48) was found suitable to asymmetrically catalyze 1,4-additions of oxindoles to β-aryl, β-heteroaryl, and β-alkenyl nitroalkenes (Eq. (9)) at room temperature in high yield (up to 99%) and high enantioselectivity (up to 96% ee) [296].

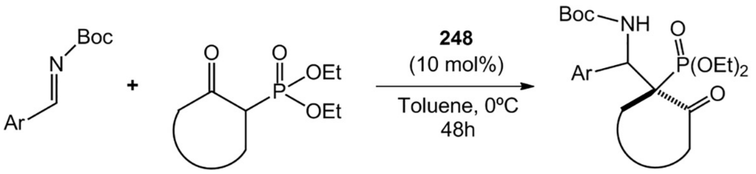


Eq. (**9**)

With the hexadentate SB ligand coordinated to nickel(II), it has been found that this Ni(II) complex **248** (Fig. 48) was a very efficient catalyst for asymmetric 1,4-addition of β-keto esters to nitroethylene (Eq. (10)) [297] and Mannich-type addition of β-keto phosphonate to aryl or heteroaryl N-Boc imines (Eq. (11)) [298].

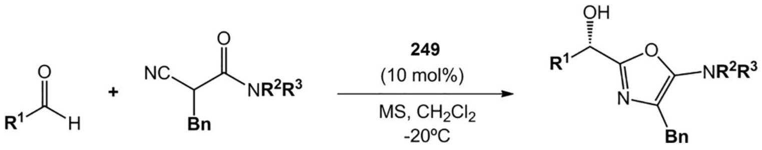


Eq. (**10**)



Eq. (**11**)

Then, the authors developed the new heterobimetallic SB complex $Ga(O^iPr)_3/Yb(OTf)_3$ **249** ($OTf = CF_3SO_3$) and found that it exhibited excellent catalytic property for asymmetric α-additions of α-isocyanoacetamides to aryl, heteroaryl, alkenyl, and alkyl aldehydes with high yield and high enantioselectivity (Eq. (12)) [299].



Eq. (**12**)

5. Conclusion and outlook

This review has highlighted the background and recent progress in the synthesis of unsymmetrically-substituted Schiff bases and their metal complexes, their structural and physico-chemical properties, and applications of some SB complexes in major organic transformations. Some typical examples are discussed in detail, like tridentate, and unsymmetrically-substituted tetradentate SB ligands and their Ni, Cu, V, Mn, Fe, Co, Zn, Ru, Pd, Pt, and U complexes. Use of SB complexes in CuAAC reaction, Henry reaction, nitro-Mannich reaction, Hetero-Ene Reaction, asymmetric aldol reaction, asymmetric cyclopropanation reaction, asymmetric synthesis of α-amino acids, hydrogen generation reaction, epoxidation of styrene, asymmetric oxidation of sulfides, asymmetric trimethylsilylcyanation of aldehydes, asymmetric hydrosilylation of ketones, asymmetric addition reaction had been clearly classified and discussed.

It is still a significant challenge to explore new applications of unsymmetrically-substituted SB ligands and their metal complexes, although great progress has been made concerning the fields of catalysis and optoelectronics. Unsymmetrical SB are being applied to synthesize controlled functional thin films on certain substrates (some kind of nanosystem) *via* the covalent molecular assembly of SB interactions with the layer-by-layer method. Moreover, this kind of nanosystems has successfully been applied in bioreactors, drug delivery, biosensors, and microarrays [300]. Unsymmetrical SBs are expected to be applied to synthesize covalent organic frameworks. Also they have been first explored for applications related to solar energy collectors, optoelectronic devices, clean energy, gas adsorption and storage [301–318]. It is consequently expected that, in the following decades, exciting progress will be made in the synthesis, catalysis, sensing, energy, and materials applications of unsymmetrical SB ligands and their metal complexes and other molecular materials for academic and industrial developments.

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