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Recent advances on ditopic ligands

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REVIEW

Recent advances on ditopic ligands†

BORIS I. KHARISOV*, PERLA ELIZONDO MARTÍNEZ, VÍCTOR M. JIMÉNEZ-PÉREZ, OXANA V. KHARISSOVA, BLANCA NÁJERA MARTÍNEZ and NANCY PÉREZ

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Recent (2000–2009) achievements on ditopic ligands are reviewed. The ditopic ligands are mainly represented by N-, P-, O-, and S-containing organic molecules or their N, O-, N, S-, and N, P-combinations with azine, azole, amine, azide, β -diketone, crown ether, carboxylate, phenanthroline, oxazoline, phosphole, and thiophene moieties, among others. A series of mono- and polynuclear transition and *f*-metal complexes with these ligands, in particular cluster- and supramolecular unit-containing complexes, have been obtained and characterized spectroscopically and electrochemically.

Keywords: Ditopic ligands; Mono- and polynuclear complexes; N-, P-, O-, and S-containing organic ligands

Abbreviations

A4-ptz	5-[N-acetato(4-pyridyl)]tetrazolate
Atz	5,5'-azotetrazolate
5,5''-azo	5,5''-azobis(2,2'-bipyridine)
4,4''-azo	4,4''-azobis(2,2'-bipyridine)
5,5''-azoxy	5,5''-azoxybis(2,2'-bipyridine)
Bbbm	1,1'-(1,4-butanediyl)bis-1H-benzimidazole
BDPQ	2,3-bis(2-pyridyl)benzo[g]quinoxaline
Bipy	bipyridine
Bpa	trans-1,2-bis(4-pyridyl)ethane
Bte	1,2-bis(1,2,4-triazole-1-yl)ethane
Btmb	1,4-bis(triazol-1-ylmethyl)benzene
DABCO	1,4-diazabicyclooctane
Dca	dicyanamide
Dedbt	2,5-diethynyl-3,4-dibutylthiophene

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†Dedicated to Prof. Dr Sci (Academician) Vladimir I. Minkin (Research Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, Russia) on the occasion of his 75th birthday.

DMeDPQ	6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline
Dpds	4,4'-dipyridyl disulfide
Dps	4,4'-dipyridyl sulfide
En	ethylenediamine
Fc	ferrocene
H ₂ BPPP	2,6-bis-(5-phenyl-1H-pyrazol-3-yl)pyridine
HOPO	hydroxypyridinone
Htza	2-(1H-1,2,4-triazol-1-yl) acetic acid
Pbbm	1,1'-(1, 5-pentanediy)bis-1H-benzimidazole
Phen	1,10-phenanthroline
pyz	pyrazolate
Pz	pyrazine
Pym	pyrimidine
Salen	2,2'-Ethylenebis(nitrilomethylidene)diphenol, N,N'-Ethylenebis(salicylimine)
Tatpp	tetraazatetrapyrido[3,2-a : 2',3'-c : 3'',2''-1 : 2''',3'''-n]pentacene
Tmp	tetramethylpyrazine
Tpp	triphenylphosphine
Tppz	tetrapyrido[3,2-a : 2',3'-c : 3'',2''-h : 2'',3''-j]phenazine
Tpy	terpyridine
Tren	2,2',2''-triaminotriethylamine

1. Introduction

Coordination chemistry gives the opportunity to explore different ways to obtain new materials possessing interesting properties. This is the case for polytopic ligands which contain multiple, separated binding sites (at least two) in their structures where cations and/or anions are bonded, enabling formation of complexes containing more than one metal center [1, 2]. A “ditopic” ligand is a receptor that possesses two remote binding regions to coordinate a metal center. Accordingly, monotopic ligands are those that contain only one binding site, assisting in the formation of discrete species by acting as terminal ligands. The term *n*-topic refers to the number of distinct binding sites, not to individual atoms capable of coordination.

Sometimes ditopic ligands, the subject of the present review, act as a zwitterion system (a chemical compound that carries a total net charge of zero, thus electrically neutral but carries formal positive and negative charges on different atoms) with positive sites binding anions and negative sites binding cations such that resulting ligands can transport metal salts. The main feature in the development of new polytopic receptors is to create a dual host system, that is, more effective than the sum of their parts. Schiff base condensation is a classic and useful route to obtain reagents with structural characteristics to act as *n*-topic ligands.

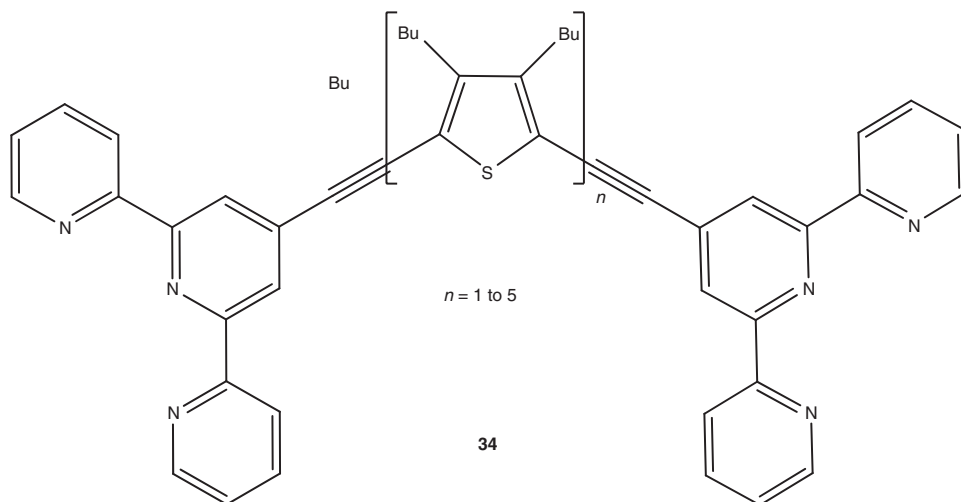
Recently, ditopic ligands and their metal complexes have been noted in a series of books [3–6], reviews [7–13], and a lot of experimental articles [14–22]. The present micro-review is devoted to the description of selected important recent achievements in this field without pretending to show the state-of-the-art in this enormous field in coordination chemistry. Attention is focused on classic N-, P-, O-, and S-containing

(or in their N, O-, N, S,- and N, P-combinations) organic molecules without examination of supramolecular compounds, described in detail in a series of above mentioned monographs, as well as in the fundamental recent book of Steed and Atwood [23]. Tables 1–3 show main moieties present in ditopic ligands and several ditopic ligands.

2. N-Containing ditopic ligands

2.1. Ditopic ligands on the terpyridine basis

Chemistry of ditopic ligands containing nitrogen is rich in comparison with O, P, and S-donor ligands. In this context, bipy and tpy have been the most widely used ligands in coordination, materials, and medicinal chemistry. Tpy is an interesting ligand due to 4'-substitution maintaining the symmetry and allowing variable coordination. However, bipy chemistry has been much more explored [24, 25]. Here we only describe the most representative recent examples of N-ditopic ligands and their metal complexes. As shown in table 1, ditopic ligands used in the last decade consist of classic N-containing moieties. According to the available bibliography, the highest number of reports has been observed for compounds with a terpyridine moiety, not only pure N-donor ligands, but also N, O, and N, S-ligands. As an example of N, S-donors based on tpy and containing thiophene, but binding guests only through nitrogens, is the soluble and rigid tpy-based ditopic ligands (**34**) bearing an increasing number of dedbt modules, which demonstrated the advantages of a single convergent strategy based on a double coupling in a final step of monoterpyridine building blocks carrying the adequate number of thiophene modules [26].



A series of ditopic ligands incorporating two 2,2':6',2''-tpy metal-binding domains linked to a central naphthalenediyl core by ethyleneoxy chains of various lengths were synthesized (reaction 1), as well as their iron complexes. The major thermodynamic complexation products are ferracycles of [1 + 1], [2 + 2] or [3 + 3] stoichiometry [27]. A similar tpy derivative (**35**) {1,4-bis(2,2':6',2''-terpyridin-4'-yl)benzene} and its

Table 1. Main N-containing ligand units present in ditopic ligands.

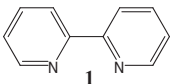
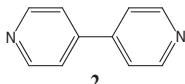
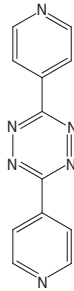
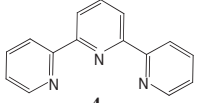


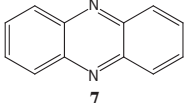






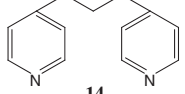
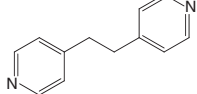
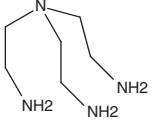
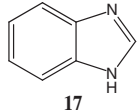
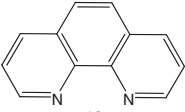
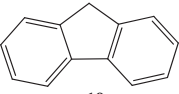
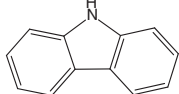
		
1	2	3
2,2'-Bipy	4,4'-Bipy	3,6-Bis(4-pyridyl)-1,2,4,5-tetrazine
		
4	5	6
Tpy	Pyrazol	Pyrazoline
		
7	8	9
Phenazine	1,2,3-Triazole	1,2,4-Triazole
		
10	11	12
Tetrazole	Pyridine	Pz
		
13	14	15
Pyrimidine	4,4'-Trimethylenedipyridine	(E)-1,2-bis(4-pyridyl)-ethane
		
16	17	18
Tren	Benzimidazole	1,10-Phen
		
19	20	
Non-N-containing fluorine 19 and its N-heteroanalogue carbazole 20		

Table 2. Main O- and N, O-containing units present in ditopic ligands.

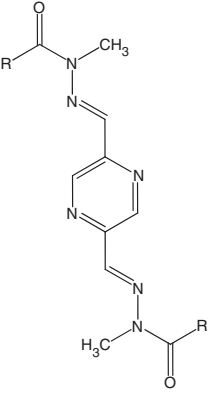
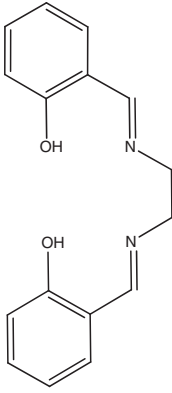
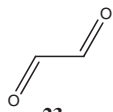
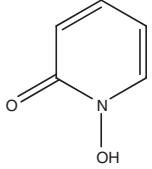
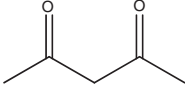
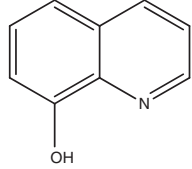

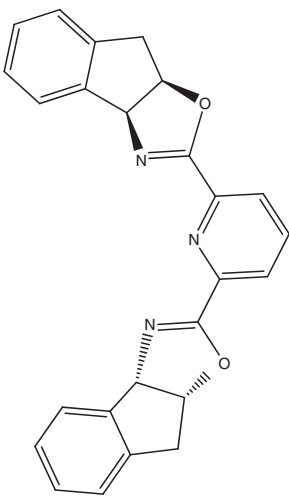
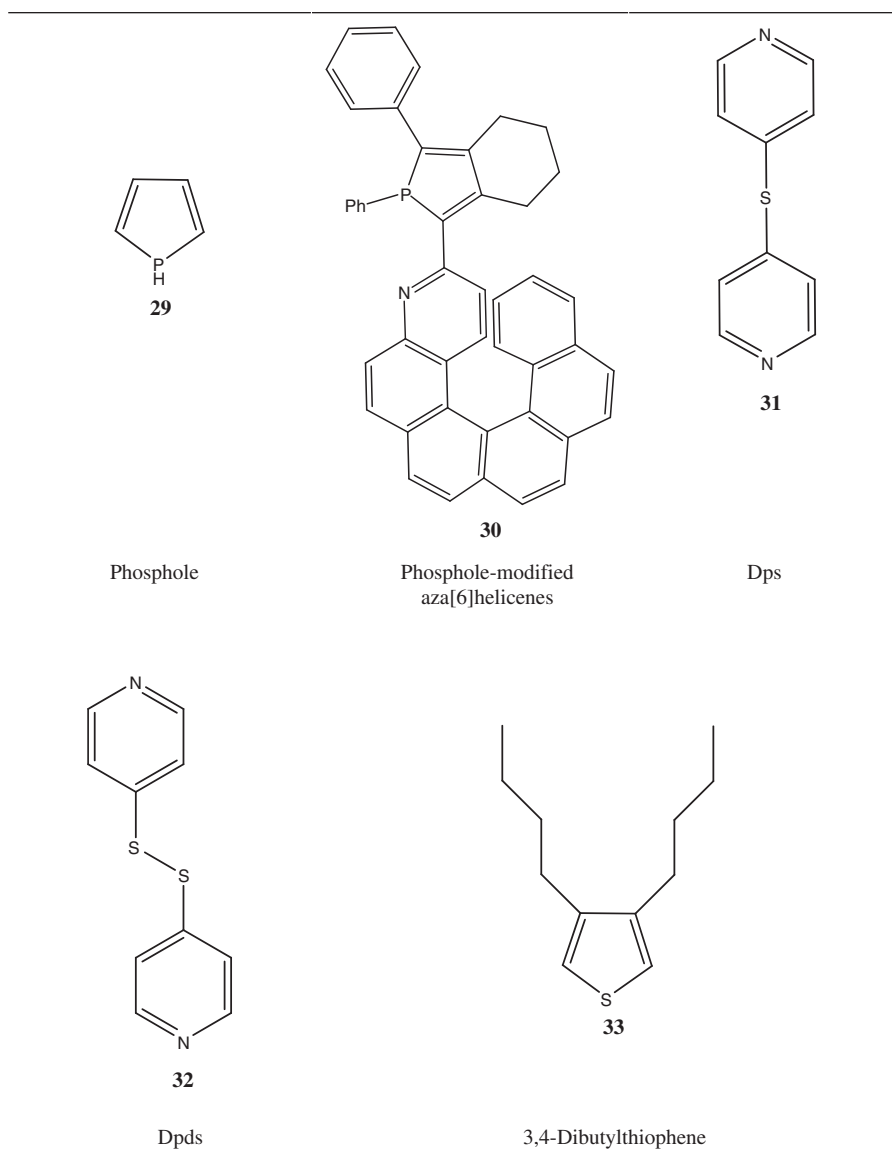
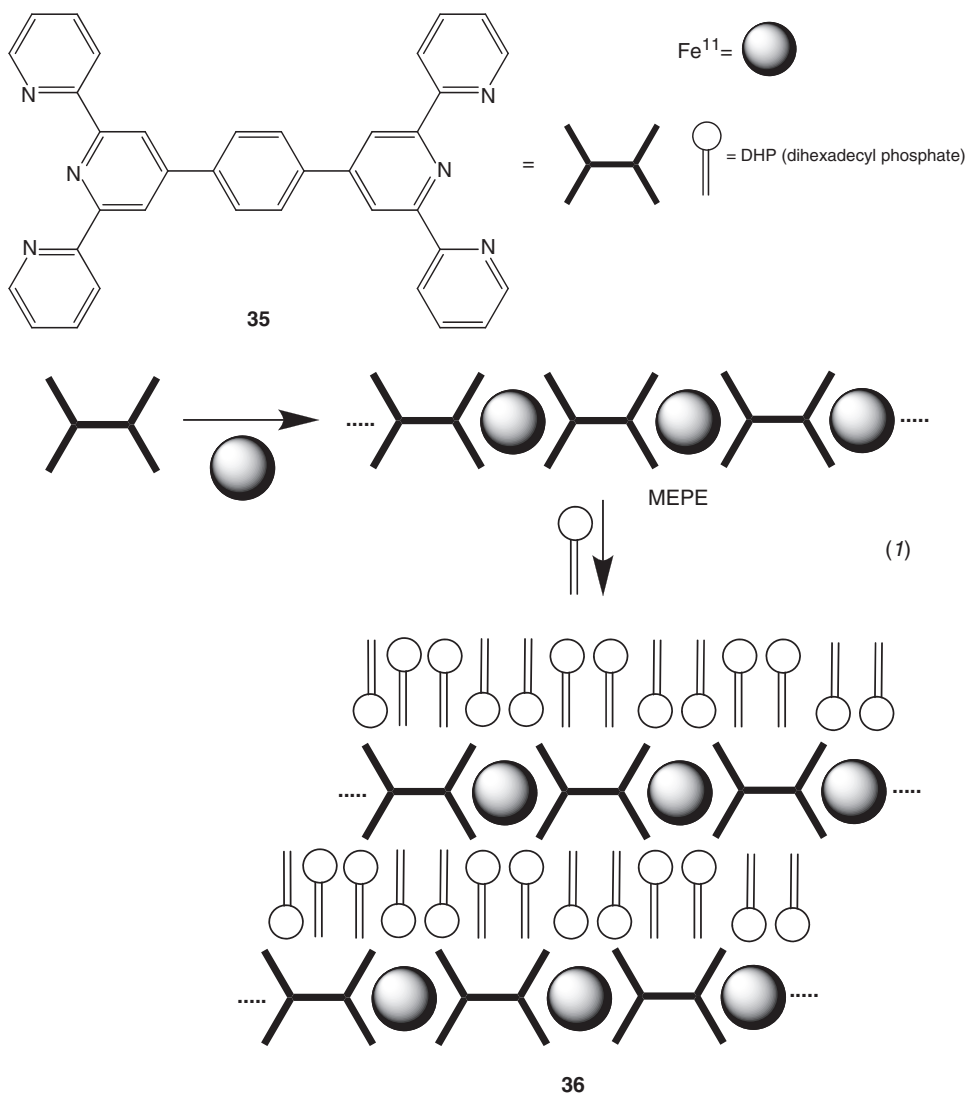
 <p>21</p>	 <p>22</p>	 <p>23</p>
<p>2,5-Pyrazine-dicarboxaldehyde - acyl-aryl-hydrazine derivatives</p>	<p>Salen</p>	<p>Glyoxal</p>
 <p>24</p>	 <p>25</p>	 <p>26</p>
<p>HOPO</p>	<p>2,4-Pentanedione, an example of a β-diketone</p>	<p>8-Hydroxyquinoline</p>
 <p>27</p>	 <p>28</p>	
<p>Oxazoline</p>	<p>Example of a pyBox ligand</p>	

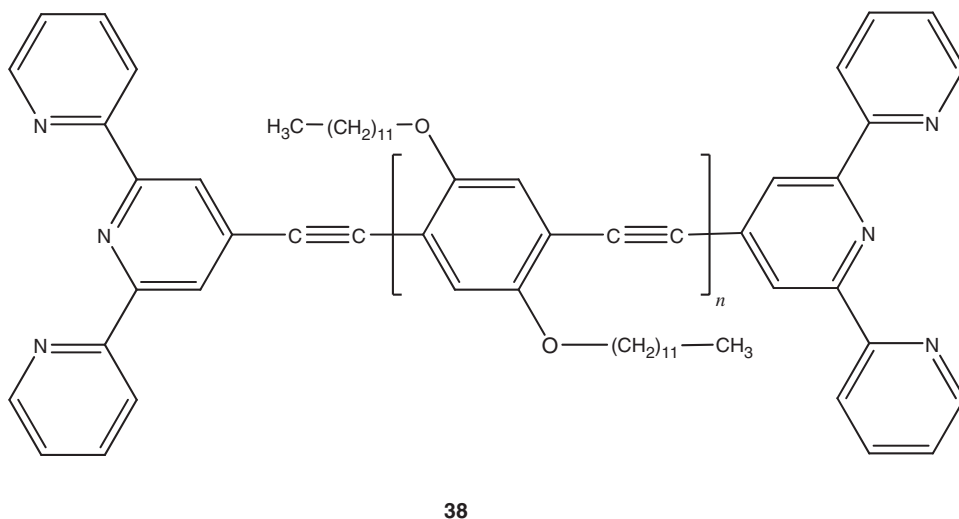
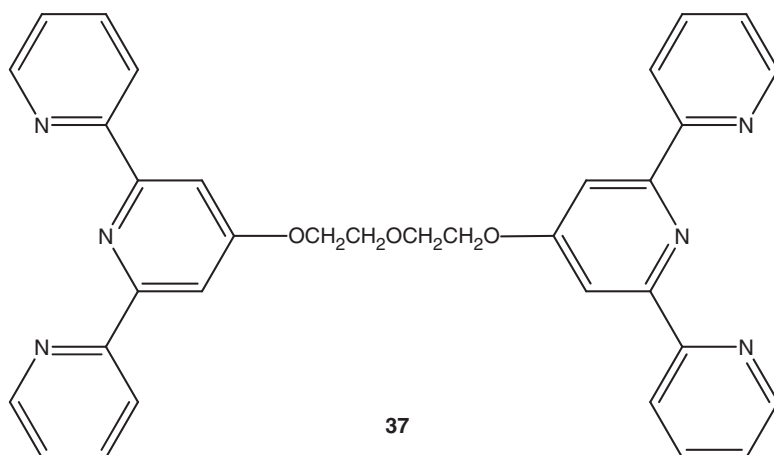
Table 3. Main P-, S-, N-, P- and N, S-containing units present in ditopic ligands.



polyelectrolyte-amphiphilic Fe complexes polyelectrolyte-amphiphile complexes (PAC) (**36**) were described by Kurth *et al.* [28–30]. The final nanostructured material which self-assembles from transition metal ions, ditopic ligands, and amphiphiles had a hierarchical architecture consisting of alternating strata of metallo units and interdigitated amphiphiles. Other metallocsupramolecular coordination polyelectrolytes (MEPEs) were described in the study carried out by Schuette *et al.* [31]. Multinuclear Co complexes of ditopic ligands with α,ω -dioxy spacers linking two tpy metal-binding domains, for example $\{[CoL](OAc)_2\}_n$ ($L = \mathbf{37}$) were found to react with alcohols to

generate mononuclear 4'-alkoxy-species, $[\text{CoL}_2](\text{PF}_6)_2$ (L = 4-methoxy/ethoxy-2,2':6':2''-terpyridine) [32, 33]. Among other tpy derivatives, we note two ditopic ligands, synthesized by coupling an amino functionalized 2,2':6':2''-tpy Ir complex to the carbonylimidazole activated dipyriddyridazine and 2,2'-bipy ligands [34], six ditopic ligands (L) which contain polyethyleneoxy-substituted naphthalene spacers connecting two 2,2':6':2''-tpy metal-binding domains, and their ruthenium complexes {linear complexes $[(\text{tpy})\text{Ru}(\text{L})\text{Ru}(\text{tpy})]^{4+}$ and metallomacrocyclic species $[\text{Ru}_n\text{L}_n]^{2n+}$ ($n=2$ or 3)} [35], and tpy-based ditopic ligands bearing one to five phenylene/ethynylene modules (**38**), attached to the tpy unit *via* an ethynylene fragment and functionalized at the 4-position with an additional ethynylene connector and in the 2,5-positions with two flexible dodecyloxy chains [36]. Other tpy complexes of transition metals were also reported [37, 38].

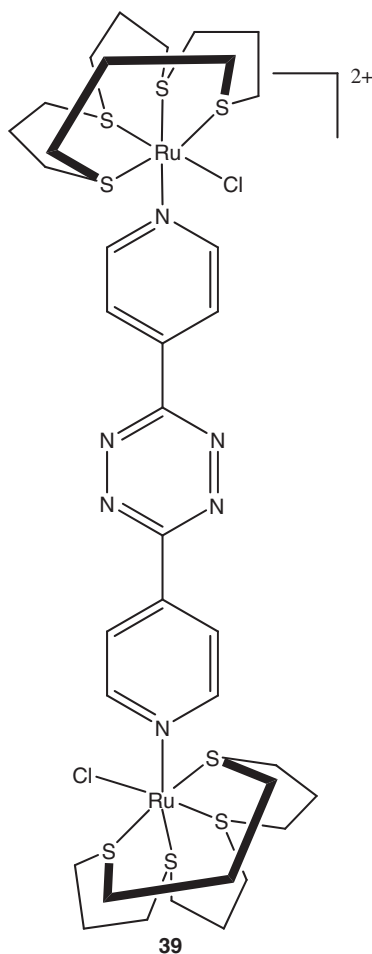


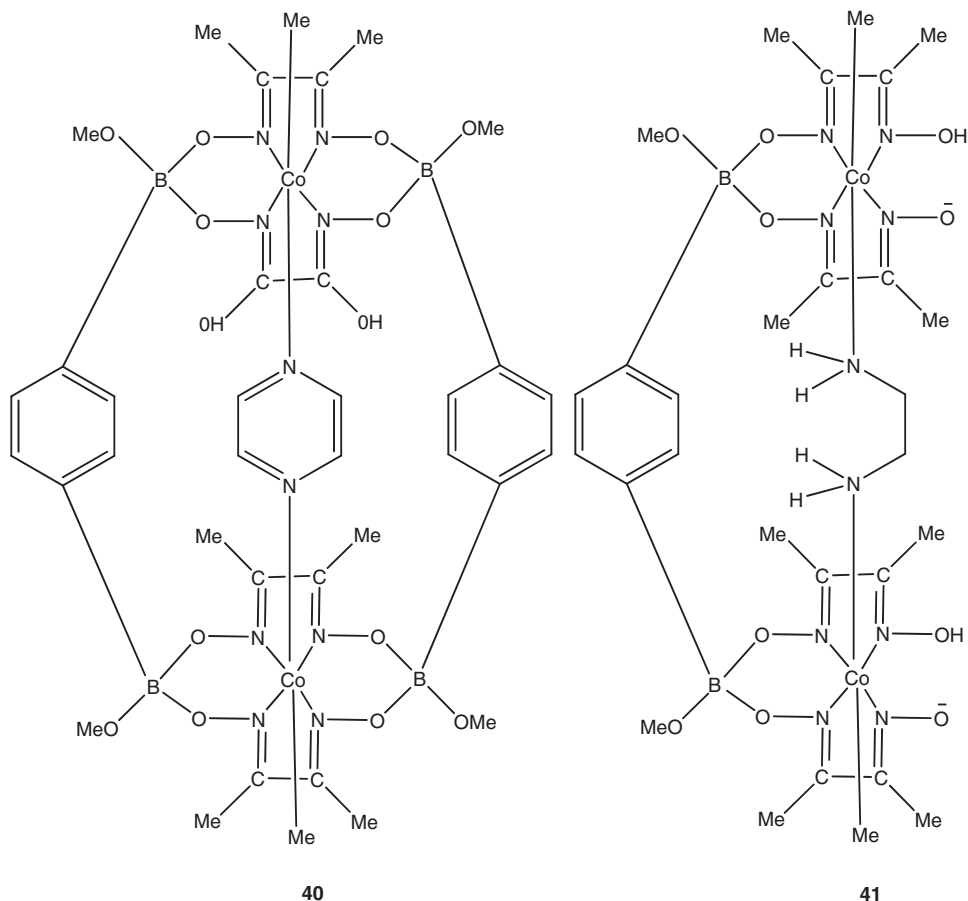


2.2. Ditopic ligands containing pyridine, bipyridine, and azine moieties

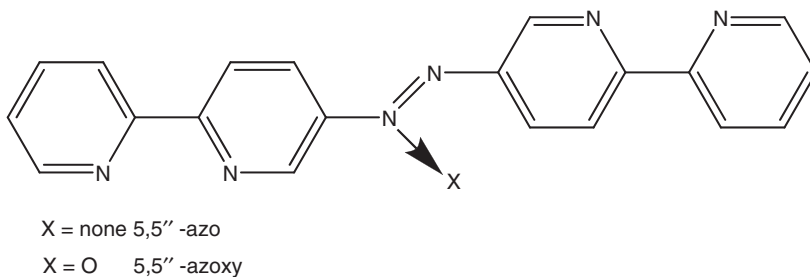
Three metallodendrimers composed of one central and six peripheral $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ core-containing clusters linked by pyridyl-based bridging ligands were reported [39]. These compounds represent the first *bonafide* cluster-supported metallodendrimers featuring cluster units at the core, within the branch, and on the periphery of a dendritic architecture. In order to expand current strategies for inorganic crystal engineering, Schultheiss *et al.* [40] designed and synthesized two asymmetric pyridyl-pyrimidine (py-pym) ligands. These ditopic ligands are suitable for binding a metal center through the py-moiety, whereas the pym-moiety provides a self-complementary hydrogen-bonding functionality capable of organizing metal ions into an extended linear 1-D network. Two copper coordination polymers, differing slightly by their structures but strongly by properties, were synthesized by reaction of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$,

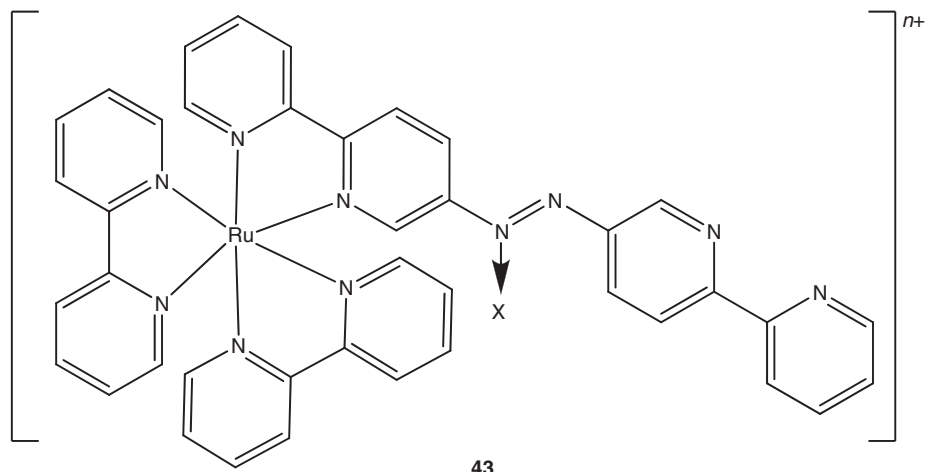
pyridine-2-carbaldehyde azine, triphenylphosphine, and diimine ligands derived from 4,4'-bipy and/or trans-1,2-bis(4-pyridyl)ethylene. The authors noted an importance of the double bond in the diimine ligand in these coordination polymers [41]. The single crystal X-ray analysis of another coordination polymer, derived from Cd with both rigid and flexible spacer ligands bpa and 4,4'-bipy, $\{[\text{Cd}(\mu\text{-bpa})(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2] \cdot (\text{ClO}_4)_2\}_n$, showed that the complex is a 1-D polymer whose 1-D chains are further self-assembled into a 3-D network *via* hydrogen bonding and π - π stacking [42]. A series of nine new complexes incorporating $[\text{RuCl}([n]\text{aneS}_4)]$ ($n = 12, 14, 16$) metal centers bridged by three ditopic ligands containing two monodentate sites {pz, 4,4'-bipy and 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine **3**}, for instance **39**, were obtained and fully characterized [43]. The guest-induced synthesis of a molecular box **40** from methyalaquacobaloxime and 1,4-phenylenebisboronic acid, with pz as guest, is described [44]. Several other ditopic ligands were tested, but none formed an analogous product. However, a second supramolecular species **41**, closely related to **40**, was formed in the case of ethylenediamine (en).





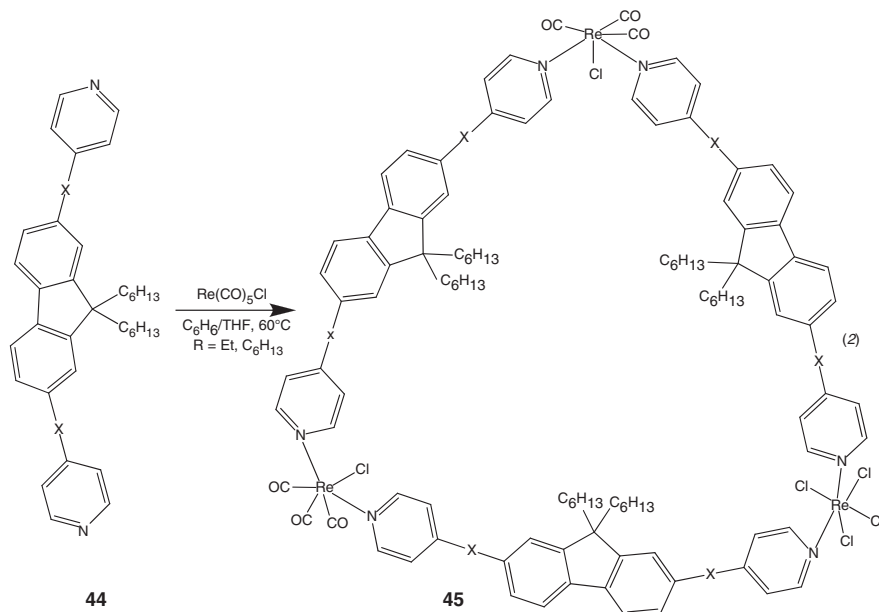
Two new ditopic ligands **42**, 5,5''-azo and 5,5''-azoxy, were prepared by the reduction of nitro precursors. Mononuclear and dinuclear Ru complexes **43** having one of these bridging ligands and 2,2'-bipy terminal ligands were also obtained; their properties were compared with similar Ru complexes having 4,4''-azo [45]. Electrochemical properties are quite similar to those of previously reported complexes involving 4,4''-azo. On the other hand, spectroscopic properties are quite different.





43

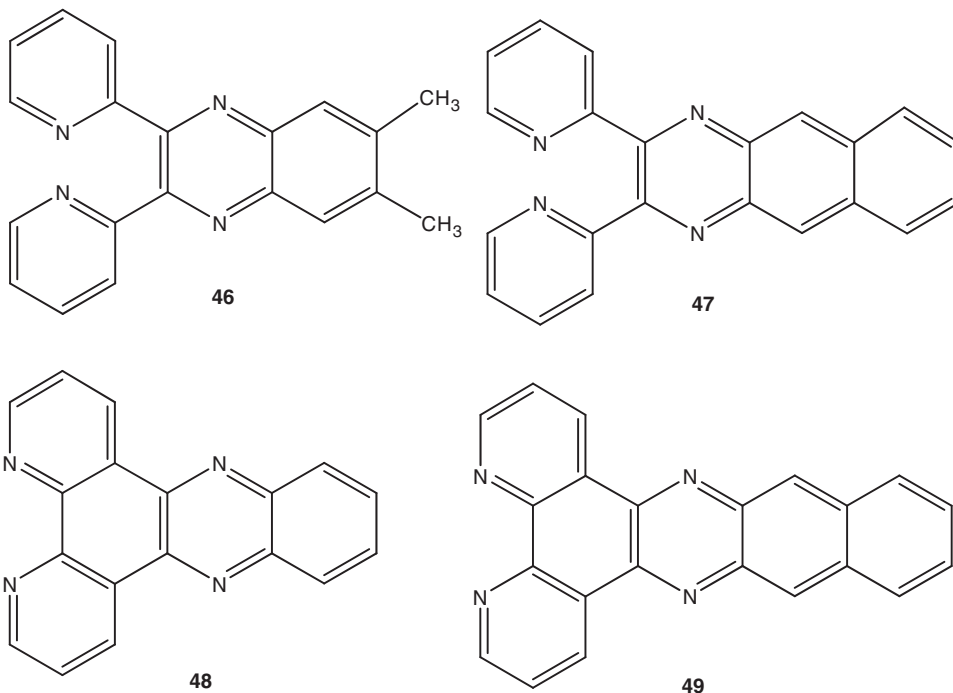
Ditopic ligands were reported [46] in which terminal 2,2'-bipy groups are connected via an ethynylene group through different sites on the pyridine ring. These terminals were capped with $[\text{Ru}(\text{bipy})_2]^{2+}$ and $[\text{Os}(\text{bipy})_2]^{2+}$ metallo-fragments to form photoactive heterodiads. Other ruthenium ditopic bipy-containing complexes were described in detail by Dunne *et al.* [47]. Fluorene- (**44**) and carbazole-bridged bipy ligands, potentially useful for the preparation of self-assembled supramolecules and synthesized by Pd-catalyzed cross-coupling reactions, undergo facile ring closure reactions (2) with $\text{Re}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) to yield **45**. Fluorene-bridged ditopic ligands facilitate the formation of trimetallic triangles while the angular carbazole-bridged ligands gave cyclic dimmers [48]. Ditopic ligands containing a 2,2'-bipy were reported by McSkimming *et al.* [49].



44

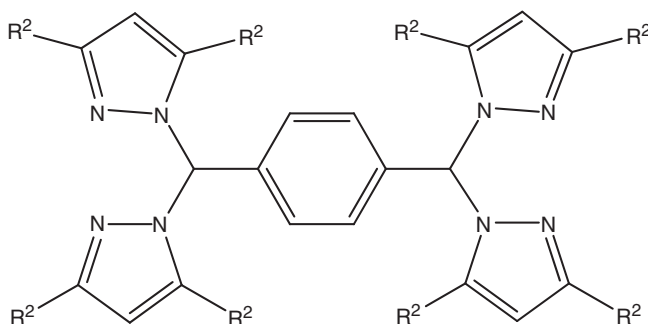
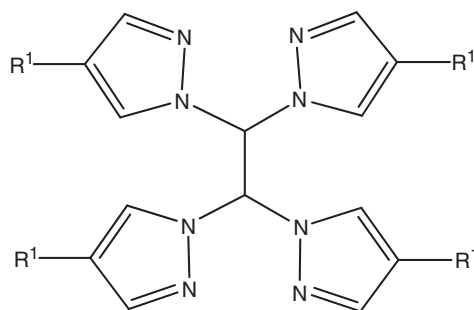
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Some complexes belonging to this group, for instance dinuclear Ru complexes based on the ditopic ligands tppz and tatpp even at high ionic strengths, bind to duplex DNA through intercalation with affinities that are higher than any other monointercalating complex and are only equaled by DNA-threaded bisintercalating complexes [50]. An extensive study on DNA and bipy derivative interactions was reported by Cusumano *et al.* [51]. Reaction of DMeDPQ (**46**) or BDPQ (**47**) with a slight excess of [Pt(bipy)Cl₂] gave the first L-shaped platinum complexes. An excess of py or 2,2'-bipy reacts with [Pt(DMePQ)Cl₂] and [Pt(BDPQ)Cl₂], respectively, forming the corresponding complexes. Finally, platinum dichloride complex derived from dipyrido[3,2-*a*:2'3'-*c*]phenazine (**48**) or benzodipyrido-[*b*:3,2-*h*:2'3'-*g*]phenazine (**49**) reacts with DMeDPQ and BDPQ, respectively, to give six platinum complexes. These complexes show an unusual L-shaped geometry which was supported by X-ray diffraction data. Based on absorption and linear dichroism spectroscopy, intercalation is possible between DNA and platinum complexes when the bidentate ligand is coplanar with the platinum coordination square.



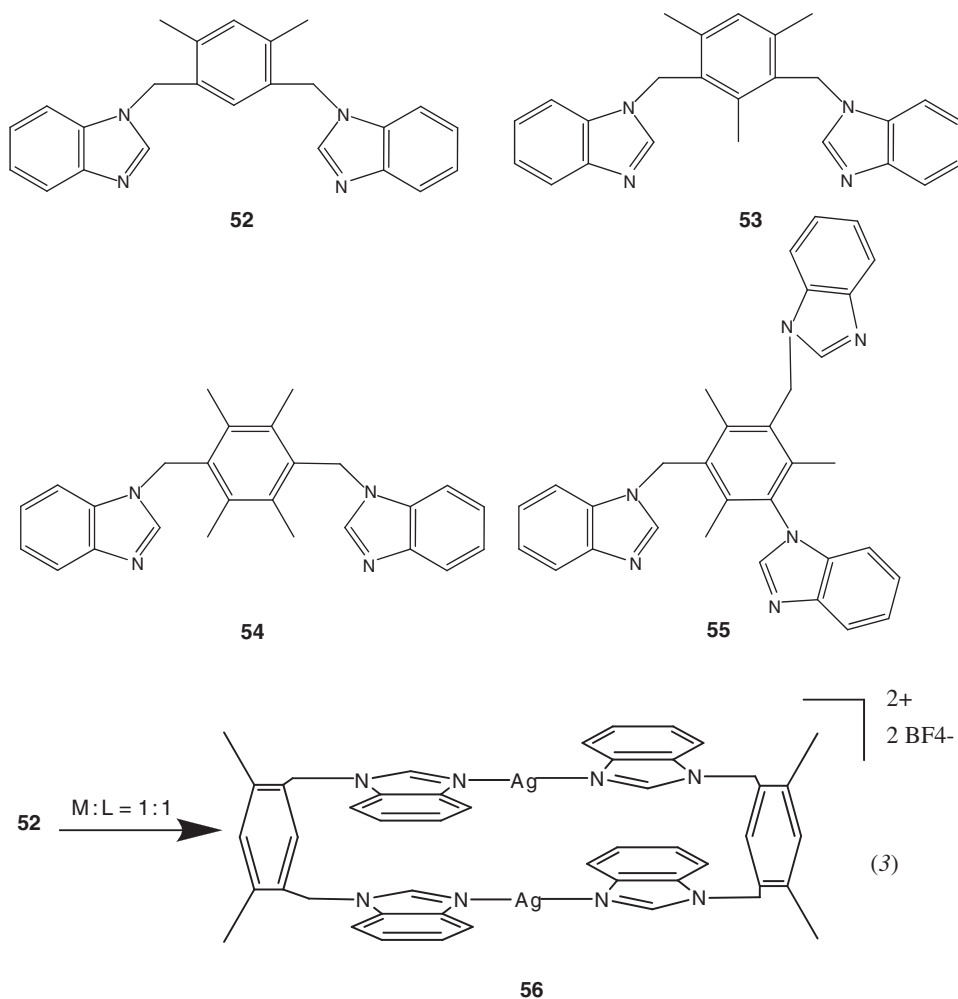
Azoles also are used widely in recently isolated ditopic ligands. Thus, new approaches for pyrazoles were proposed for the synthesis of compounds containing two bis(1H-pyrazol-1-yl)methane fragments. Nucleophilic replacement of bromides from appropriate tetrabromo derivatives by pyrazoles in the basic system KOH-DMSO gave ditopic chelating ligands: 1,1,2,2-tetrakis(1H-pyrazol-1-yl)ethane (**50**, $R^1 = \text{H}$), 1,4-bis[bis(1H-pyrazol-1-yl)methyl]benzene (**27**, $R^2 = \text{H}$), and 1,4-bis[bis(3,5-dimethyl-1H-pyrazol-1-yl)methyl]benzene (**51**, $R^2 = \text{Me}$) [52]. The practical synthesis of ditopic

ligands containing both 1-R-tetrazole and 4-R-1,2,4-triazole moieties linked by an R–R alkyl spacer, $((\text{CH}_2)_n, n = 3, 4)$ was reported as very useful for coordination chemistry. Such ligands are suitable for building multidimensional polynuclear coordination assemblies and for the observation of thermal spin state crossover behavior with iron ions [53]. Reliable strategies were applied for the preparation of binary co-crystals by design of two ditopic ligands, 1,4-bis[(pyrazol-1-yl)methyl]benzene and 1,4-bis[(triazol-1-yl)methyl]benzene [54]. Orthorhombic system (space group *Pbca*) was reported for a pyrazolate-bridged quasi-hexacopper complex $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pyz})_3(\text{pyzH})_3(\mu_3\text{-ClO}_4)_2(\mu\text{-ClO}_4)_2 \cdot (\text{CH}_3\text{OH})_{0.33} \cdot (\text{C}_2\text{H}_5\text{OH})_{0.66} \cdot \text{H}_2\text{O}]$ [55]. For a bis-pyrazole derivative, H_2BPPP , and two d^{10} metal complexes, $[\text{Zn}(\text{H}_2\text{BPPP})\text{Cl}_2](\text{DMF})_2$ and $[\text{Cd}(\text{H}_2\text{BPPP})\text{Cl}_2](\text{DMF})_2$, a tautomeric equilibrium of the bis-pyrazole compound in solution and transfer of the H atom of pyrazolyl NH to the adjacent nitrogen were established [56]. A large series of metal-pyrazoline derivatives, complexes with 5(2'-hydroxyphenyl)-3-(4-X-phenyl)pyrazolines, $\text{M}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2$ [$\text{M} = \text{Cu}, \text{Co}, \text{Ni}, \text{Zn}$; $\text{X} = \text{-H}, \text{-Cl}, \text{-CH}_3, \text{-OCH}_3$], $\text{SbCl}_2(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})$, and $\text{SbCl}(\text{C}_{15}\text{H}_{12}\text{N}_2\text{OX})_2$, as well as some of their addition complexes with 2,2'-bipy, 1,10-phen and tpp, were prepared and square-planar geometry around the metal was suggested with two bidentate pyrazoline ligands. In the case of $\text{M} = \text{Cu}, \text{Zn}, \text{Ni}$, and Co the bidentate and monodentate behaviors of pyrazoline ligands (in addition complexes pyrazoline is monodentate) was confirmed. All complexes were tested for *in vitro* antibacterial and antifungal activities and they exhibit very good antibacterial and antifungal activities; coordination has a pronounced effect on the microbial activities [57–61].



Such classic cyclic N-containing ligands with higher number of nitrogen atoms as triazoles and tetrazoles are also widely represented in the last decade as moieties in ditopic ligands and their complexes, frequently forming unusual structures proved by X-ray single crystal diffraction. Thus, treatment of 2-(1H-1,2,4-triazol-1-yl) acetic acid (Htza) with AgClO_4 resulted in $[\text{Ag}_3(\text{tza})_2(\text{ClO}_4)]_n$. In its crystal structure, resolved by X-ray crystallography, each pair of adjacent Ag atoms, separated at 2.954 Å, is bridged by the bidentate carboxylate [62]. In another silver-triazole complex, $\{\text{K}[\text{Ag}_2\text{L}_2(\mu_3\text{-Cl})(\mu_2\text{-Cl})_2]\}_n$, obtained from 3,5-dimethyl-4-amino-1,2,4-triazole (L) and corresponding Ag and K salts under ammonia solution and hydrothermal conditions, $\mu_3\text{-Cl}$, $\mu_2\text{-Cl}$, and L bridge Ag ions form a rare 1-D $[\text{Ag}_2\text{L}_2(\mu_3\text{-Cl})(\mu_2\text{-Cl})_2]^-$ anion while K^+ cations are located between neighboring anion chains [63]. A 2-D silver complex, $\{[\text{Ag}_4(\mu_4\text{-bte})(\mu_2\text{-H}_2\text{O})_2](\text{SiF}_6)_2\}_n$, prepared from the flexible ligand bte and corresponding silver salts crystallizes in the orthorhombic *Pcca* space group [64]. In addition to Ag complexes with triazole ligands, cobalt-triazole-ferrocene $\{[\text{Co}(\text{btmb})_2(\text{H}_2\text{O})_2] \cdot (\text{Fc}(\text{SO}_3)_2)\}_n$, and cadmium-benzimidazole-ferrocene $\{[\text{Cd}(\text{bbm})(\text{H}_2\text{O})_4] \cdot (p\text{-FcC}_6\text{H}_4\text{SO}_3)_2(\text{CH}_3\text{OH})\}_n$ coordination polymers were synthesized as cocrystals [65]. Among tetrazole compounds, a U mononuclear coordination complex $[\text{UO}_2(\text{a4-ptz})_2 \cdot (\text{H}_2\text{O})_3]$ (a slightly distorted pentagonal bipyramid around each U center) and a Zn 1-D coordination polymer $[\text{Zn}(\text{a4-ptz})_2 \cdot (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (octahedral with four a4-ptz and two water ligands) were described. In the Zn compound, each Zn is linked by carboxylate-O(1) and tetrazolate-N(2) of a4-ptz forming a 1-D polymeric chain. Both complexes are self-assembled to form 3-D supramolecular structures through hydrogen bonds [66]. A monoclinic complex, $\text{Pb}(\text{atz})(\text{phen})_2 \cdot 3\text{H}_2\text{O}$, suggested by the authors as energetic, was explored as an additive to promote thermal decomposition of ammonium perchlorate [67].

For benzimidazoles, two 1-D chain metal-organic polymers, $[\text{Mn}(\text{SCN})_2(\text{pbbm})_2]_n$ and $\{[\text{HgCl}_2(\text{pbbm})] \cdot \text{DMF}\}_n$, were obtained using a flexible building unit pbbm. Considerable difference in their metal-organic frameworks (parallel ribbons of rings for Mn and a 1-D zig-zag chain based on tetrahedral mercury bridged by pbbm and terminally coordinated by two chlorides for the Hg compound) indicates that the flexible pbbm adjusts its conformation to meet the coordination preference of the metal center [68]. Similar polymers, $[\text{PbI}_2(\text{pbbm})]_n$ and $[\text{HgI}_2(\text{pbbm})] \cdot (\text{DMF})_{1/2}\}_n$, were also reported [69]. Three angular ditopic ligands (1,3-bis(benzimidazol-1-ylmethyl)-4,6-dimethylbenzene, (**52**), 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene, (**53**), and 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene, (**54**) and one tripodal ligand (1,3,5-tris(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene, (**55**) were described by Su *et al.* [70]. Reaction of these shape-specific ligands with different metal salts affords discrete molecular architectures: $[\text{Ag}_2\text{L}_2^1](\text{BF}_4)_2$ (**56**) (reaction 3), $[\text{Ag}_2\text{L}_2^2](\text{CF}_3\text{SO}_3)_2$, $[\text{CF}_3\text{SO}_3\text{Ag}_2\text{L}_2^3]\text{CF}_3\text{SO}_3$, among others. Bis{1-ethyl-2-[6-(N,N-diethylcarbamoyl)-4-halopyridin-2-yl]benzimidazol-5-yl}methane (halo = Cl, Br) were synthesized as ditopic receptors for the development of lanthanide-containing helicates [71].

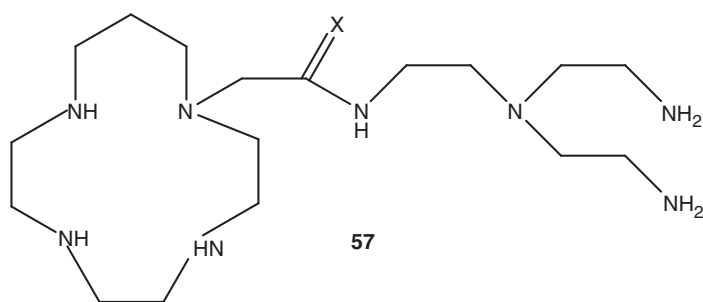


Reaction of 5,6-dihydroxy-1,10-phen with various poly(ethylene)glycol-ditosylates affords ligands in which a phen-binding site is attached to an adjacent crown ether unit. The resulting NN chelating site may be coordinated to $\{\text{Ru}(\text{bipy})_2\}^{2+}$ to afford $[\text{Ru}(\text{bipy})_3]^{2+}$ derivatives with pendant crown ether units, which can bind alkali metal ions [72].

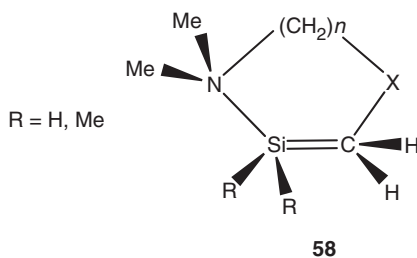
2.3. Amines and azides

The cluster $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_6]^{4-}$, which consists of a Nb_6 octahedron edge bridged by 12 inner chlorides and has six apical chlorides, was isolated and then equipped with ditopic ligands by substitution of all apical chlorides by azides (N_3^-) to form $[\text{Nb}_6\text{Cl}_{12}(\text{N}_3)_6]^{4-}$ in which azides have the ability to act as bridging ligands leading to

the formation extended framework materials [73]. Two heteroditopic ligands (**57**, X = O or 2H) containing the macrocyclic unit cyclam and the open chain ligand tren, as well as the pendant macrocycle 1-(2-methylaminoethyl)-1,4,8,11-tetraazacyclotetradecane, were prepared. Both ligands form mononuclear MLH_n ($n=3, 2, 1, 0$) and dinuclear M_2LH_p ($p=0, -1, -2$) species, and in some cases also dimeric complexes $(ML)_2H_m$ ($m=2, 1, 0$) [74].



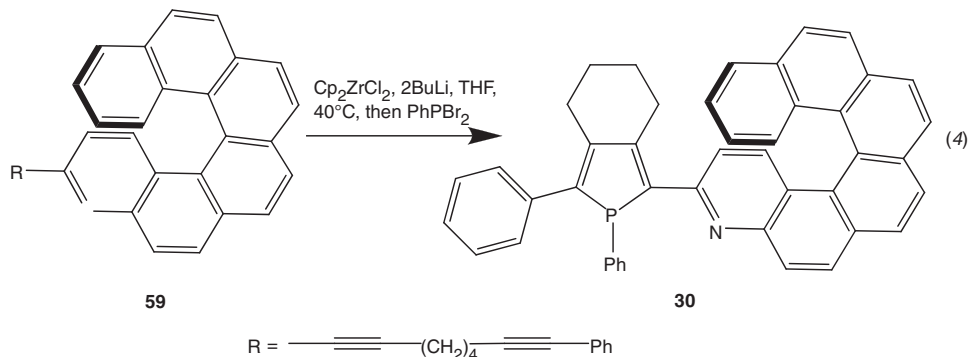
Complexation of ditopic aminoligands $Me_2N(CH_2)_nX$ ($n=0-2$; X = BF_2 , SiF_3) containing both donor and acceptor sites was studied at the MP4/6-311G(d,p)//MP2/6-31G(d,p)+ZPE level of theory to estimate their capability of simultaneously binding to both ends of silenes, $R_2Si=CH_2$ (R = H, Me), to give cyclic complexes **58** [75].



3. P-Containing ditopic ligands

Variety of reported phosphorus-containing ditopic ligands is considerably less (table 3) than those with the N-ligands discussed above. Thus, phosphole-modified aza[6]helicenes (**30**), obtained (reaction 4) from aza[6]helicenes (**59**) (the benzologues of phenanthrene in which the extra ortho-condensed rings give rise to a cylindrical helix) and complexation of these π -conjugated ditopic ligands with metallic ions (Pd, Cu) forming the corresponding complexes were described by Graule *et al.* [76]. It was shown that because of their peculiar properties (ease of inversion at P, polarizable π systems, etc.), phospholes are unique building blocks for the tailoring of azahelicene

derivatives that can be assembled on metal centers.

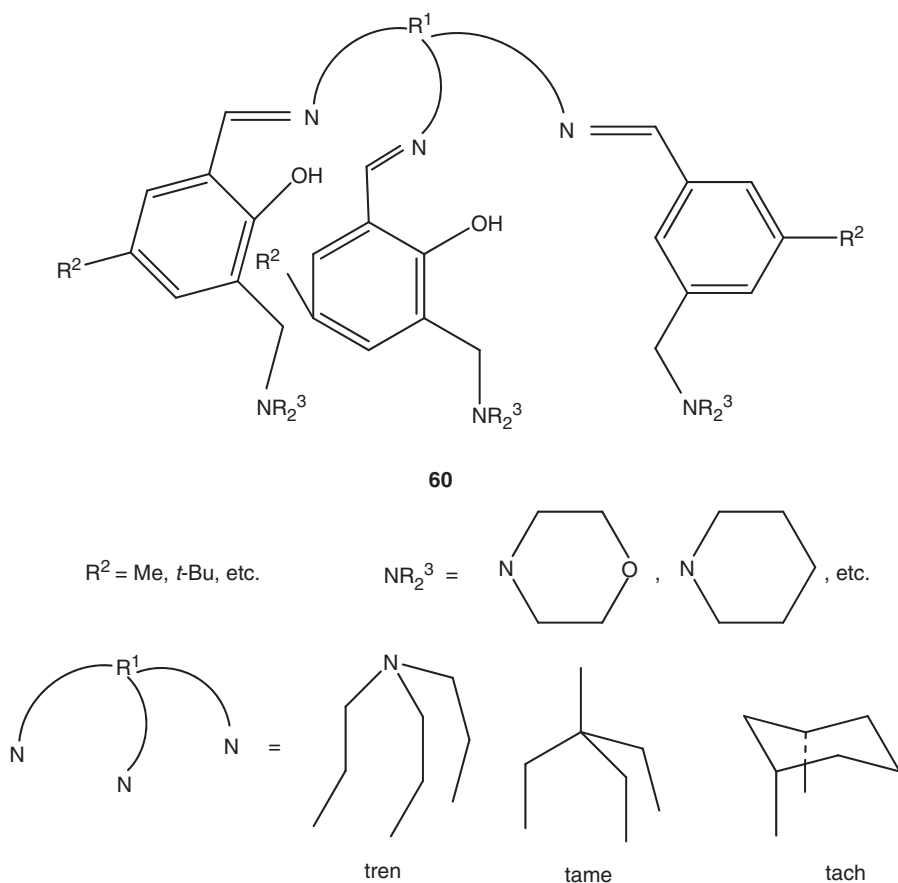


Ditopic ligands comprising an anionic N-O or N-N moiety and a phosphine were shown to assemble with hard and borderline hard-soft metal ions, such as zinc to form bidentate phosphine ligands. This approach led to Rh catalysts for selective hydroformylation of 1-octene with linear-to-branched ratio up to 21:1 and rate comparable to that of covalently bound wide bite-angle diphosphine ligands [77, 78]. Synthesis of a series of phosphine-functionalized macrocycles yielding ligands with combination of N- and O-sites with P- and S-sites is described by Carroy *et al.* [79]. The resulting ligands may bind transition or non-transition metal ions; as a consequence, they give access to dinuclear complexes containing both a Lewis acid and a redox metallic site. Some obtained compounds are heterodinucleating ligands capable of binding two dissimilar metals in proximity. Among a few of other similar P-containing ligands, the new ditopic ligands bis(phosphinito) [$\{2\text{-Ph}_2\text{PO-3,5-(Me}_3\text{C)}_2\text{C}_6\text{H}_2\}_2\text{S}$] and chiral bis(phosphite) [$\{p\text{-}[(\text{C}_{10}\text{H}_6\text{O})_2\text{PO}]\text{C}_6\text{H}_4\}_2\text{CMe}_2$] and their metal complexes with Pd(II), Pt(II), and Cu(I) substrates were studied [80].

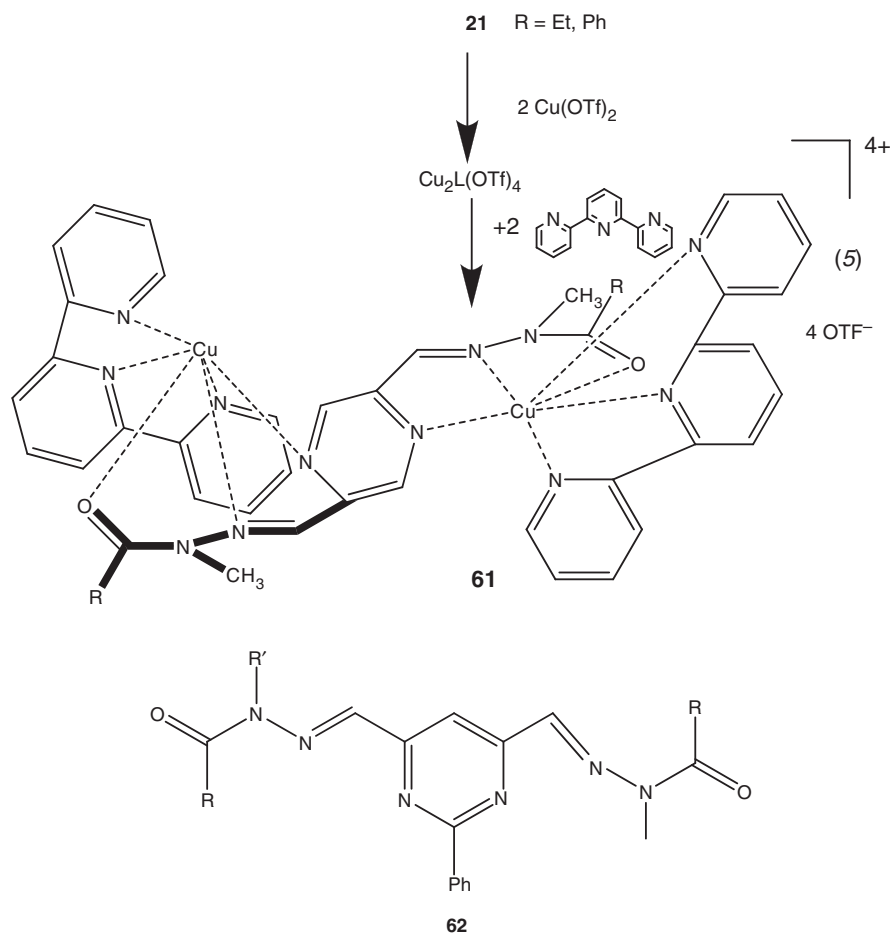
4. O-Containing ditopic ligands

O-containing ditopic ligands and their complexes (table 2) are represented by a considerably lower number of examples in comparison with N-ligands; some ligands are a combination containing simultaneously a nitrogen (O,N-donors), as well as in the case of P-containing ligands described above (P,N-ligands). A number of reports is dedicated to *salen* **22** and related ligands. Thus, reaction of chiral and achiral salen ditopic ligands with sodium in dry *i*-propanol generated remote O,O-dianions. The dianions thus generated *in situ* are trapped by suitable phosphorus dielectrophiles to yield 2-oxo and 2-thioxo-1,3,7-dioxazaphosphadecines and 2-oxo and 2-thioxo-1,3,7,10-dioxadiazaphosphatridecines in moderate to good yield [81]. The pentameric cluster-based (as well as in case of azide-containing ligands, see above) supramolecular units $\{[\text{Mn}(\text{L})]_4[\text{Nb}_6\text{Cl}_{12}(\text{CN})_6]\}$ ($\text{H}_2\text{L} = 7\text{-Me-salen}$) can be extended into 1-D coordination polymers through either formation of Mn dimers or through ditopic ligands [82, 83]. Tetradentate salicylaldimine ligands of the H_2salen -type bearing ortho-N-morpholinomethyl substituents function as ditopic ligands, bonding to Ni or Cu ions

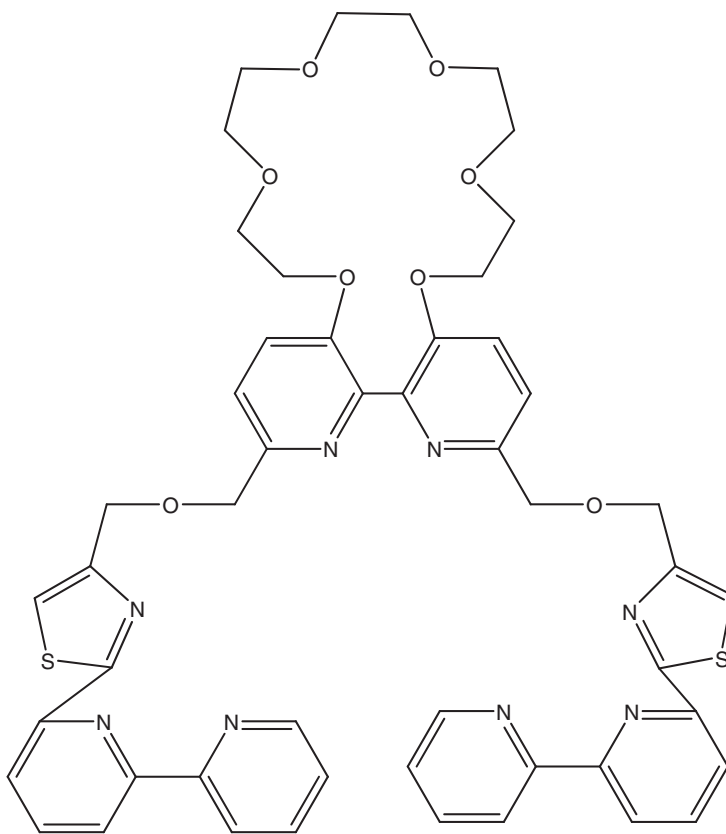
with the $[\text{N}_2\text{O}_2]^{2-}$ donor set of the salen unit and a sulfate or two nitrate anions with the protonated morpholine units [84]. Binding of the metal salt by the zwitterionic form of the ligand provides a novel approach to transport of metal sulfates in metal recovery processes. Hexadentate tris-salicylaldimine ligands (**60**) (derivatives of the ligands tren, tame, and tach) bearing ortho-*N*-dialkylaminomethyl substituents function as ditopic ligands for NiSO_4 or NiCl_2 [85]. Formulation as complexes of the trianionic/tricationic ligand is supported by X-ray structure data of some nickel complexes. Tetradentate salicylaldimine ligands of the H_2 -salen type bearing pendant tertiary amines undergo a zwitterionic transformation when binding metal salts to form overall neutral assemblies which can be transferred into non-polar, water-immiscible solvents [86]. Among other related compounds, two $\text{Fe}(\text{salen})$ complexes, $\text{FeL}^1\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ and FeL^2ClO_4 [$\text{L}^1 = \text{N}, \text{N}'$ -ethylenebis(3-formyl-5-methylsalicylaldimine) and $\text{L}^2 = \text{N}, \text{N}'$ -cyclohexenebis(3-formyl-5-methylsalicylaldimine)], possess catalytic activity for epoxidation of alkenes [87]. The formation constants and free energies for the interaction of R_2SnCl_2 ($\text{R} = \text{Me}, n\text{-Bu}, \text{Ph}$) as acceptors, with nickel Schiff-base complexes ($[\text{NiL}]$, where $\text{L} = \text{salen}$ and a large series of its derivatives in chloroform) have been studied [88]. Preparation of some Co, Cu, Ni, and uranyl Schiff-base complexes from salicylaldehyde, ammonium hydroxide, aliphatic aldehydes, and transition metal salts through one-pot four component reactions was reported by Naeimi *et al.* [89].

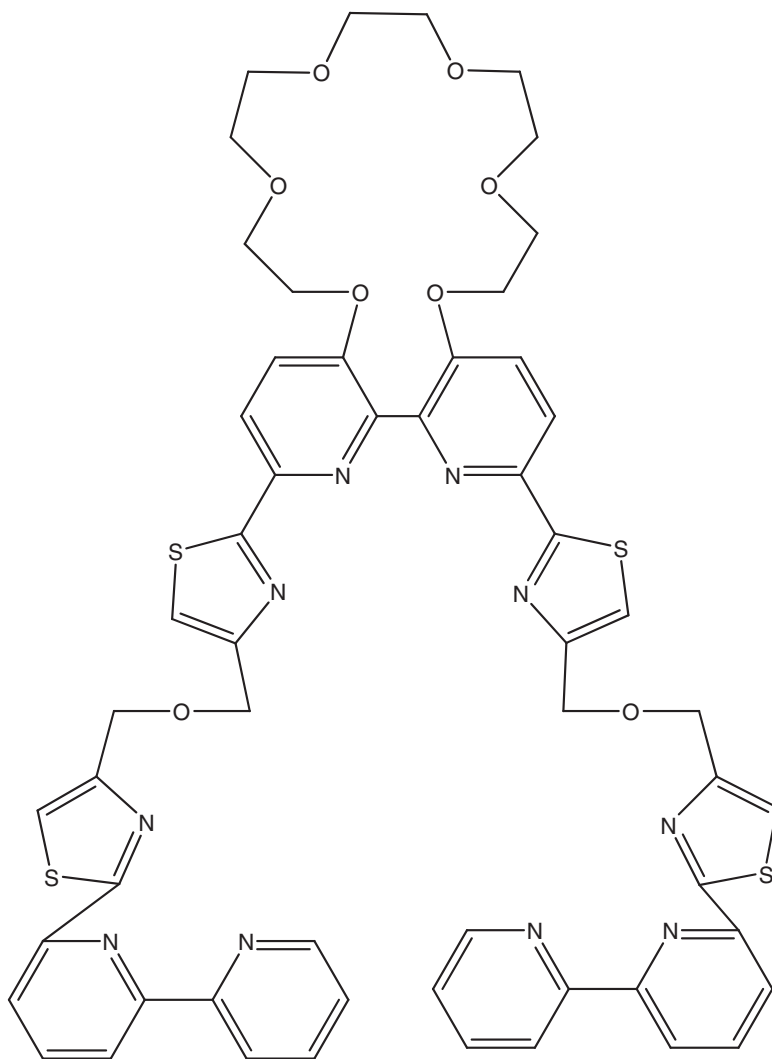


A class of ditopic ligands (**21**) was synthesized by reaction of 2,5-pyrazine-dicarboxaldehyde with two equivalents of acyl-/aryl-hydrazine. They gave heteroleptic Cu(II) dinuclear rack-like complexes (**61**), $[\text{Cu}_2\text{L}(\text{tpy})_2](\text{OTf})_4$ (reaction 5). Magnetic measurements performed on the complexes revealed the presence of antiferromagnetic intramolecular interactions [90]. The ditopic ligands, containing one N_2O_2 or N_3O_2 Schiff base and one O_2O_3 or O_2O_4 crown ether-like chamber, obtained by condensation of the formyl precursors 3,3'-(3-oxapentane-1,5-diylidioxo)bis(2-hydroxybenzaldehyde) or 3,3'-(3,6-dioxaoctane-1,8-diylidioxo)bis(2-hydroxybenzaldehyde) with en or 1,5-diamino-3-azamethylpentane, were designed and used for selective complexation of d and/or s metal ions, respectively, into the Schiff base and the crown ether chamber [91]. Ditopic bis(acylhydrazone) ligands ($\text{LH}_2 = \mathbf{62}$ (the structure similar to **21**); $\text{R} = \text{Me}$, Et, C_7H_{15} , Ph, MeC_6H_4 , CH_3OCH_2 , $\text{MeOCH}_2\text{CH}_2\text{OCH}_2$; $\text{R}' = \text{H}$, Me) derived from reactions of carbohydrazides with 2-phenylpyrimidine-4,6-dicarbaldehyde exhibited a varied coordination chemistry depending upon the degree of deprotonation [92]. Their transition metal (Zn, Cu, Ni, Fe, and Co) complexes containing varying degrees of deprotonation of the bis(acylhydrazone) ligands were isolated and characterized (for instance, $[\text{Ni}_4(\text{LH}_2)_4](\text{ClO}_4)_8$ ($\text{R} = \text{Ph}$, $\text{R}' = \text{H}$), $[\text{Co}_4(\text{LH})_4](\text{BF}_4)_4$ ($\text{R} = \text{Ph}$, $\text{R}' = \text{H}$), $[\text{Zn}(\text{L})_4]$ ($\text{R} = \text{C}_7\text{H}_{15}$, $\text{R}' = \text{H}$)).



A novel class of ditopic ligands (L) built on bis- and tris-phenolic platforms {several bis- and tris-HOPO **24**} that are capable of simultaneously binding an anion and a target metal ion to give neutral complexes (MLX), was reported by Gopalan *et al.* [93]. In these ligands, the HOPO moieties are anchored to the polyphenol platform *via* a carboxamide or sulfonamide linkage. Such ligands should be efficient extractants of the target cation to organic media from aqueous media if the extended ditopic complex is neutral. Dinuclear lanthanide(III) helicates were formed by self-assembly from symmetric and unsymmetric ditopic ligands based on diketonate-(**25**) or 8-hydroxyquinolate-(**26**)-binding sites [94]. Polynuclear complexes can be synthesized, such as homodinuclear *f-f* as well as heterodinuclear *p-f*, and *d-f* complexes. According to the authors, coordination compounds of this type are of interest because of their emitting properties and to investigate energy transfer processes. Crown ethers as classic building blocks in coordination chemistry were also reported in discussions on ditopic ligands. Thus, multidentate ditopic ligands **63** and **64** which contain both N-donor and crown ether units were synthesized. The potentially octadentate ligand L¹ **63** forms a trinuclear heterometallic double helicate with Cu and Zn ions ($[\text{Zn}_2\text{Cu}(\text{L}^1)_2]^{5+}$), whereas **64** forms a tetranuclear heterometallic double helicate with the same metal ions ($[\text{Zn}_2\text{Cu}_2(\text{L}^2)_2]^{6+}$) [95].

**63**

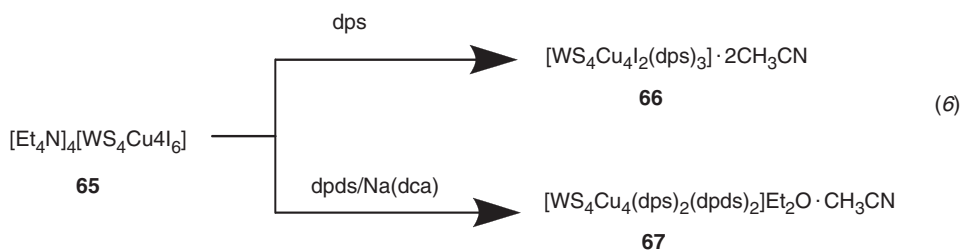


64

Crystalline 2:2 condensation product (“glytham”) of glyoxal **23** and tris(hydroxymethyl)aminomethane was isolated [96] and used as starting material for the synthesis of ditopic ligands for metal ions. Dimeric Ag carboxylates $\text{Ag}_2(\text{CF}_3\text{CO}_2)_2$ permit further elaboration into neutral coordination networks through linkage of the Ag centers *via* ditopic ligands [97], giving $\text{Ag}(\text{O}_2\text{CCF}_3)\text{L}$ [$\text{L} = \text{DABCO}$, tmp or pz]. In each reported compound pairs of silver centers are linked *via* carboxylate bridges and each silver ion is further coordinated by two neutral ditopic ligands that provide linkages to two further silver ions. Starting from easily available Pybox **28** derivatives, chiral ditopic ligands with pendant Lewis basic sites consisting of amine or phosphine oxide functions attached in the 4-positions of the oxazoline 27 rings were isolated [98].

5. S-Containing ditopic ligands

A set of new $[\text{WS}_4\text{Cu}_4]^-$ or $[\text{MoOS}_3\text{Cu}_3]$ -based supramolecular assemblies were obtained from reactions of preformed cluster compounds $[\text{Et}_4\text{N}]_4[\text{WS}_4\text{Cu}_4\text{I}_6]$ (**65**) and $[\text{Bu}_4\text{N}]_2[\text{MoOS}_3\text{Cu}_3\text{X}_3]$ ($\text{X}=\text{I}, \text{SCN}$) with flexible ditopic ligands, such as dps 31, dpds 32, and their combinations with dca anion and 4,4'-bipy. The cluster precursor **65** reacted with dps or dpds and Na-dca in MeCN (reaction 6) to produce $[\text{WS}_4\text{Cu}_4\text{I}_2(\text{dps})_3] \cdot 2\text{MeCN}$ (**66**) and $[\text{WS}_4\text{Cu}_4(\text{dps})_2(\text{dpds})_2]\text{Et}_2\text{O} \cdot 2\text{MeCN}$ (**67**), respectively [99].



Based on thiophene, 10 ditopic ligands containing pyridine, quinoline, or acridine metal-binding domains linked by 2,5-thiophenediyl or poly(2,5-thiophenediyl) spacers were described [100]. Single crystal structures of 2,5-bis(4-pyridyl)thiophene, 2,5-bis(9-acridinyl)thiophene, 5,5'-bis(4-quinolyl)-2,2'-bithiophene, and 5-(9-acridinyl)-5'-(4-pyridyl)-2,2'-bithiophene were determined.

6. Conclusions

The material presented above shows only a small part of a large area in coordination chemistry, focused mainly on derivatives of classic N-, O-, S-, and P-containing ligands and their combinations without examination of macrocyclic structures. During the last decade, the N-containing ligands prevail; a considerable number of N-ligand examples correspond to terpyridine, bipyridine, and azoles. For O-containing ditopic ligands, main attention is paid to various Schiff-base complexes and less to β -diketonates, 8-hydroxyquinolates, and carboxylates. The P- and S-containing ditopic ligands are represented by very few compounds (mainly disulfide, thiophene, phosphine, and phosphole derivatives). Mixed N, O-, N, S-, and N, P-ditopic ligands and their metal complexes have been reported and structurally characterized. PAC and MEPEs have received attention.

For many reported complexes of ditopic ligands, their crystal structures were elucidated by X-ray single crystal diffraction. Some possess useful properties, for instance antimicrobial/antifungal activity and capacity for DNA binding, or those functioning as switches or for selective extractions, exchange or binding cations or anions. Some units in the ditopic ligands have special properties, for example the phospholes are unique building blocks for tailoring azahelicene derivatives that can be assembled on metal centers. The field of ditopic ligands and their complexes is

a dynamically developing part of coordination chemistry promising various practical applications.

Acknowledgements

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