This is the Author's accepted manuscript version of the following contribution:

Massimiliano Arca,* Anna Pintus,* "1,2-Diselenolene Ligands and Related Metal Complexes: Design, Synthesis and Applications", *Coord. Chem. Rev*., **464**, 214444 (2022). ISSN: 00108545

The publisher's version is available at:

http://dx.doi.org/10.1016/j.ccr.2022.214444

When citing, please refer to the published version.

1,2-Diselenolene Ligands and Related Metal Complexes: Design, Synthesis and Applications

Anna Pintus,* Massimiliano Arca*

*Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, S.S. 554 bivio per Sestu, 091042 Monserrato (CA), Italy. * E-mail: apintus@unica.it; marca@unica.it*

ABSTRACT

1,2-Diselenolene metal complexes show a variety of chemical and physical properties, such as redox activity, visible–near-infrared absorption, optical nonlinearity, conductivity, and magnetism, which render them attractive for applications spanning from new generations of devices to catalysis. This review provides an extensive report on the synthetic pathways leading to the different classes of homoleptic and heteroleptic metal complexes featuring 1,2-diselenolene ligands, discussing their structural features, properties, and main applications. A comparison between this class of coordination compounds and their much more widely investigated 1,2-dithiolene isologues illustrates similarities and differences.

Contents

1. Introduction

"Dichalcogenolene" represents a general term to describe unsaturated bidentate chalcogen donor ligands $E^\wedge E^{x-}$ (E = S,[1,2] dithiolene; Se,[3,4] diselenolene; Te,[5,6,7] ditellurolene), whatever the charge x. This general class includes both ene-1,1-[8,9] and ene-1,2-dichalcogenolates[1-7] ($x = 2$) and the corresponding oxidized species ($0 \leq x < 2$). To date, the number of metal complexes featuring 1,1-dichalcogenolene ligands is dramatically lower than that of 1,2-dichalcogenolene metal complexes: the Cambridge Crystallographic Data Centre reports about 200 crystal structures of 1,1-dichalcogenolene complexes and more than 4700 structure of metal complexes featuring at least one 1,2-dichalcogenolene ligand.

The first reports on 1,2-dichalcogenolene ligands date back to the mid-1930s,[10,11,12] but it was not before the early 1960s, with the seminal works by Schrauzer and Mayweg,[13] and by Gray[14] on 1,2-dithiolene complexes (E = S), that the chemistry of these systems started to attract the interest of researchers. Since then, a plethora of different 1,2-dithiolene ligands and their complexes with numerous metal ions have been reported, and the interest towards 1,2-dithiolene metal complexes was further enhanced by the discovery of a large variety of applications, in fields ranging from material chemistry[15,16,17,18,19,20,21,22,23,24,25,26] to biology.[27,28,29,30,31] On the other hand, it was only in 1967 that Davison and Shawl[32] succeeded in synthesizing several 1,2-diselenolene (E = Se) transition metal complexes. 1,2-Diselenolene metal complexes have been studied much less as compared to their fully sulphured congeners, partly due to the lack of general synthetic methods for the ligands and/or their complexes.[33] Tellurium analogues (E = Te) are even more rare and to date only twelve 1,2-ditellurolene metal complexes have been described since the first report in 1986.[6,7,34,35,36,37,38,39,40] Despite this, a significant number of systems containing 1,2-diselenolene ligands were reported over the past 60 years, and, similarly to their sulphured analogues, 1,2-diselenolene metal complexes have been studied for applications involving conductivity,[41,42,43,44,45,46] magnetism,[47,48,49,50,51,52] linear[53] and nonlinear optics,[54] and, more recently, catalysis[55,56] and quantum information science.[57] The properties of 1,2-diselenolene metal complexes have most often being compared to those of 1,2-dithiolene analogues, and for a long time it was thought that the nature of the chalcogen donor atoms did not significantly affect the chemistry of such complexes.[58,59] On the other hand, over the past years, an increasing number of experimental and theoretical reports have indicated that the subtle differences that do indeed exist between 1,2-dithiolene and 1,2-diselenolene ligands can have considerable effects on the chemistry of their complexes, thus allowing for a fine-tuning of their properties. In fact, the substitution of sulphur with selenium affects the eigenvalues of the frontier molecular orbitals of 1,2-dichalcogenolene species, which is reflected in their electrochemical,[58,60,61] linear[62,63,64,] and nonlinear[65,66] optical properties, and leads to an increase in the strength of intermolecular interactions and dimensionality in the solid state, thus affecting their magnetic[49,50,67,68] and conductive behavior.[41,69,70,71] Moreover, it was recently found that these fine differences in their electronic structure also render 1,2-diselenolene complexes better candidates for some of their most promising and recently developed catalytic applications, such as the photocatalytic splitting of water to form hydrogen gas,[55,72,73] electrochemical proton reduction,[74] olefin purification[56,75] or biomimetic oxo-transfer.[76] Based on these findings, a renewed interest on the chemistry of metal 1,2-diselenolene complexes can be expected.

Considering this and given the lack of a comprehensive review specifically dealing with the chemistry of 1,2-diselenolene complexes, this paper attempts to summarize all the work that has been carried

out on these systems over the past six decades. In particular, the first section of this review will deal with 1,2-dichalcogenolene ligands and their precursors, with a particular focus on their long sought-after synthesis. The following section (3.1) will deal with the synthesis and structural features of homoleptic and heteroleptic 1,2-diselenolene metal complexes. The properties and prospects of application of these compounds in such areas as molecular electronics, magnetic molecular materials, and catalysis will be outlined in the final section (3.2) of the review.
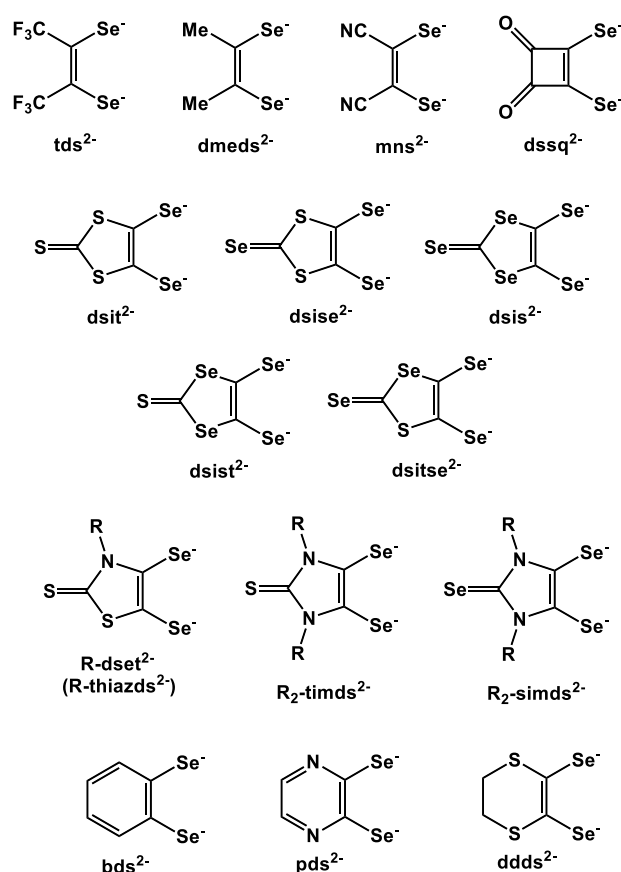
2. 1,2-Diselenolene ligands

1,2-Diselenolene ligands formally derive from 1,2-disubstituted alkene- or arene-1,2-diselenolate dianions or the corresponding oxidized species. 1,2-Diselenolene species show a rich redox chemistry, formally existing as neutral, radical monoanionic, and diamagnetic dianionic species, which can be considered formally derived by deprotonation of disubstituted 1,2-diselenols (Scheme 1). Because of their redox properties, it is often difficult to partition the charge of 1,2-diselenolene metal complexes between the metal ion and the ligands (*non-innocence*), which led to a heated debate in the past.[77]
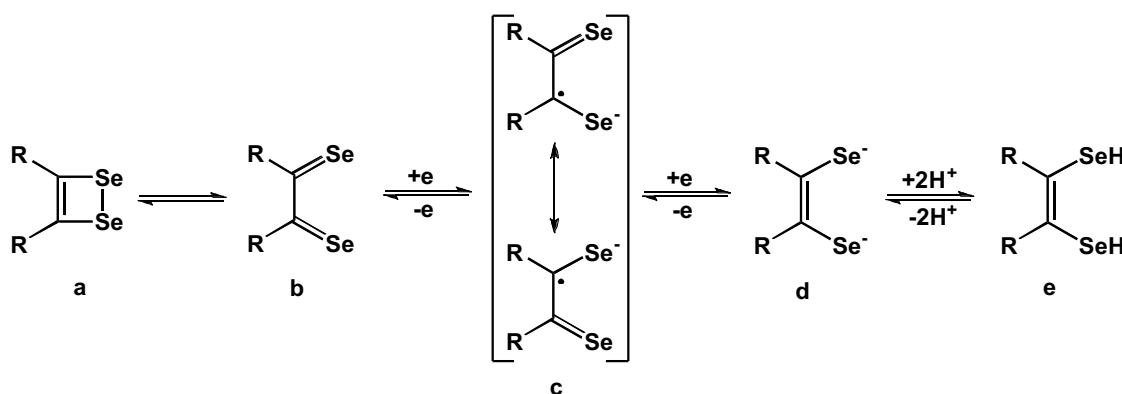
Scheme 1. Equilibria between disubstituted 1,2-diselenolene ligands: 1,2-diselenete (a), 1,2-diselone (b), radical monoanionic (c) and dianionic (d) ene-1,2-diselenolate, and ene-1,2-diselenol (e).

In Scheme 2, a selection of the most common 1,2-diselenolene ligands, represented in their dianionic form, and their commonly used acronyms is reported. These systems can be divided into four main classes, namely: (1) 1,2-disubstituted ene-1,2-diselenolates (such as tds^{2-}, dmeds^{2-}, and mns^{2-}), (2) arene-1,2-diselenolates (bds^{2-} and derivatives), (3) 1,3-dichalcogenole-2-chalcogenone-4,5-diselenolates (dsit^{2-} and isologues),[78] and (4) larger cyclic 1,2-diselenolene ligands such as ddds^{2-}.

F_3C Se⁻ / F_3C Se⁻ **tds²⁻**   Me Se⁻ / Me Se⁻ **dmeds²⁻**   NC Se⁻ / NC Se⁻ **mns²⁻**   O / O Se⁻ Se⁻ **dssq²⁻**

dsit²⁻   **dsise²⁻**   **dsis²⁻**

dsist²⁻   **dsitse²⁻**

R-dset²⁻
(R-thiazds²⁻)   **R₂-timds²⁻**   **R₂-simds²⁻**

bds²⁻   **pds²⁻**   **ddds²⁻**

Scheme 2. Selected 1,2-diselenolene ligands and commonly used acronyms. All ligands have been drawn in their 1,2-diselenolate form.

It is worth mentioning that the well-known 1,2-dicarba-*closo*-dodecarborane-1,2-diselenolato systems, extensively studied by the groups of Jin,[79,80,81,82,83,84,85,86,87,88,89,90,91,92,93,94,95,96,97,98,99,100,101,102,103,104,105,106,107] Herberhold and Wrackmeyer,[108,109,110,111,112,113,114,115,116,117,118,119] and Yan[120,121,122,123,124,125,126] also formally fall in the definition of 1,2-diselenolene ligands. This notwithstanding, the forcedly long C–C distances renders these compounds different from typical 1,2-diselenolene derivatives, and hence their description is beyond the scope of the present paper. The reader is referred to reviews already existing on this topic.[127,128,129,130,131,132,133]

As mentioned in the introduction, 1,2-diselenolene species are more rarely encountered as compared to their sulphured analogues, largely because of the lack of generally applicable synthetic methods for the ligands and/or their complexes, which has hampered the development of the research on these systems especially until the late 1980s. This was mainly due to unpleasant odor of the starting materials, the extreme conditions needed for the synthesis, and/or the low stability of the ligands towards oxidation.[134]

6

Only in few cases 1,2-diselenolates were reported in stable salts. Most often, 1,2-diselenolates and the corresponding oxidized species are not stable species, and they are generated from protected forms of the ligands (proligands) belonging to a variety of classes. The deprotection of proligands is typically achieved in the presence of a transition metal source (see Section 3.1), thus directly providing the corresponding 1,2-diselenolene metal complex. Therefore, in the following and in Schemes 3–14 the ligand synthesis preludes to the reaction with a suitable metal salt or complex, unless differently stated.

The first reports on 1,2-diselenolene metal complexes date back to the late 1960s, when Davison and Shawl[3,32] reported on the synthesis of several compounds containing the 1,2-*bis*(trifluoromethyl)ethane-1,2-diselenolate ligands (tds^{2-}, Scheme 2), obtained starting from *bis*(trifluoromethyl)-1,2-diselenete (route i in Scheme 3). The main difficulty with this procedure rested in the preparation of the latter heterocycle, which was synthesized by the reaction of hexafluorobut-2-yne with refluxing selenium (b.p. 685 °C!).[135] The crude product was formed as an impure red oil containing foul-smelling organoselenium contaminants, and the procedure was limited to the preparation of compounds bearing electron-withdrawing functional groups that could endure the drastic conditions involved. As a consequence, tds^{2-} remained the only 1,2-diselenolene ligand for about fifteen years, until in 1982 Bolinger and Rauchfuss achieved the *in situ* synthesis of 1,2-diselenolene mixed-ligand complexes via the addition of selenium to activated alkynes,[136] thus developing an alternative route to tds^{2-} and introducing the 1,2-*bis*(carboxymethyl)-ethylene-1,2-diselenolate (Se$_2$C$_2$COOMe^{2-}) ligand (i in Scheme 4). This route was subsequently revised and extended to different ene-1,2-diselenolato ligands (routes ii-iv in Scheme 4).[137,138,139,140,141,142,143,35,144,145,146,147,33] A further synthetic path to tds^{2-} was introduced by Wudl and coworkers in 1985,[148] involving the synthesis of a stable 1,3-diselenolene-2-selone precursor by reaction of DMAD (dimethyl acetylenedicarboxylate) with 1,3-diselenolane-2-selone[149] (ii in Scheme 3). The same authors[150] also developed the *in situ* preparation of different ene-1,2-diselenolato ligands starting from the corresponding iminiumdithiocarbonate precursors[151,152,153] (iii in Scheme 3). The unsubstituted member of the series (ethylene-1,2-diselenolate) was obtained by two cycles of lithiation and subsequent selenation of (*Z*)-1,2-*bis*(trimethylstannyl)ethane, prepared in turn by reacting acetylene with hexamethylditin (HMDT; route iv in Scheme 3).[38] The *cis*-1,2-dicyanoethene-1,2-diselenolato ligand (mns^{2-}, selenated analogue of mnt^{2-}, one of the most commonly reported 1,2-dithiolene ligands) was synthesized for the first time in 1996 by Almeida and coworkers[154] through the nucleophilic ring opening of 4,5-dicyano-1,3-diselenole-3-one (route v in Scheme 3).[155] The synthesis of the latter precursor[156] involves several steps as well as the use of CSe$_2$ and dicyanoacetylene, both being difficult reagents to synthesize and handle.[157] An alternative route was

developed by Ibers a few years later, leading to the *in situ* synthesis of mns^{2-} starting from CH_3CN and elemental selenium.[157] Despite this, very few examples of complexes featuring the mns^{2-} ligand have been reported in the literature to date.[158,159,160]
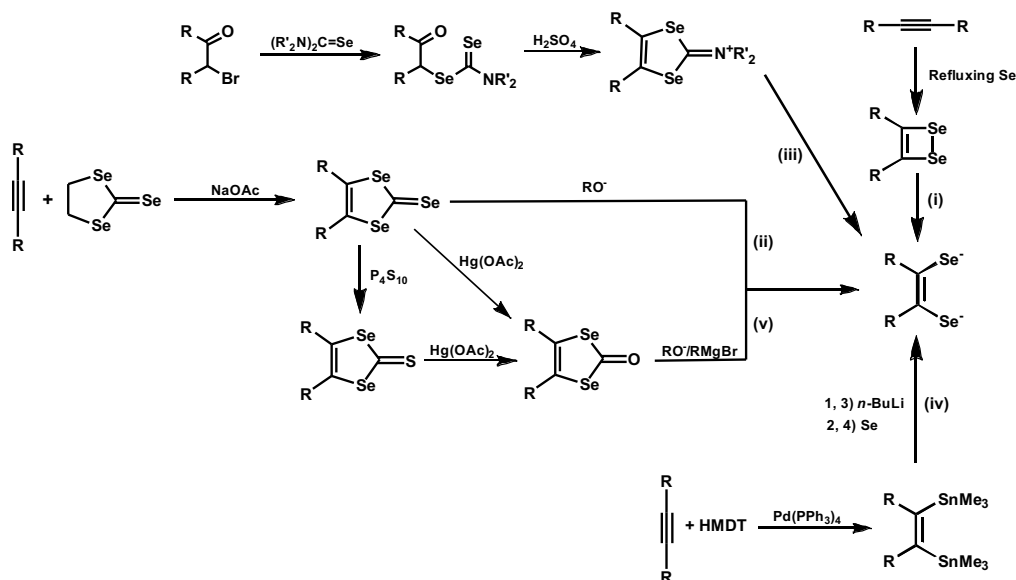
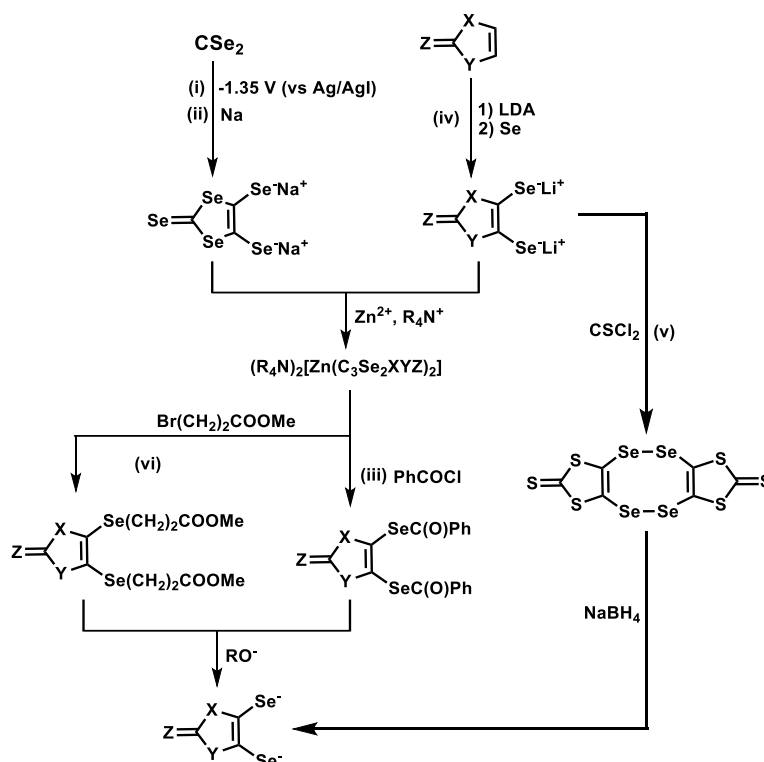**Scheme 3**. Strategies for the synthesis of ene-1,2-diselenolato ligands.
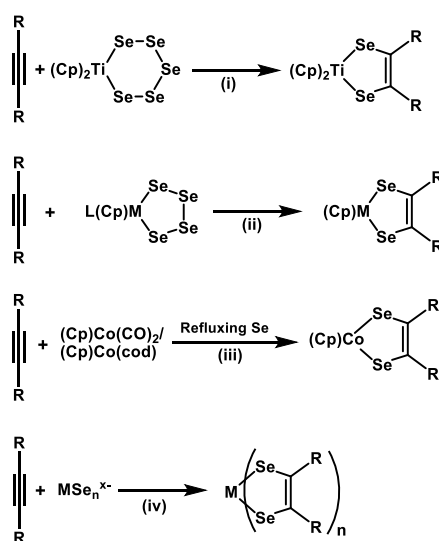
Scheme 4. Strategies for the *in situ* synthesis of ene-1,2-diselenolato ligands from acetylene derivatives.

The *in situ* synthesis of the ethenetetraselenolate bridging group starting from [(triphos)RhCl(η^2-CSe$_2$)] was also reported,[161,162] and the bonding properties of this ligand were studied by means of DFT calculations [triphos = 1,1,1-*tris*(diphenylphosphinomethyl)ethane].[163]

The first reports on the synthesis of the other two most common classes of 1,2-diselenolene ligands, namely arene-1,2-diselenolates and 1,3-dichalcogenole-2-chalcogenone-4,5-dithiolates, also date

back to the early 1980s. In 1982, Papavassiliou[164,165] first reported on the synthesis of the dsis^{2-} ligand through the chemical or electrochemical reduction of CSe$_2$ (routes i and ii in Scheme 5). This synthetic route was further developed by Matsubayashi[166] and Hoyer,[167,168] who also managed to obtain the same ligand in a stable form through the reaction of the corresponding Zn complexes with benzoylchloride, leading to 4,5-benzoylseleno-1,3-diselenole-2-selone (route iii in Scheme 5). A few years later, Nigrey[169,170] achieved the replacement with selenium of the exocyclic sulfur of vinylene trithiocarbonate (1,3-dithiole-2-thione)[171] by lithiation followed by reaction with elemental selenium, thus obtaining the dsit^{2-} ligand (Scheme 2; route iv in Scheme 5). This ligand could also be obtained in a stable, protected form from the corresponding zinc complex (to give the benzoyl-substituted system),[172,173,174] or through reaction with thiophosgene to give the corresponding 1,2,5,6-tetraselenocin (route v in Scheme 5).[175] The same synthetic route was extended to different 1,3-dichalcogenole-2-chalcogenones by Hoyer[176,177,178] and Poleschner[179] in the 1990s, thus providing an alternative route to the dsis^{2-} ligand, and extending the family of analogues of the latter compound with the introduction of dsise^{2-} and dsitse^{2-} (Scheme 2).

Scheme 5. Strategies for the synthesis of the dsit^{2-} ligand and its analogues and derivatives (X, Y, Z = chalcogen atom).

By the same synthetic route, extended 1,2-diselenolene ligands featuring tetrathiafulvalene moieties could also be prepared (route i in Scheme 6).[180] The latter were also obtained[69] from precursors such as *bis*(2'-cyanoethylseleno)-diethylthiotetrathiafulvalene (route ii in Scheme 6).[69,181]

9
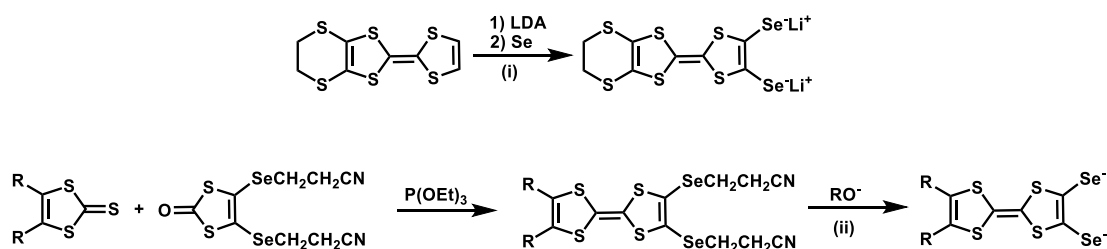
Scheme 6. Strategies for the synthesis of 1,2-diselenolene ligands featuring the tetrathiafulvalene moiety.

4,5-*Bis*(2-methoxycarbonylethylthioseleno)-1,3-diselenole-2-chalcogenones were reported as a further class of precursors for the dsis^{2-} and dsist^{2-} ligands (Scheme 2; route vi in Scheme 5).[182,183]

The reaction of *N*-substituted 1,3-thiazole with lithium diisopropylamide (LDA) followed by selenium was exploited to prepare zinc, nickel and palladium complexes of the R-thiazds^{2-} ligands (N-substituted 1,3-thiazoline-2-thione-4,5-diselenolate, route i in Scheme 7). By reacting the alkylammonium salts of [Zn(R-thiazds)$_2$]$^{2-}$ complexes with Br(CH$_2$)$_2$CN the corresponding *N*-substituted 4,5-*bis*(2'-cyanoethylseleno)-1,3-thiazol-2-thiones were obtained, thus affording stable precursors for these ligands (route ii in Scheme 7; R = Me, Et).[184] The direct synthesis of the latter precursors from *N*-substituted 1,3-thiazole was also developed (route iii in Scheme 7),[185,186] and extended to the 2-one analogues (route iv in Scheme 7).[41] A further series of related ligands (namely Me$_2$-timds^{2-} and Me$_2$-simds^{2-}, Scheme 2) were recently obtained *in situ* through a similar pathway, involving the lithiation followed by selenation of the *N,N'*-disubstituted-2-chalcogenoxoimidazole precursors (route v in Scheme 7).[187]
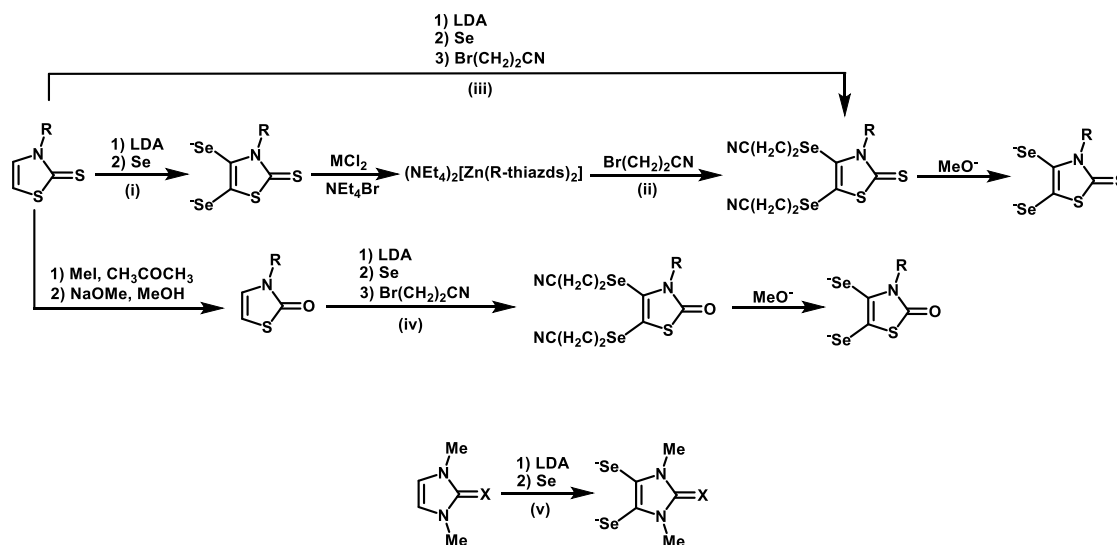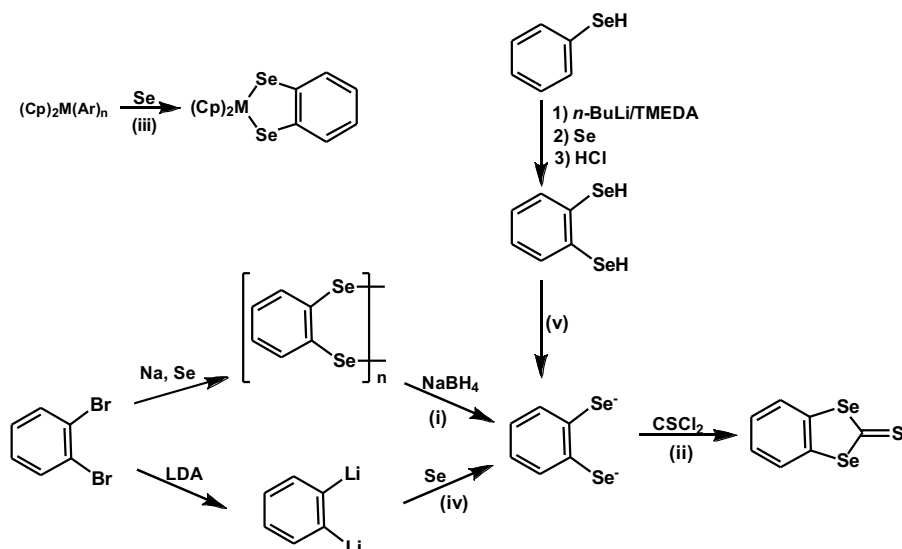

Scheme 7. Strategies for the synthesis of N-substituted 1,3-thiazoline-2-thione-4,5-diselenolate R-thiazds^{2-} (R = Me, Et; route i–iii), the corresponding N-substituted 1,3-thiazoline-2-one-4,5-diselenolate (route iv), Me$_2$-timds^{2-}, and Me$_2$-simds^{2-} ligands (X = S, Se; route v).

It is worth mentioning that the reaction with Br(CH$_2$)$_2$CN was also employed on (Et$_4$N)$_2$[Zn(dsit)$_2$] to obtain the corresponding 4,5-*bis*(2'-cyanoethylseleno)-1,3-dithiol-2-thione;[188] the latter was subsequently reacted with Hg(OAc)$_2$ to form its 2-one derivative, whose hydrolysis with potassium methoxide allowed for the *in situ* formation of 1,2-selenoethene-1,2-dithiol, the only tetradentate mixed 1,2-dithiolene/1,2-diselenolene anion known to date (Scheme 8).[189]
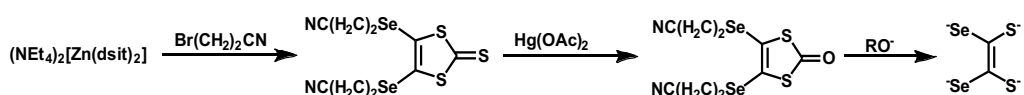

Scheme 8. Synthesis of 1,2-selenoethene-1,2-dithiol.

In 1983, Sandman and coworkers[190] prepared poly-*o*-phenylenediselenide by reacting 1,2-dibromobenzene with Na$_2$Se in DMF; the reduction of this stable precursor with NaBH$_4$ led to the formation of the bds^{2-} anion (Scheme 2; route i in Scheme 9) that can be subsequently protected by conversion to 4,5-benzo-1,3-diselenole-2-thione by using thiophosgene (route ii in Scheme 9).[191,192] In the same year, Gautheron and coworkers[193] developed alternative routes for the *in situ* formation of the bds^{2-} anion and some variously substituted derivatives by treating the corresponding diarylmetallocenes with elemental selenium (route iii in Scheme 9).[194,39,195,196] In 1986 Köpf[197] reported the use of dilithium benzene-1,2-diselenolate[198,199] as a starting material for the preparation of 1,2-diselenolene metal complexes, in analogy to what previously described for dsit^{2-} and its analogues (route iv in Scheme 9). More recently, 1,2-benzenediselonol[200] was also used as a source for the preparation of 1,2-diselenolene ligands (route v in Scheme 9).[201]

Scheme 9. Strategies for the synthesis of benzene-1,2-diselenolate (bds^{2-}).

The synthesis of variously substituted benzene-1,2-diselenolato ligands was also achieved by a sequence of bromination, selenation, trimethylsilyl protection, *ortho* lithiation, and further selenation of *para*-disubstituted benzene derivatives (route i in Scheme 10).[202,203,204,205,206,207] Substituted derivatives of bds^{2-} were also obtained starting from the corresponding benzotriselenoles,[208] after conversion to the *bis*(cyanoethylseleno)-derivatives (route ii in Scheme 10)[209] or the 1,2-diselenete form (route iii in Scheme 10).[210,211]
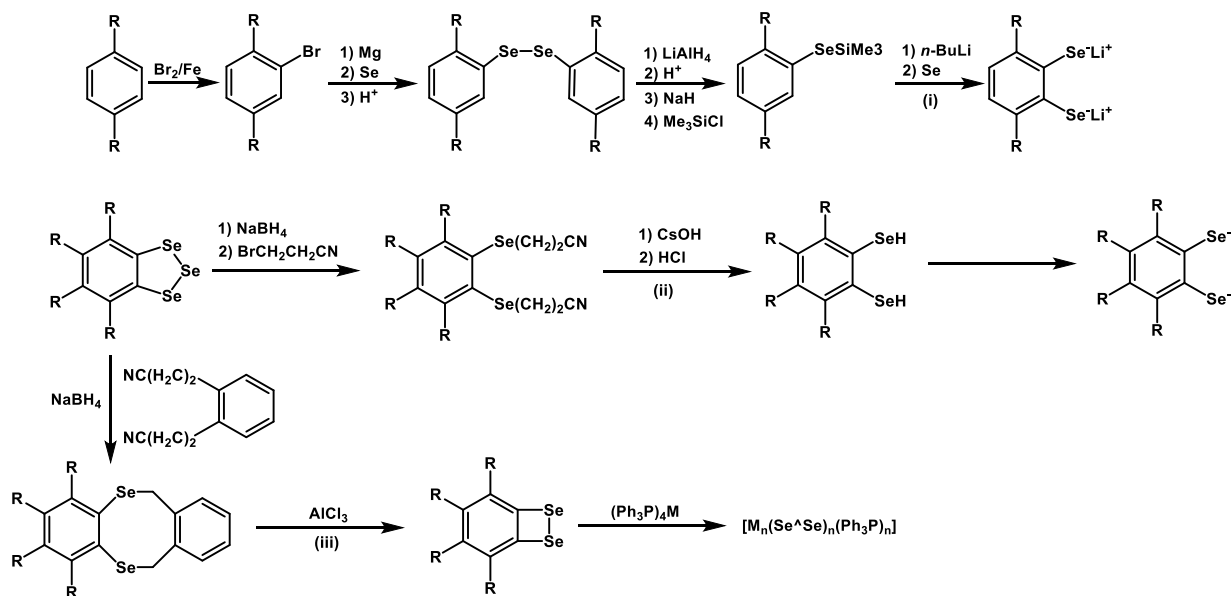
Scheme 10. Strategies for the synthesis of substituted 1,2-arenediselenolato ligands (R = H, Br, Et, OMe, iPr, CN).

Recently, the synthesis of tetradentate ligands featuring two 1,2-diselenolene donor groups (1,2,4,5-benzenetetraselenolate)[73,212] from a selenoacetate precursor was also reported (i in Scheme 11), while

the preparation of the hexadentate benzenehexaselenolate was achieved through an intermediate diselenaborole (route ii in Scheme 11).[213,214] The latter synthetic approach was extended to 1,2,4,5-benzenetetraselenolate and 2,3,6,7,10,11-triphenylenehexa(selenolate).[213]
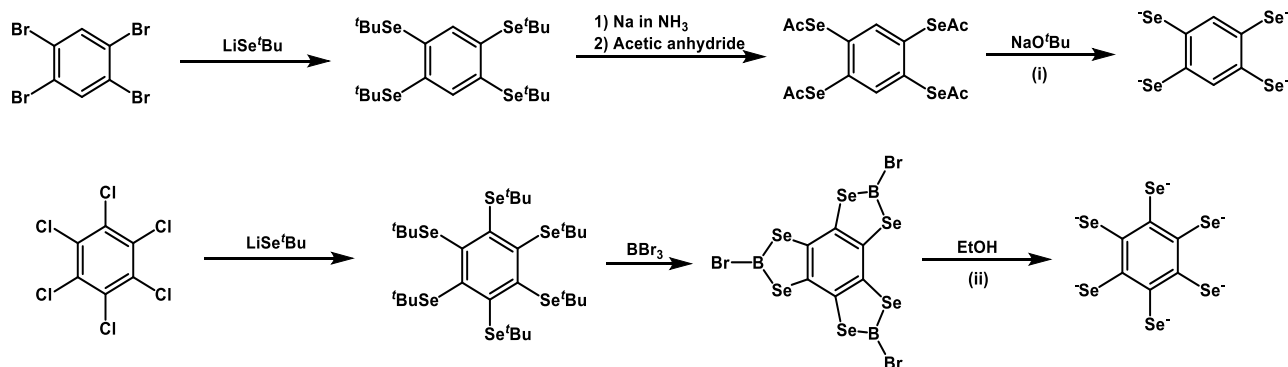
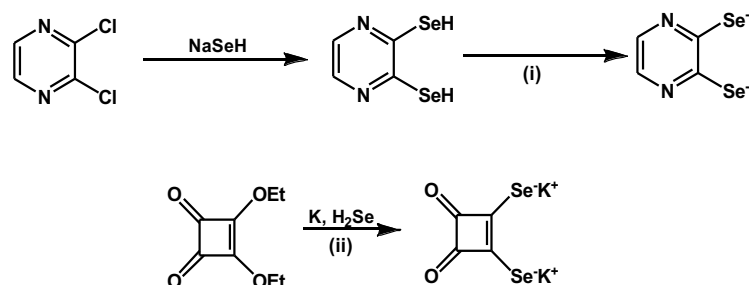**Scheme 11**. Strategies for the synthesis of benzene-1,2,4,5-tetraselenolate (i) and benzenehexaselenolate (ii) ligands.

Pyrazine-2,3-diselenolato ligand (pds^{2-}, Scheme 2) was first obtained by Papavassiliou[215] and coworkers in 1987 by reacting 2,3-dichloropyrazine with NaSeH (route i in Scheme 12), while 1,2-diselenosquarate (dssq^{2-}; Scheme 2) was isolated in 1998 as a potassium salt, obtained by the reaction of 1,2-diethoxysquarate with H$_2$Se (route ii in Scheme 12).[216,217]

Scheme 12. Strategies for the synthesis of pds^{2-} (top) and dssq^{2-} (bottom).

In 1991, the lithiation/selenation synthetic pathway discussed above was extended by Kato[218] and coworkers to 5,6-dihydro-1,4-dithiin-2,3-diselenolate (ddds^{2-}, Scheme 2; route i in Scheme 13), the first example of a cyclic 1,2-diselenolene ligand.[155,219,220] Also for this ligand, a protected 1,3-diselenole-3-one or 3-thione form could be prepared, obtained in this case from the corresponding titanocene complexes (route ii in Scheme 13).

13
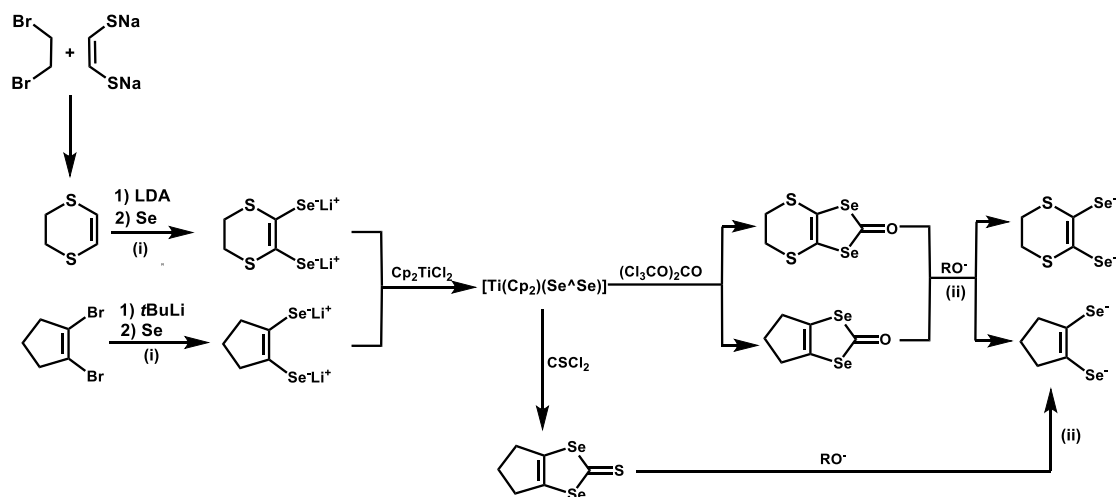
Scheme 13. Strategies for the synthesis of ddds^{2-} and other cyclic 1,2-diselenolene ligands.

Starting from 1988, Morley[221] reported on the use of 1,2,3-selenadiazoles[222,223,224] as proligands for the *in situ* synthesis of various cyclic 1,2-diselenolene ligands (route i in Scheme 14).[225] These could also be obtained in a protected form as 1,2-diselenins (route ii in Scheme 14).[226,227,228,229,230] The same route was also extended to ene-1,2-diselenolato ligands.[135,231,232]
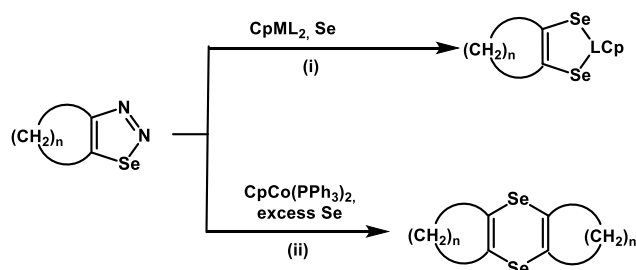
Scheme 14. Synthesis of cyclic 1,2-diselenolene ligands from 1,2,3-selenadiazoles.

3. 1,2-Diselenolene metal complexes

1,2-Diselenolene complexes can be categorized into four main categories: (1) *bis* or *tris* homoleptic metal complexes [M(Se^Se)$_n$], featuring two ($n = 2$) or three ($n = 3$) identical 1,2-diselenolene ligands (Se^Se); (2) *bis*(1,2-dichalcogenolene) heteroleptic metal complexes [M(Se^Se)(S^S)], featuring a 1,2-diselenolene (Se^Se) and a 1,2-dithiolene (S^S) ligand; (3) mixed-ligand heteroleptic complexes [M(Se^Se)$_m$(L)$_n$], featuring m 1,2-diselenolene ligands in combination with n ligands of different nature (L), such as diimines or phosphines (m, $n \geq 1$); (4) mixed-ligand 1,2-diselenolene

organometallic complexes, that incorporate a 1,2-diselenolene ligand along with cyclopentadienyl (Cp) systems, CO, or different classes of C-bonded organic ligands (Scheme 15).
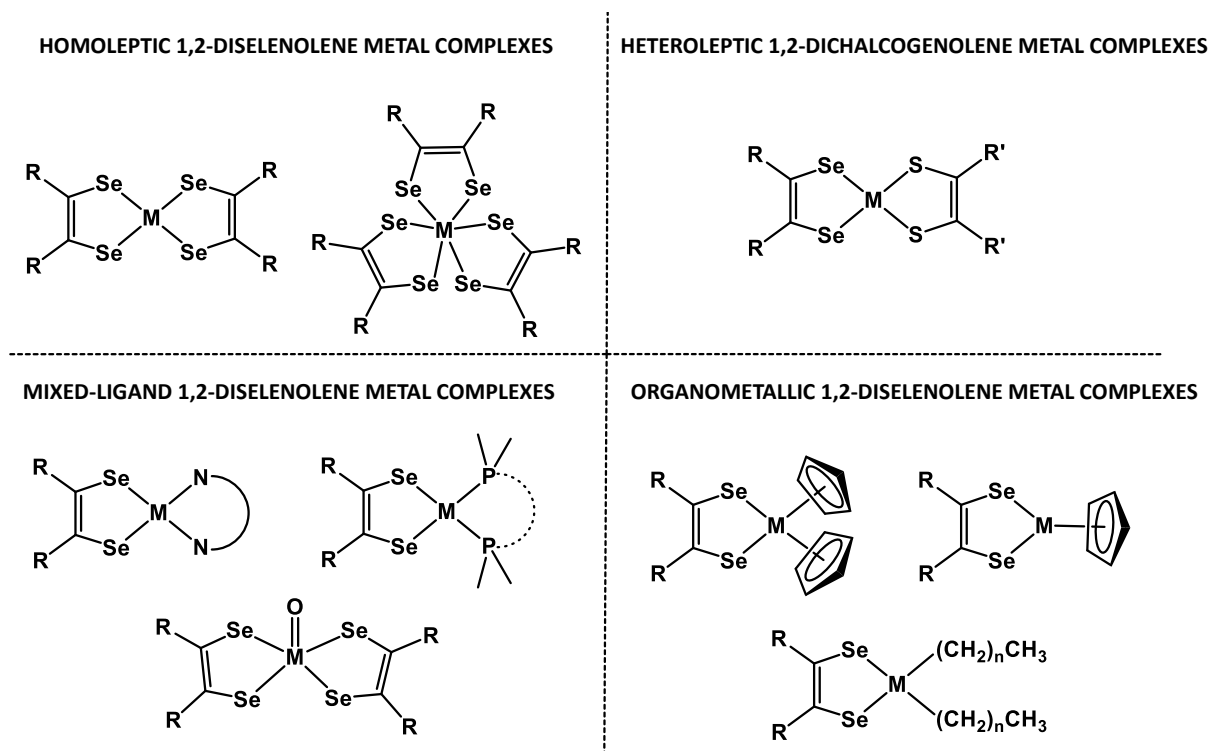
Scheme 15. Different types of homoleptic and heteroleptic 1,2-diselenolene metal complexes. 1,2-Diselenolene ligands are depicted in their 1,2-diselenolate form.

3.1. Synthesis and structural features

3.1.1. Homoleptic 1,2-diselenolene metal complexes

Homoleptic 1,2-diselenolene complexes include *bis* and *tris*(1,2-dichalcogenolene) complexes (Figure 1), and only a few examples of dinuclear complexes[233] or clusters.[159,234,235]

Figure 1. Distribution and frequency of homoleptic *bis* and *tris*(1,2-diselenolene) metal complexes (in gray and orange, respectively).

In homoleptic *bis*(1,2-diselenolene) metal complexes, the *noninnocent* nature of the ligands makes it difficult to assign clearly separated formal charges 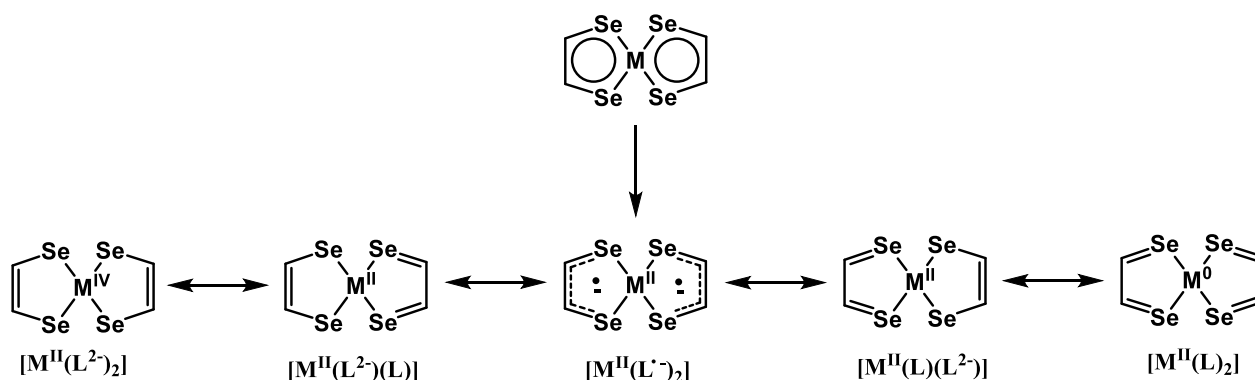to the metal and to the ligands, as illustrated in Scheme 16 for neutral square-planar *bis*(1,2-diselenolene) complexes of d^8 metal ions. The formal oxidation state of the central metal atom varies between 0, II, and IV, depending on the resonance form assigned to the ligand.

Scheme 16. Structures and formal oxidation state of the central metal in neutral *bis*(1,2-diselenolene) complexes of d^8 metal ions.

Moreover, *bis*(1,2-diselenolene) metal complexes have the ability to carry different molecular charges, typically ranging between –2 and 0, reversibly accessible by chemical and electrochemical means. These features have rendered the understanding of the electronic structure of *bis*(1,2-dichalcogenolene) complexes a challenging task, and the object of a heated debate, and in the past many efforts were made to elucidate this issue by means of different experimental techniques, including magnetic measurements (see section 3.2.4) and ^{77}Se-NMR spectroscopy.[236,237]

In particular, an intensely discussed question is whether 1,2-dichalcogenolene ligands can exist as a neutral dichalcogenoketone (L), radical monoanion (L$^{•-}$), or dianionic dichalcogenolate (L^{2-}) in the corresponding metal complexes. For the description of neutral *bis*(1,2-dithiolene) complexes of group 10 metal ions, two models have mainly been proposed, resulting in an oxidation state of II for the metal: a singlet diradical ground state [M^{II}(L$^{•-}$)$_2$] (open shell) featuring two radical monoanionic ligands whose spins are antiferromagnetically coupled; and a singlet closed shell ground state based on the two resonance hybrid structures [M^{II}(L^{2-})(L)] and [M^{II}(L)(L^{2-})] (Scheme 16). Recent DFT calculations performed by different researchers,[238,239] often associated with experimental studies,[240,241,242,243] clearly indicate a degree of singlet diradical character for the investigated systems, whose amount depends on the nature of the ligand and the central metal ion, and suggest that the singlet diradical character is smaller for 1,2-diselenolenes than for 1,2-dithiolenes.[65,66,244]

Homoleptic *bis*(1,2-diselenolene) complexes have been obtained for transition metals such as Co, Fe, Ni, Cu, Zn, for the first row; Pd, Ag, and Cd, for the second row; and Pt, Au, and Hg for the third row. In addition, *bis*(1,2-diselenolene) complexes with *p*-block elements such as Pb, Sb, and Ge have also been reported. The much fewer homoleptic *tris*(1,2-diselenolene) complexes reported feature group 3 and 4 metal ions (namely V, Mo, and W),[57,70,141,245] but examples featuring Pt[233] or *p*-block metals such as In[134] and Sn[246] also exist. Most commonly *bis* and *tris*(1,2-diselenolene) complexes are reported as anionic species, counterbalanced by a large variety of organic and inorganic cations. These include cryptand complex cations such as [K([2.2.2]-cryptand)][+],[158,157,159] and several cationic metal complexes, such as [M(Cp*)$_2$][+] (M = Fe, Mn, Cr; Cp* = pentamethylcyclopentadienyl),[47,247,248,249] [Ni(DMF)$_6$][2+] (DMF = dimethylformamide),[43] or spin-crossover salts of the type [Fe(L)$_2$][2+] [L = bpp = 2,6-*bis*(pyrazol-3-yl)pyridine;[48,70,250] qsal = N-(8-quinolyl)salicylaldimine].[251]

As compared to their sul

phured analogues and as highlighted in the previous section, very few 1,2-diselenolene ligands exist as stable salts (as in the case of K$_2$dssq)[217,216] or as the corresponding 1,2-diselenoles (H$_2$pds, H$_2$bds),[57,200,252,253,44,254,255,233] capable of yielding the corresponding homoleptic *bis* or *tris*(1,2-diselenolene) complexes when reacted with metal halides,[57,216,217,253,44,254,233] such as NiCl$_2$, Ni(ClO$_4$)$_2$[254], PtCl$_2$, K$_2$PtCl$_4$, K$_2$PdCl$_4$, CuCl$_2$, Cu(ClO$_4$)$_2$,[252,255] or different metal salts such as ZnSO$_4$, Cd(CH$_3$COO)$_2$,[217] VO(acac)$_2$, or Ti(NMe$_2$)$_4$,[57] (route i in Scheme 17). The synthesis of homoleptic *bis* and *tris*(1,2-diselenolene) complexes thus exploits stable proligands, including the vinylene di- or tri-chalcogenocarbonates[68,256,154,148,192,258] described above and iminiumdiselenocarbonates,[148] which are prone to hydrolysis in alkaline media, yielding the corresponding complexes in the presence of suitable metal salts. As mentioned above, [M(dsit)][2−] complexes were first synthesized through the chemical or electrochemical reduction of CSe$_2$ followed by addition of the appropriate metal chloride,[166,167,164] while ligands such as dsit[2−] and its isologues[174] and derivatives,[180] R-thiazds[2−], or R$_2$-timds[2−] and R$_2$-simds[2−] could be obtained both by selenation of the corresponding heterocyclic precursors in the presence of the metal (route ii in Scheme 17),[169,172,170,182,175,179,60,62,49,176] or starting from the *in situ* generated ligands from protected precursors (route iii in Scheme 17)[134,168,175,257,183,173,258,259,260,261,262,70,69,60,41,178,45,186] On the other hand, *bis*(trifluoromethyl)-1,2-diselenete and poly-*o*-phenylenediselenide[32,3,263] were used as precursors of homoleptic 1,2-diselenolene complexes featuring the bds[2−] and tds[2−] ligand, respectively; the former precursor could be reacted directly with the desired metal salt (often a metal carbonyl or a mixed salt; route iv in Scheme 17), while in the case of the latter, a reductive ring opening was induced by reaction with NaBH$_4$ before addition of the metal salt (route v in Scheme 17).[191] As mentioned above, the reactions of electrophilic alkynes such as DMAD with metal per- and poly-selenido complexes was also

exploited for the synthesis of homoleptic 1,2-diselenolene complexes (route vi in Scheme 17). For example, the reaction of $[WSe_9]^{2-}$ or $[WSe_4]^{2-}$ with DMAD afforded $[W(Se_2C_2COOMe_2)_3]^{2-}$,[141] while the reaction of DMAD with $(PPh_4)_2[Pd(Se_4)_2]$ led to the isolation of $[Pd(Se_2C_2COOMe_2)_2]^{2-}$.[144] On the other hand, homoleptic complexes featuring the mns^{2-} ligand were obtained both by the direct reaction of KNH_2, K_2Se, Se and a metal source in acetonitrile,[157,160] and starting from a heteroleptic *mono*(1,2-diselenolene) complex (route vii in Scheme 17).[159,158] The same approach allowed for the preparation of several *bis*(1,2-diselenolene) germanium complexes featuring bds^{2-} and variously substituted derivatives, starting from the corresponding diselenophenylene zirconocene and $GeCl_4$.[196,264,265] Finally, homoleptic *bis*(1,2-diselenolene) complexes were also obtained by means of metal exchange reactions (route viii in Scheme 17).[71,246,258,266]
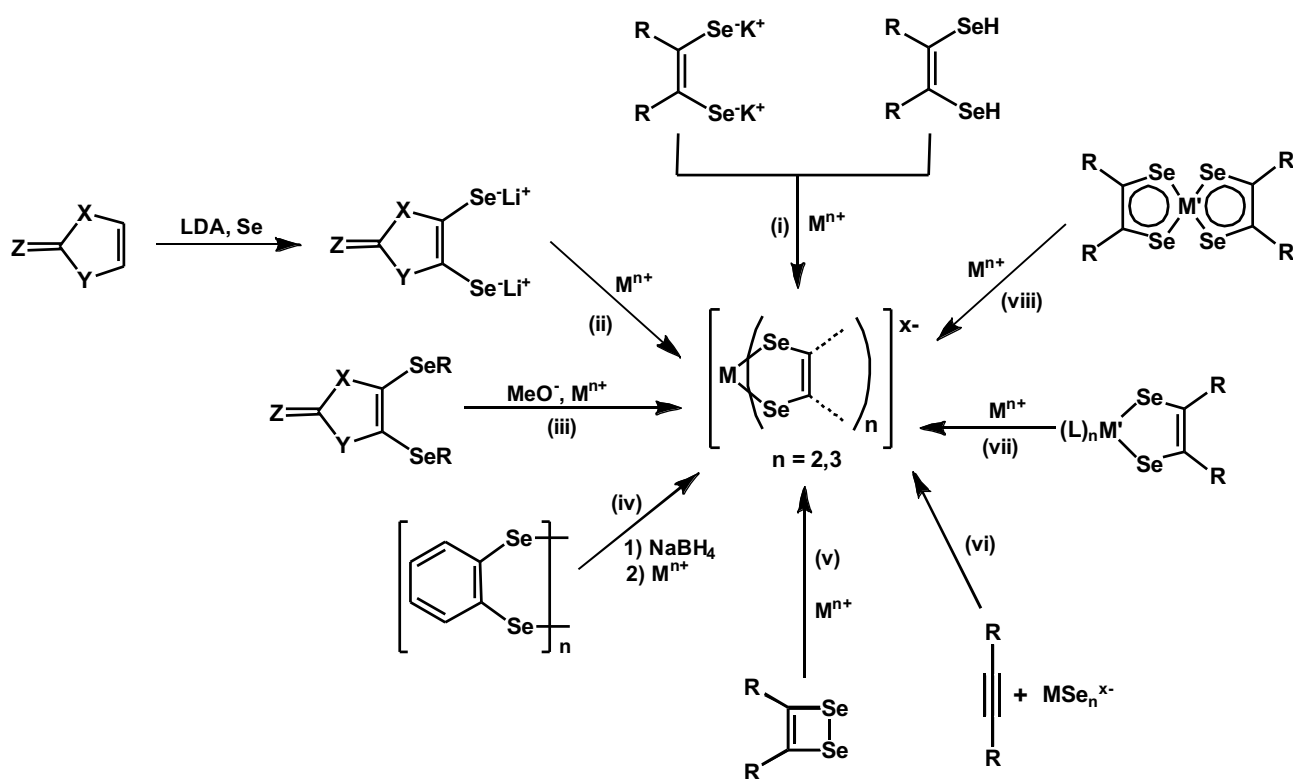
Scheme 17. Strategies for the synthesis of homoleptic *bis* and *tris*(1,2-diselenolene) metal complexes.

Whatever the synthetic procedure adopted, the isolated homoleptic *bis* or *tris*(1,2-diselenolene) complexes undergo oxidation to higher oxidation states by reaction with diiodine,[69,70,262] NaI/I$_2$ 1:1 mixture,[262] CH_3COOH/O_2,[170,262] H_2O_2,[148] $FeCp_2PF_6$,[60,276] $FeCp*_2BF_4$,[70,276] TCNQ (7,7,8,8-tetracyanoquinodimethane),[262] and $(TTF)_3[BF_4]_2$ (TTF = tetrathiafulvalene),[70,276] or reduction by hydrazine,[3,263] $SnCl_2$,[263] acetone,[3,267] or sodium amalgam.[3]

The first report on the structure of a homoleptic *tris*(1,2-diselenolene) metal complex dates back to 1971, when Eisenberg reported the crystal structure of $[Mo(tds)_3]$ (Figure 2).[245] Since then, just four

more crystal structures of coordination compounds featuring *tris*(1,2-diselenolene) complexes, namely $(AsPh_4)_2[W(Se_2C_2(COOCH_3)_2)_3]\cdot C_7H_8\cdot\frac{1}{2}DMF$,[141] $(PPh_4)_2[Ti(bds)_3]$, $(PPh_4)_2[V(bds)_3]$,[57] and $Na_2[Pt(pds)_3]\cdot 6H_2O$ (where the central metal ion features an authentic IV oxidation state)[233] have been reported (Table 1).

Table 1. Selected average bond distances (Å) and angles (°) for homoleptic *tris*(1,2-diselenolene) metal complexes.

CCDC Code	Complex	M–Se	Se–C	C–C	Se–M–Se	M–Se–C	Se–C–C	ϕ^a	η^b	Ref.
QIMXAO	$[Ti(bds)_3]^{2-}$	2.541	1.907	1.400	83.71	106.49	121.29	82.32	5.96	57
QIMXIW	$[V(bds)_3]^{2-}$	2.489	1.904	1.397	84.35	106.95	120.63	56.61	6.08	57
TFMESM	$[Mo(tds)_3]$	2.491	1.871	1.379	83.42	105.16	121.16	90.00	18.50	245
JAPSUO	$[W(Se_2C_2(COOCH_3)_2)_3]^{2-}$	2.500	1.882	1.337	81.77	107.85	120.93	82.32	3.74	141
PAFKEN	$[Pt(pds)_3]^{2-}$	2.463	1.902	1.397	90.06	101.29	123.24	56.61	3.67	233

[a] Average dihedral angle between the SeMSe and SeSeSe planes (see text). [a] Average bend angle between the SeMSe and SeCCSe planes of each 1,2-diselenolene ligand (see text).

In order to determine the coordination geometry of *tris*(1,2-diselenolene) complexes, the average dihedral angle (ϕ) between the SeMSe plane (passing through the metal ion and two Se atoms of one of the ligands) and the SeSeSe plane (passing through Se atoms belonging to the three different ligands) can be used (Figure 2).[268]

The ϕ angle can be in fact used as a direct measure of a structural tendency toward trigonal-prismatic ($\phi = 90°$) or octahedral ($\phi \sim 55°$) coordination geometry. The analysis of ϕ shows that three of the *tris*(1,2-diselenolene) complexes structurally characterized, namely $[Mo(tds)_3]$,[245] $[Ti(bds)_3]^{2-}$,[57] and $[W(Se_2C_2(COOCH_3)_2)_3]^{2-}$,[141] feature a trigonal prismatic geometry (slightly distorted in the case of the latter two), while in $[Pt(pds)_3]^{2-}$ and $[V(bds)_3]^{2-}$,[57, 233] the central metal ion displays a distorted octahedral coordination environment, thus testifying the possibility of observing both possible coordination geometries in these hexacoordinated systems. The average bend angle (η) between the coordination plane SeMSe and the ligand plane SeCCSe of a chelate is $< 7°$ in all structures but in that determined for $[Mo(tds)_3]$,[245] showing a high degree of planarity of the ligands in these compounds. Average M–Se, C–Se and C–C distances show small variations of 0.078 (2.463–2.541 Å), 0.036 (1.871–1.907 Å), and 0.063 Å (1.337–1.400 Å), respectively, thus suggesting that, in the case of *tris*(1,2-diselenolene) complexes, average bond lengths are not very sensitive to overall molecular charge, the nature of the transition metal or that of the 1,2-diselenolene ligand, in agreement with what previously observed for 1,2-dithiolene metal complexes.[268]
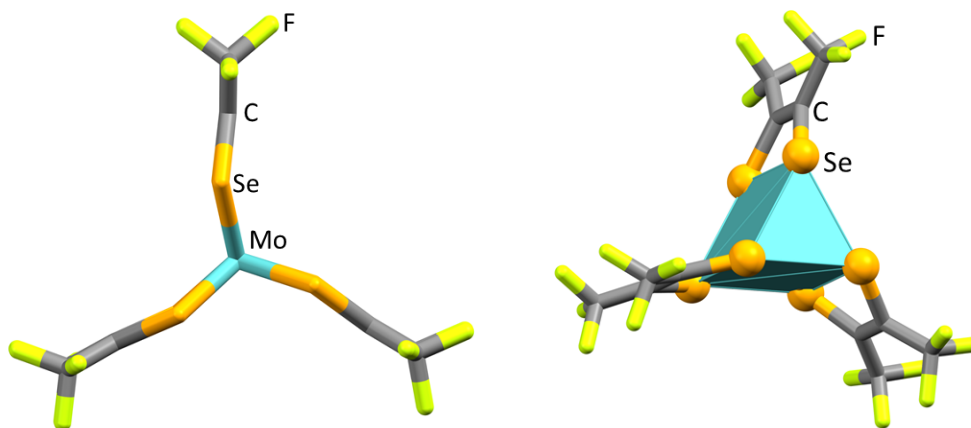
Figure 2. Capped stick (left) and polyhedral (right) representation of $[Mo(tds)_3]$ (CCDC code TFMESM, ref. 245) showing its characteristic "pin-wheel"-like appearance due to the partial bending of the three 1,2-diselenolene ligands (η = 18.50°), and the perfect trigonal prismatic coordination around the central molybdenum ion (ϕ = 90.00°).

The first structural reports on *bis*(1,2-diselenolene) complexes, namely TBA[Ni(bds)$_2$],[192,269] [Fe(C$_5$Me$_5$)$_2$][Ni(bds)$_2$]· CH$_3$CN,[52] (TMTSF)$_2$[Ni(tds)$_2$],[270] (PPh$_4$)[Pt(tds)$_2$],[263] and (TBA)$_n$[Ni(dsit)$_2$][173] (n = 1, 2; TMTSF = tetramethyltetraselenafulvalene) were published in the late 1980s. To date, 69 crystal structures of (1,2-diselenolene) metal complexes have been deposited at the Cambridge Crystallographic Data Center, featuring 39 different *bis*(1,2-diselenolene) complexes (Table 2). The vast majority of the reported structures feature the dsit^{2-} ligand and its analogues (dsit^{2-} : 5 structures; dsis^{2-}: 4 structures; dsise^{2-}: 3 structures; dsiste^{2-}: 1 structure), or the pds^{2-} (16 structures), bds^{2-} (6 structures), tds^{2-} (9 structures), mns^{2-} (8 structures), ddds^{2-} (7 structures), and dssq^{2-} (3 structures) ligands. As for the metal, almost half of the reports (30 structures) feature a nickel metal ion, and among the remaining structures most contain a group 10 (M = Pd: 4 structures; M = Pt: 5 structures), 11 (M = Ag: 1 structure; M = Cu: 11 structures; M = Au: 10 structures), or 12 (M = Zn: 5 structures) metal ion. Exceptions include (PPh$_4$)[Co(bds)$_2$][55] and the main-group metal complexes [Ge(bds)$_2$][265] and [K([2.2.2]cyptand)]$_3$[Sb(mns)$_2$]· 2CH$_3$CN.[157] In 64 out of the total 69 structures, the metal complex carries a negative charge. Two compounds featuring the mns^{2-} ligand, namely [K([2.2.2]cryptand)]$_3$[Sb(mns)$_2$]· 2CH$_3$CN and its silver analogue,[159] carry a –3 molecular charge. The number of neutral *bis*(1,2-diselenolene) metal complexes structurally characterized so far is limited to the germanium complex mentioned above, the gold complex [Au(Et-thiazds)$_2$] and its analogue featuring an *N*-ethyl-1,3-thiazoline-2-one-4,5-diselenolate ligand,[41] and the dimeric system [Ni(ddds)$_2$]$_2$.[68] The structures of two compounds featuring complexes with non-integer oxidation states, namely (Me$_4$N)[Pd(dsit)$_2$]$_2$[271] and (Me$_4$N)[Ni(dsise)$_2$]$_2$,[262] were also reported.

Table 2. Selected average bond distances (Å) and angles (°) for homoleptic *bis*(1,2-diselenolene) metal complexes.

CCDC code	Complex	M–Se	Se–C	C–C	Se–M–Se	M–Se–C	Se–C–C	λ[a]	η[b]	Ref.
CAFZOZ	[Ni(tds)$_2$]$^-$	2.248	1.870	1.366	92.18	103.84	120.06	0.02	0.80	247
COHREX		2.245	1.842	1.353	92.33	103.02	120.80	0.00	1.34	47
COHROH		2.245	1.869	1.342	92.05	103.61	120.36	0.02	0.93	47
FUXKOY		2.255	1.874	1.354	92.42	103.28	120.48	0.00	1.02	270
FUXKOY01		2.262	1.853	1.426	93.22	103.19	120.11	1.58	1.94	270
TODDAR	[Ni(mns)$_2$]$^-$	2.286	1.875	1.357	92.79	102.10	121.38	0.00	4.96	154
WAQVEP	[Ni(mns)$_2$]$^{2-}$	2.292	1.874	1.349	93.17	101.32	121.90	0.00	5.85	158
OBETUK		2.289	1.888	1.342	93.00	101.59	121.60	0.00	7.68	160
JIMCOY	[Ni(dsit)$_2$]$_2^{2-}$	2.331	1.871	1.376	92.62	100.77	122.14	22.93	10.49	249
WACNOD		2.329	1.882	1.342	92.94	100.10	122.71	27.55	8.59	272
WACNOD01		2.333	1.885	1.332	92.33	99.80	122.66	24.57	14.17	272
JEVDAP	[Ni(dsis)$_2$]$^-$	2.276	1.865	1.325	93.24	101.27	122.11	3.79	0.60	45
VOZRIL	[Ni(dsise)$_2$]$^-$	2.277	1.880	1.359	94.34	101.05	121.78	0.02	0.00	259
VOZREH	[Ni(dsise)$_2$]$^{2-}$	2.305	1.883	1.363	93.48	101.11	121.95	0.00	5.90	259
PIKVUA	[Ni(dsise)$_2$]$_2^-$	2.330	1.877	1.338	92.60	99.80	122.73	19.71	19.71	262
DESBOS10	[Ni(bds)$_2$]$^-$	2.259	1.891	1.354	92.66	103.24	120.32	3.82	1.79	192
QIMXUI		2.296	1.897	1.396	91.36	104.34	119.84	0.00	4.96	Pr. Com.
JECDOK		2.266	1.890	1.383	92.79	103.42	120.15	0.03	2.36	52
NUSXIK	[Ni(L)$_2$]$^{-c}$	2.277	1.867	1.363	93.48	101.64	121.54	0.00	3.78	69
IZORUK	[Ni(pds)$_2$]$^{2-}$	2.290	1.879	1.417	91.85	104.14	119.90	0.00	2.60	254
IZOSAR		2.300	1.895	1.411	92.27	103.51	119.99	0.00	3.37	254
IZOSEV	[Ni(pds)$_2$]$^-$	2.317	1.888	1.399	91.17	102.44	120.36	22.14	14.30	254
RAMQAX	[Ni(dssq)$_2$]$^{2-}$	2.341	1.845	1.395	95.03	98.57	123.90	0.00	1.73	217
RONSIW	[Ni(ddds)$_2$]$^-$	2.267	1.873	1.367	92.22	103.04	120.48	15.65	7.52	256
RONSIW01		2.247	1.877	1.302	91.92	103.05	120.89	0.02	2.11	273
RONSIW02		2.267	1.873	1.367	92.22	103.04	120.48	15.65	7.52	68
SUHQOB		2.267	1.885	1.351	92.22	102.68	120.56	0.02	11.02	68
SUHQUH		2.272	1.887	1.347	91.70	103.51	120.45	0.04	5.31	68
SUHWIB	[Ni(ddds)$_2$]$_2$	2.302	1.877	1.376	91.09	102.81	120.59	21.31	13.71	68
SUHWIB01		2.300	1.877	1.361	91.10	102.52	120.82	20.86	14.18	68
OBEVAS	[Pd(mns)$_2$]$^{2-}$	2.402	1.871	1.366	91.61	100.33	123.73	0.03	4.63	160
SUVBAM	[Pd(C$_2$Se$_2$COOMe$_2$)$_2$]$^{2-}$	2.403	1.894	1.347	90.03	101.69	122.79	0.03	9.55	144
LEHPAP	[Pd(dsit)$_2$]$_2^-$	2.409	1.865	1.363	90.96	100.71	123.74	6.99	2.59	271
FODGEK	[Pd(dssq)$_2$]$^{2-}$	2.444	1.844	1.387	93.66	96.98	126.19	0.00	0.20	216
CAFZUF	[Pt(tds)$_2$]$^-$	2.361	1.877	1.358	90.00	103.11	121.88	0.02	1.17	247
COHRIB		2.364	1.878	1.355	90.09	102.89	122.06	0.00	0.45	47
COHRUN		2.363	1.897	1.308	90.03	102.38	122.11	0.54	0.73	47
GAMVUL		2.367	1.883	1.367	90.30	102.92	121.87	7.38	1.25	263
OBEVEW	[Pt(mns)$_2$]$^{2-}$	2.401	1.892	1.393	91.42	101.46	122.65	0.00	4.70	160
QUCGEA	[Cu(mns)$_2$]$^{2-}$	2.383	1.880	1.351	91.93	100.27	123.47	0.00	7.28	159
KESGIY	[Cu(dsis)$_2$]$^{2-}$	2.365	1.898	1.204	95.60	94.89	127.31	53.02	0.03	257
KESGIY10		2.365	1.898	1.204	95.60	94.89	127.31	53.02	0.03	71
JIMDUF	[Cu(pds)$_2$]$^-$	2.295	1.895	1.399	93.21	102.32	120.68	14.26	6.45	251
LATDUG		2.299	1.892	1.366	93.04	101.96	121.33	1.87	3.57	50
AWOFOH		2.304	1.885	1.407	92.89	102.66	120.76	0.00	2.56	255
AWOFUN		2.304	1.896	1.396	92.64	102.65	120.70	0.00	7.59	255
AHAROQ		2.300	1.888	1.408	92.54	103.18	120.40	0.00	0.62	252
SOJKUY		2.296	1.889	1.413	93.75	101.75	120.83	11.64	5.62	48
BIMVUP	[d]	2.300	1.872	1.444	93.33	101.91	120.53	0.17	12.92	274
QIMYAP	[Cu(bds)$_2$]$^{2-}$	2.396	1.898	1.396	90.04	103.17	121.68	0.00	4.90	Pr. Com.
QUCFUP	[Ag(mns)$_2$]$^{3-}$	2.658	1.888	1.368	87.96	97.11	127.96	79.90	10.76	159
HEZNUX	[Au(Et-thiazds)$_2$]$^-$	2.444	1.893	1.342	92.68	96.84	125.43	0.04	16.79	41
HEZPIN	[Au(Et-thiazds)$_2$]	2.439	1.868	1.374	92.92	98.10	125.30	0.02	2.73	41
HEZNOR	[Au(L)$_2$]$^{-e}$	2.439	1.891	1.339	93.20	97.56	125.68	0.02	5.71	41
HEZPEJ	[Au(L)$_2$]	2.430	1.868	1.420	93.38	98.75	124.38	0.03	0.49	41
JIMFAN	[Au(pds)$_2$]$^-$	2.426	1.901	1.405	91.11	101.13	122.79	6.38	7.71	251
ECOQES		2.430	1.889	1.431	90.43	101.60	122.31	0.53	10.71	44
ECOQIW		2.428	1.896	1.430	91.17	101.58	122.54	0.31	6.02	44
ECOQIW01		2.424	1.899	1.410	91.42	101.19	122.79	2.40	5.67	44
OLABUY		2.424	1.888	1.397	91.40	100.91	123.27	2.17	2.49	253
OLABUY01		2.429	1.905	1.391	91.46	100.83	123.24	0.00	6.05	242
QANFOD	[Co(bds)$_2$]$^-$	2.290	1.910	1.388	92.01	104.04	119.92	0.00	1.92	55
CIRDUD	[Zn(dsit)$_2$]$^{2-}$	2.444	1.883	1.353	96.80	93.88	127.67	82.55	2.32	Pr. Com.
KEKJAL	[Zn(dsis)$_2$]$^{2-}$	2.443	1.898	1.318	96.51	93.87	127.80	81.74	3.82	166
VOZPAB	[Zn(dsitse)$_2$]$^{2-}$	2.448	1.883	1.378	96.90	93.88	127.36	89.21	6.42	179
JIVWIV	[Zn(Me-thiazds)$_2$]$^{2-}$	2.475	1.885	1.362	96.30	93.63	127.81	82.92	8.94	60
RAMQEB	[Zn(dssq)$_2$]$^{2-}$	2.485	1.839	1.396	98.46	90.54	130.06	88.27	5.89	217
LELPAT	[Ge(bds)$_2$]	2.325	1.914	1.373	99.31	95.79	124.54	83.45	0.16	265
NOLXER	[Sb(mns)$_2$]$^{3-}$	2.655	1.866	1.367	87.81	96.70	128.30	79.73	11.72	157

[a] Dihedral angle between the two SeMSe planes, each defined by two Se atoms within a ligand and the central atom. [b] Average bend angle between the SeMSe and SeCCSe planes of each 1,2-diselenolene ligand. [c] L = diethylthiotetrathiafulvalenyldiselenolate. [d] The complex is part of a 2D layered coordination polymer where the Cu^I countercations coordinated by both the pyrazine N and Se atoms intercalate between complex molecules. [e] L = *N*-ethyl-1,3-thiazoline-2-one-4,5-diselenolate.

The coordination geometry about the central metal atom in the majority of the structures is square-planar or nearly tetrahedral (Figure 3).
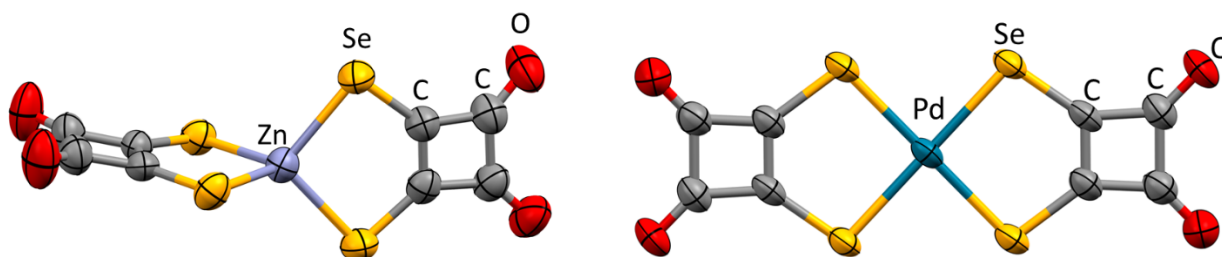

Figure 3. Drawings of the 1,2-diselenolene complex anions in $(PPh_4)_2[Zn(dssq)_2]$ (left; CCDC code RAMQEB, ref. 217) and $(PPh_4)_2[Pd(dssq)_2]$ (right; CCDC code FODGEK, ref. 216), showing a tetrahedral ($\lambda = 88.27°$) and square-planar ($\lambda = 0.00°$) coordination, respectively; thermal ellipsoid are shown at the 50% probability level.

A structural parameter reflecting the coordination geometry at the central metal ion is the dihedral angle (λ) between the two SeMSe planes, each defined by two Se atoms within a ligand and the central atom.[268] The vast majority of the structures feature a square-planar geometry (λ in the range 0–10°), including all of the complexes featuring Pd, Pt, Au or Co. The 8 structures showing a tetrahedral geometry (λ in the range 80–90°) include all of the Zn complexes, and few complexes featuring Ag, Sb, and Ge, and, in a single case, Ni. The remaining 13 structures, showing an intermediate situation (λ in the range 10–53°) all feature Cu and Ni, thus illustrating the large degree of variability in the coordination geometries sported by these two metals. The distortion from the square-planar coordination is in some cases due to the formation of dimeric structures, such as in the case of $[Fe(Cp^*)_2]_2[Ni(dsit)_2]_2$,[249] $(TBA)_2[Ni(dsit)_2]_2$,[272] $[(CH_3)_4N][Ni(dsise)_2]_2$,[262] $[Ni(ddds)_2]_2$,[68] and $(Me_4N)[Pd(dsit)_2]_2$.[271] In fact, analogously to their sulphured analogues, square-planar bis(1,2-diselenolene) metal complexes can form dimeric structures, held together by intermolecular M–Se[42,68,249,262] or M–M bonds,[271] sometimes interacting with each other through intermolecular interactions (Figure 4).
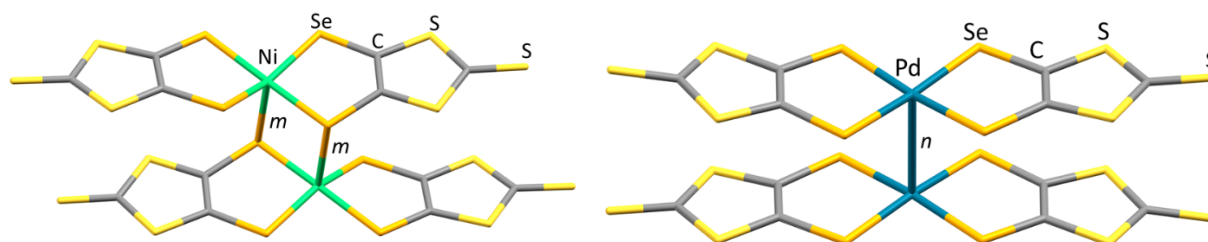

Figure 4. Capped stick representation of the complex anion dimers in $[Fe(Cp^*)_2]_2[Ni(dsit)_2]_2$ (left, CCDC code JIMCOY, ref. 249) and $(Me_4N)[Pd(dsit)_2]_2$ (right, CCDC code LEHPAP, ref. 271) showing Ni–Se and Pd–Pd interactions, respectively ($m = 2.556$ Å, $n = 3.173$ Å).

The average bend angle (η) between the SeMSe and SeCCSe planes of a 1,2-diselenolene chelate is < 10° in all but 11 of the structures. In the latter cases, the distortion is occasionally ascribable to the formation of dimers. The nature of the central metal ion shows a great influence on the structural parameters of *bis*(1,2-diselenolene) metal complexes especially as regards M–Se bond lengths (Figure 5). Overall, average M–Se bond lengths found among the existing structural examples range between 2.245 and 2.658 Å. Nickel complexes display the shortest M–Se average bond distances, and the small number of complexes based on Ag, Sb and Zn the longest ones. Within complexes of a single metal element, and analogously to what observed for 1,2-dithiolene complexes,[268] M–Se bond lengths roughly depend on the charge on the complex. Less oxidized complexes typically show longer M–Se bond lengths. For example, all dianionic Cu complexes exhibit longer Cu–Se bond lengths than monoanionic ones. The other bond lengths within the metallacycles are quite constant in homoleptic *bis*(1,2-diselenolene) complexes, with average C–Se and C–C distances covering a range of 0.074 (1.839–1.914 Å) and 0.239 Å (1.204–1.444 Å), respectively. As far as angles are concerned, Se–M–Se angles have been found to range between 87.8 and 99.3°, while the range of M–Se–C and S–C–C angles are between 90.5 and 104.1° and 119.9 and 130.1°, respectively (Figure 5).
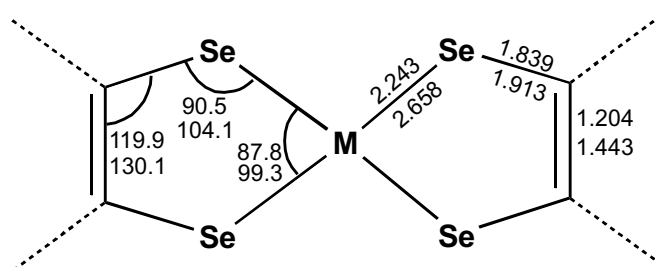

Figure 5. Ranges of average bond distances (Å) and angles (°) for *bis*(1,2-diselenolene) metal complexes.

In the solid state, the crystal packing of 1,2-diselenolene complexes shows a variety of interactions. In the case of charged complexes, the nature and size of the counterion often play a crucial role, and in many cases the complex molecules are isolated from one another by bulky countercations preventing any contact between them. Therefore, in (Ph$_4$P)[Pt(tds)$_2$] (Figure 6a),[263] (Et$_4$N)$_2$[Zn(Me-thiazds)$_2$],[60] [Fe(qsal)$_2$][M(pds)$_2$] [M = Cu, Au; qsal = N-(8-quinolyl)salicylaldimine],[251] (TBA)[M(pds)$_2$] (M = Cu, Ni; Figure 6b),[254,255] (TBA)[Ni(bds)^2],[192] [N(C$_6$H$_{13}$)][Ni(L)$_2$] (L = diethylthiotetrathiafulvalenyldiselenolate),[69] (TBA)$_2$[Ni(dsit)$_2$]$_2$,[272] (Ph$_4$P)[Ni(dssq)$_2$],[217] (TBA)[Ni(ddds)$_2$],[256] and (TBA)$_2$[Ni(dsise)$_2$]^{259} the crystal packing mainly arises from anion-cation interactions.

(a)   (b)
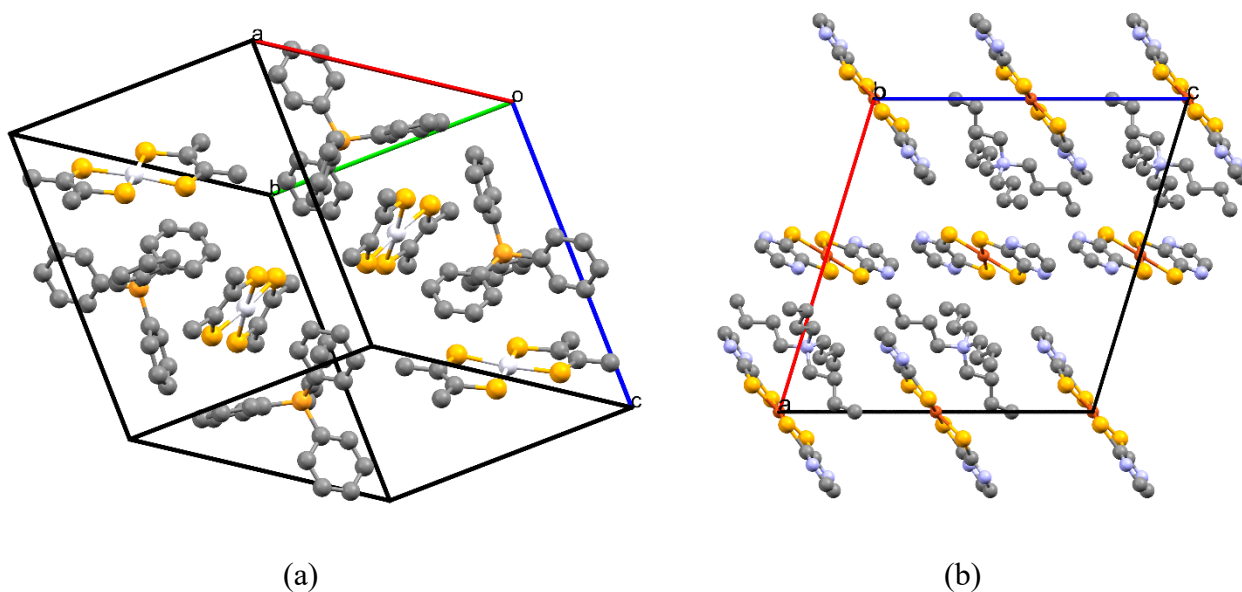
Figure 6. View of the packing of (Ph$_4$P)[Pt(tds)$_2$] (a; CCDC code GAMVUL, ref. 263) and (TBA)[Cu(pds)$_2$] (b; CCDC code AWOFUN, ref. 255). Hydrogen and fluorine atoms were omitted for clarity.

In other cases, chalcogen···chalcogen contacts (Se···Se, or S···Se and S···S for sulphur-containing 1,2-diselenolene ligands), shorter or close to the sum of van der Waals radii (1.80 and 1.90 Å for S and Se, respectively),[275] have been reported to occur between complex molecules arising from different layouts of the anions. These determine arrangements (a) in a zig-zag fashion, as found in the case of (Me$_4$N)[Ni(ddds)$_2$] (see Figure 25b);[68] (b) with formation of layers or chains alternating with those hosting the counteractions, where neighboring complex molecules or dimers are stacked, as in (Me$_4$N)[Pd(dsit)$_2$]$_2$ (Figure 7a)[271,359] and [Fe(bpp)$_2$][Cu(pds)$_2$]$_2$ (bpp = 2,6-*bis*(pyrazol-3-yl)pyridine);[48] or (c) with side-by-side interactions, as for (Et$_4$N)[Ni(ddds)$_2$],[68] [Ni(dmf)$_6$][Ni(dsit)$_2$]$_2$,[43] (R$_4$N)[Ni(dsise)$_2$] (R = Me, Bu),[259,262] (Bu$_4$N)[Ni(dsis)$_2$],[71] (Me$_4$N)$_2$[Cu(dsis)$_2$]·2MeCN (Figure 7b),[71] and (Me$_4$N)$_2$[Cu(dsis)$_2$].[257]

(a)   (b)
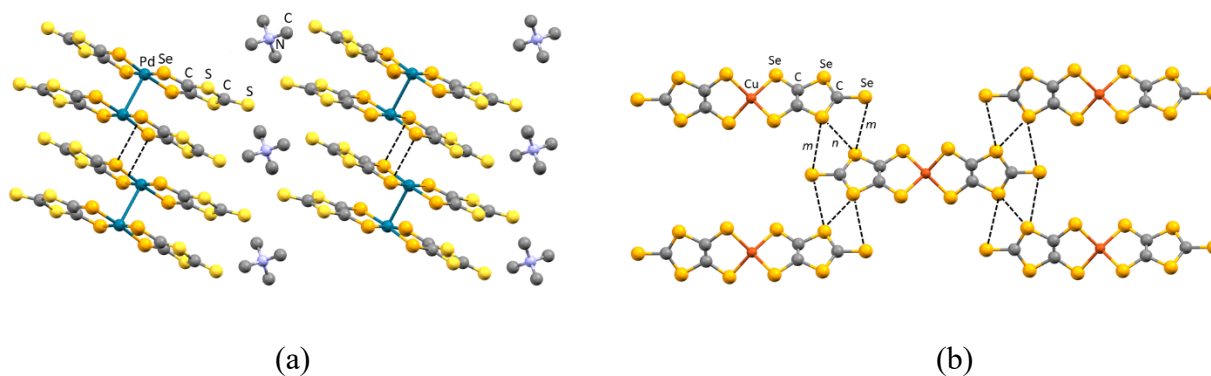
Figure 7. (a) View of the unit cell of (Me$_4$N)[Pd(dsit)$_2$]$_2$ (CCDC code LEHPAP, ref. 271) along the *b* axis, showing the interdimer Se···Se contacts (3.862 Å); (b) selenium-selenium contacts among the [Cu(dsis)$_2$]$^{2-}$ moieties in (Me$_4$N)$_2$[Cu(dsis)$_2$]·2MeCN (CCDC code KESGIY10, ref. 71), projected along the *c* axis (*m* = 3.469, *n* = 3.915 Å). Hydrogen atoms were omitted for clarity.

24

Similarly, the solid-state structures of Charge-Transfer (CT) salts often consist of chains or two-dimensional layers of alternating donor and acceptor molecules. In the case of compounds such as [Fe(Cp*)$_2$][M(tds)$_2$] (M = Ni, Pt),[247] [Fe(Cp*)$_2$][Ni(bds)$_2$],[52] (DT-TTF)$_4$[M(pds)$_2$]$_3$ (M = Au, Cu)[50,253] and (TMTSF)$_2$[Ni(tds)$_2$][270] (Figure 8) this arrangement prevents short contacts between acceptors, while in [Fe(Cp*)$_2$][Ni(dsit)$_2$]$_2$ (Figure 23a)[249] and [M(Cp*)$_2$][M'(tds)$_2$] (M = Cr, Mn; M' = Ni, Pt)[47] Se···Se contacts between complex molecules belonging to neighboring chains or adjacent layers can be observed.[249]
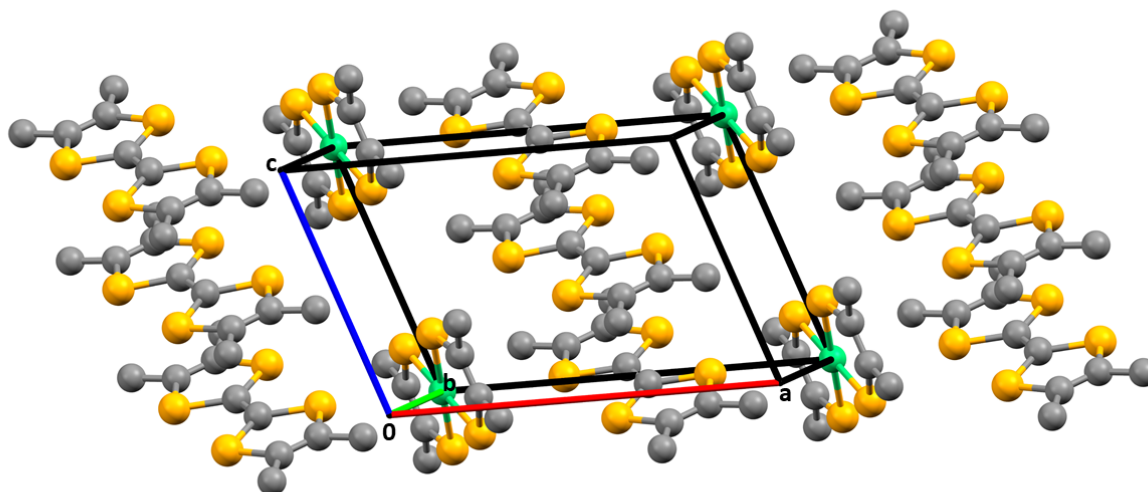
Figure 8. View of the packing of (TMTSF)$_2$[Ni(tds)$_2$] (CCDC code FUXKOY, ref. 270). Hydrogen and fluorine atoms were omitted for clarity.

Se···Se or S···Se contacts are also responsible for the packing in the few neutral 1,2-diselenolene metal complexes reported, such as [Au(Et-thiazds)$_2$], [Au(L)$_2$] (L = *N*-ethyl-1,3-thiazoline-2-one-4,5-diselenolate; Figure 9),[41] [Ge(bds)$_2$],[265] and [Ni(ddds)$_2$]$_2$.[68]

(a)   (b)
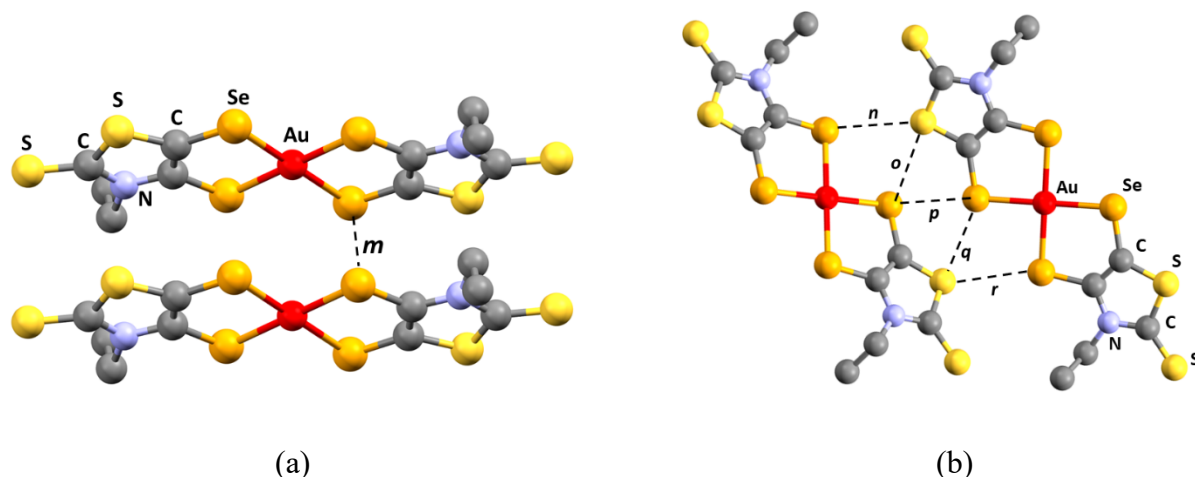
Figure 9. View of Se···Se and Se···S contacts between neighboring [Au(L)$_2$] molecules [L = N-ethyl-1,3-thiazoline-2-one-4,5-diselenolate, m = 3.970(5) Å] within (a) and between (b) stacks [CCDC code HEZPIN, ref. 41; n = 3.803(1), o = 3.472(2), p = 3.440(1), q = 3.623(2), r = 3.725(1) Å]). Hydrogen atoms were omitted for clarity.

In some cases, it was observed that the Se···Se contacts between 1,2-diselenolene metal complexes lead to an extension in the dimensionality of the packing interactions as compared to the S···S contacts of 1,2-dithiolene analogues, as expected from the more diffused p and d orbitals of selenium.[68,71,249] Finally, *bis*(1,2-diselenolene) metal complexes are also found in a series of coordination polymers obtained through the coordination of the pyridine nitrogen of pds^{2-} ligands to metal ions such as Na$^+$ and Cu$^+$, as in Na$_2$[M(pds)$_2$]·2H$_2$O (M = Cu, Ni; Figure 10),[252] Na$_2$[Ni(pds)$_2$]·4H$_2$O,[254] and Cu[Cu(pds)$_2$] [274]. The resulting complex supramolecular architectures affect the solid-state properties of the resulting molecular materials (see sections 3.2.3 and 3.2.4).
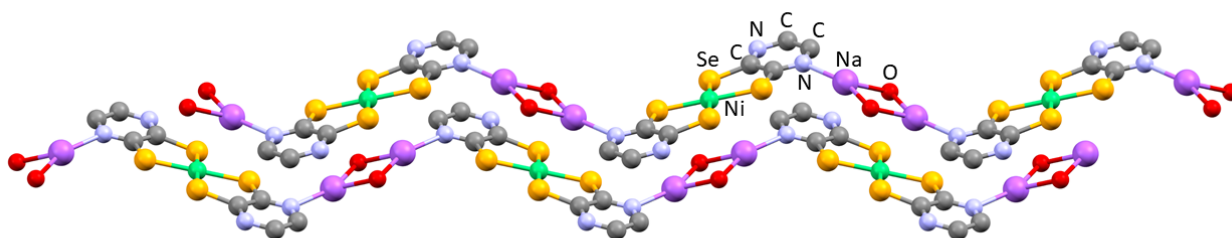
Figure 10. View of the infinite chain along the c axis in Na$_2$[Ni(pds)$_2$]·2H$_2$O (CCDC code IZOSAR, ref. 254). Hydrogen atoms were omitted for clarity.

3.1.2. *Heteroleptic bis(1,2-diselenolene) metal complexes*

The number of heteroleptic *bis*(1,2-dichalcogenolene) metal complexes featuring a single 1,2-diselenolene ligand is limited to 19 examples, namely (TBA)$_2$[M(dmit)(dsis)] (M = Ni, Pd),[276] (Me$_4$N)[Ni(dsit)(mnt)], (TBA) [Ni(ddds)(mnt)],[277] (TBA)[Ni(ddds)(dmit)],[273] [Ni(ddds)(edo)] (edo^{2-}

26

= 5,6-dihydroxo-1,4-dioxine-2,3-dithiol),[278] [M(R$_2$pipdt)(dsit)] (R$_2$pipdt^{2-} = 1,4-disubstituted piperazine-3,2-dithione; R = Me, Bz, ^{i}Pr: M = Ni, Pd, Pt),[54,279,280] [Ni(dmeds)(dmit)], [Ni(dpedt)(dsit)],[42] (TBA)$_2$[Cu(dsis)(mnt)], (TBA)$_2$[Cu(dsis)(dmit)], (TBA)$_2$[Cu(dsis)(dto)],[281] and [Ge(bds)(bdt)][265] (Scheme 2; dmit^{2-} = 1,3-dithiole-2-thione-4,5-dithiolato; dpedt^{2-} = diphenylethylene-1,2-dithiolate; dto^{2-} =1,2-dithioxalate). These compounds were obtained through three main synthetic strategies (Scheme 18): i) by reacting the two ligands (or more often their precursors deprotected *in situ*) in the presence of the desired metal ion; ii) through ligand-exchange reactions between the corresponding homoleptic *bis*(1,2-dichalcogenolene) complexes; iii) by reacting a *mono*(1,2-dichalcogenolene), usually featuring chloride ancillary ligands, with the other 1,2-dichalcogenolene ligand or proligand. A disadvantage of these synthetic pathways is that in most cases the homoleptic by-products need to be removed by recrystallization or chromatographic techniques.
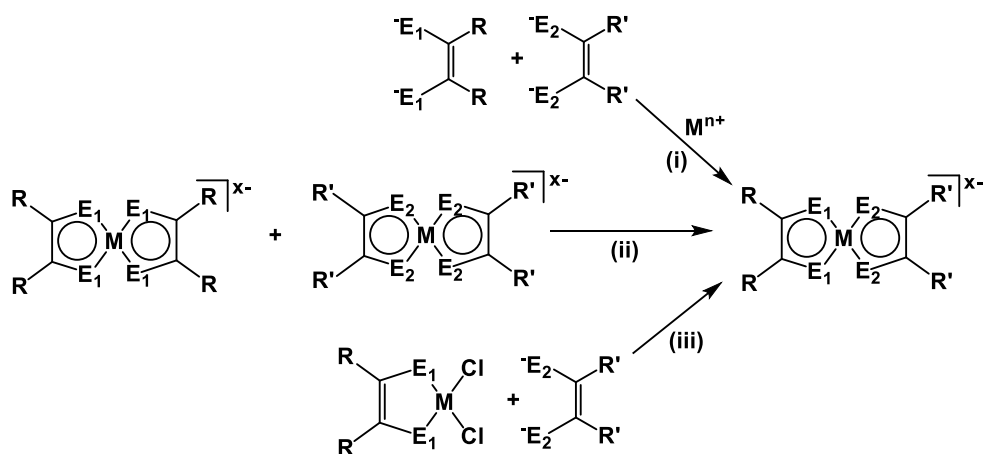
Scheme 18. Synthetic strategies for the preparation of heteroleptic *bis*(1,2-dichalcogenolene) metal complexes (E = S, Se).

Among the 19 heteroleptic *bis*(1,2-dichalcogenolene) metal complexes reported to date, [Ni(dmeds)(dmit)],[42] [Ni(Bz$_2$pipdt)(dsit)], and [Pt(Bz$_2$pipdt)(dsit)][54] were structurally characterized (Table 3).

Table 3. Selected average bond distances (Å) and angles (°) for heteroleptic *bis*(1,2-diselenolene) metal complexes.

CCDC code	Complex	M–Se	Se–C	C–C	Se–M–Se	M–Se–C	Se–C–C	λ^a	η^b	Ref.
RICSOM	[Ni(dmeds)(dmit)]	2.298	1.859	1.356	89.25	104.66	120.22	18.38	9.47	42
ZEGTUC	[Ni(Bz2pipdt)(dsit)]	2.282	1.879	1.353	94.44	100.65	122.10	0.27	2.25	54
ZEGVAK	[Pt(Bz2pipdt)(dsit)]	2.399	1.891	1.345	92.22	99.89	123.96	0.57	2.94	54

[a] Dihedral angle between the two EME planes, each defined by two chalcogen atoms E within a ligand and the central metal ion M. [b] Average bend angle between the SeMSe and SeCCSe planes of the 1,2-diselenolene ligand.

In [Ni(Bz2pipdt)(dsit)] and [Pt(Bz2pipdt)(dsit)] the central metal ion shows a square-planar coordination,[54] while [Ni(dmeds)(dmit)] features a dimeric structure (Figure 11).[42]
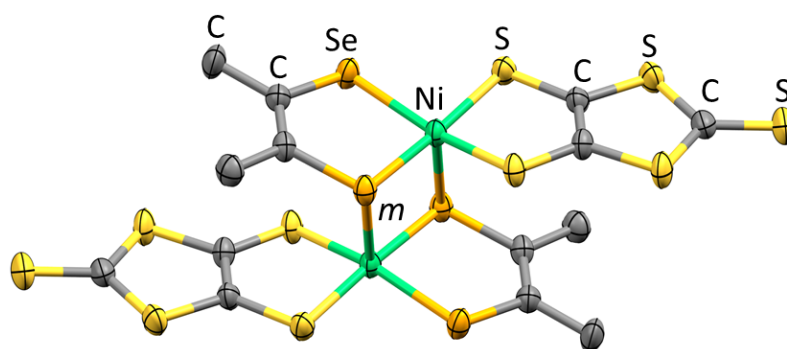
Figure 11. Drawing of the [Ni(dmeds)(dmit)]₂ dimer (CCDC code RICSOM, ref. 42, m = 2.562 Å). Hydrogen atoms were omitted for clarity, thermal ellipsoids shown at the 50% probability level.

A particular class of heteroleptic metal complexes including 1,2-diselenolene and 1,2-dithiolene ligands is that of bimetallic systems featuring the tetrathiooxalato (tto) ligand, in complexes such as (TBA)₂[M(tto)(dsit)₂] (M = Ni, Cu),[282,283,284] synthesized through ligand-exchange reactions (Figure 12).
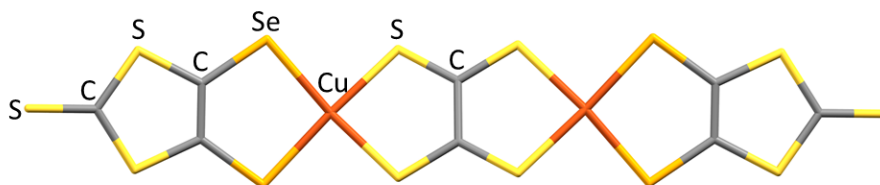
Figure 12. Capped stick representation of the complex anion in (TBA)₂[Cu(tto)(dsit)₂] (CCDC code TINNAF, ref. 42).

3.1.3. Mixed-ligand 1,2-diselenolene metal complexes

Most examples of mixed-ligand 1,2-diselenolene metal complexes include neutral diimine-diselenolate complexes of the type [M(N^N)(Se^Se)] (where N^N is an aromatic diimine such as 2,2'-bipyridine or 1,10-phenanthroline), and complexes featuring mono- or bidentate phosphine ligands.

While several hundreds of diimine-dithiolate metal complexes [M(N^N)(S^S)], especially with M = Pt, have been reported,[285,286,287,288] the number of [M(N^N)(Se^Se)] complexes is limited to only eight examples, namely [Pt(bipy)(dsit)], [Pt(Et-pa)(dsit)], [Pt(Pr^i-pa)(dsit)],[289] [Pt(bipy)(bds)], [Ni(bipy)(bds)],[58] [Pt(4,4'-tBu$_2$bipy)(bds)],[64] [Pt(bipy)(Me-thiazds)], and [Pt(phen)(Me-thiazds)][63] (bipy = 2,2'-bipyridine; Et-pa and Pr^i-pa = N-ethyl- and N-isopropyl-2-methylpyridine-2-carbaldimine; 4,4'-tBu$_2$bipy = 4,4'-di-$tert$-butyl-2,2'-bipyridine; phen = 1,10-phenanthroline). These complexes, analogously to the sulphured congeners, were synthesized as neutral species by reaction of the corresponding diimine-dichloro metal complexes [M(N^N)Cl$_2$] with the desired 1,2-diselenolene ligands (Scheme 19).
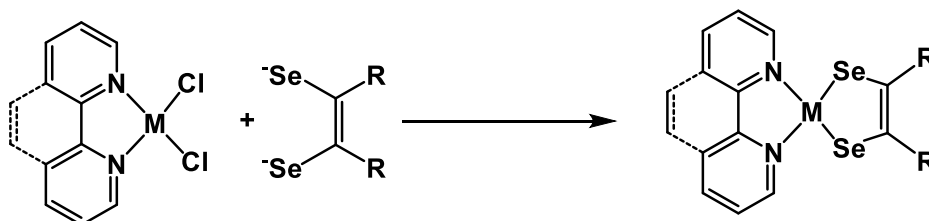
Scheme 19. Synthetic strategy for the synthesis of diimine-diselenolate metal complexes.

The crystal structures of [Pt(bipy)(bds)]·CH$_2$Cl$_2$, [Pt(bipy)(bds)]·DMSO,[58] and [Pt(phen)(Me-thiazds)][63] (Figure 13) all feature the central Pt ion in a square-planar coordination (Table 4).

Table 4. Selected average bond distances (Å) and angles (°) for the 1,2-diselenolene unit in diimine-diselenolate metal complexes.

	Complex	M–Se	Se–C	C–C	Se–M–Se	M–Se–C	Se–C–C	λ^a	η^b	Ref.
EVEWEH	[Pt(bipy)(bds)]	2.372	1.906	1.388	89.72	104.11	120.91	1.46	4.73	58
EVEWIL	[Pt(bipy)(bds)]	2.378	1.926	1.414	89.51	105.02	120.13	0.45	3.05	58
ZUQGEZ	[Pt(bipy)(Me-thiazds)]	2.387	1.882	1.331	91.26	100.12	123.56	2.99	11.50	63

^{a} Dihedral angle between the two SeMSe and NMN planes, each defined by two donor atoms within a ligand and the central atom. ^{a} Average bend angle between the SeMSe and SeCCSe planes of the diselenolene ligand.
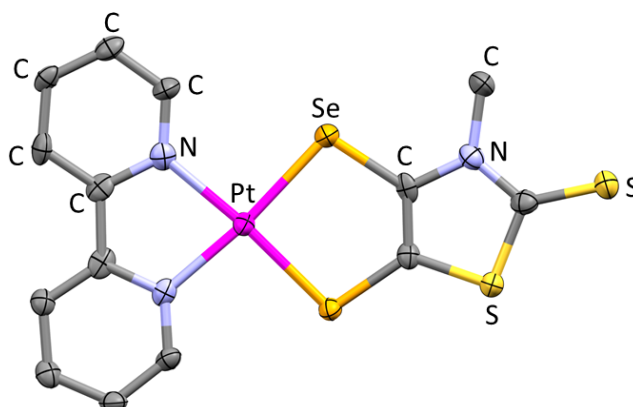
Figure 13. Drawing of [Pt(bipy)(Me-thiazds)] isolated in [Pt(bipy)(Me-thiazds)]·CH$_2$Cl$_2$ (CCDC code ZUQGEZ, ref. 63). Hydrogen atoms were omitted for clarity; thermal ellipsoids drawn at the 50% probability level.

Starting from 1999,[229,230] Morley and coworkers reported on a series of mono- and di-nuclear Pd and Pt complexes featuring cyclic 1,2-diselenolene ligands in combination with mono- or bi-dentate phosphines.[53,227,228,290] These complexes were obtained as neutral species by reacting the corresponding 1,4-diselenines or 1,2,3-selenadiazole (Scheme 14) with the desired phosphine metal complex, or with a different metal source (such as [Pd$_2$(dba)$_3$], dba = dibenzylideneacetone) in the presence of the desired phosphine (route i in Scheme 20). Ligand-exchange reactions were also performed starting from the mono- or di-nuclear complexes, leading to the formation of compounds of the type [M(Se^Se)(P^P)], featuring bidentate phosphine P^P ligands (route ii in Scheme 20).[228] Heteroleptic platinum complexes featuring ene-1,2-diselenolate ligands could also be synthesized *in situ* by reaction of [PtSe$_4$(dppe)] and DMAD [route iii in Scheme 20; dppe = 1,2-bis(diphenylphosphino)ethane],[146] or by means of ligand-exchange reactions (route iv in Scheme 20).[136] An alternative route involves aromatic 1,2-diselenetes (route v in Scheme 20).[210,211] The few further 1,2-diselenolene metal complexes featuring phosphine ligands reported in the literature were all synthesized by similar procedures, involving the reaction of the 1,2-diselenolene ligand or seldom a *mono*(1,2-diselenolene) complex, such as [Ti(Cp$_2$)(Se$_2$C$_2$(COOMe)$_2$)][136] and [AgSe$_6$(mns)]$^{3-}$,[158] with a phosphine metal complex,[38] or a different source of the metal ion in the presence of the desired phosphine.[74]
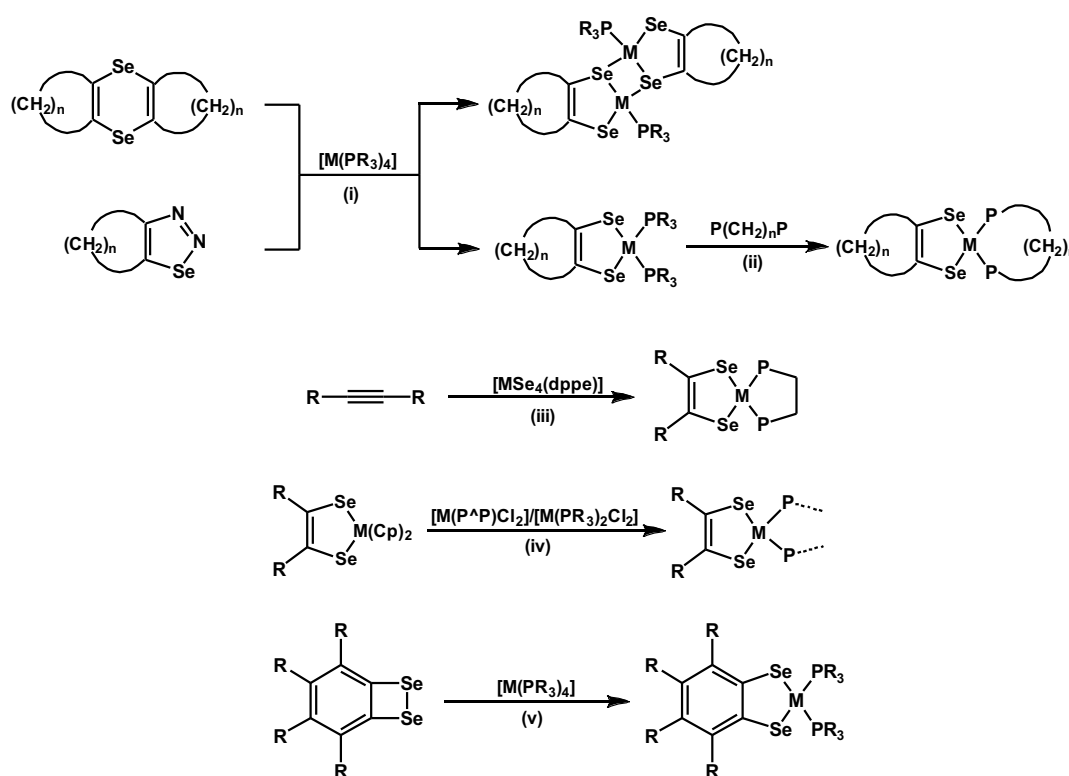
Scheme 20. Synthetic strategies for the synthesis of mixed-ligand heteroleptic 1,2-diselenolene metal complexes featuring mono- or bidentate phosphines.

The crystal structures of 9 such complexes are reported in the literature (Table 5), namely [Pt(Se$_2$C$_8$H$_{12}$)(dppm)], [Pt(Se$_2$C$_8$H$_{12}$)(PEt$_3$)$_2$], [Pt(Se$_2$C$_7$H$_{10}$)(PEt$_3$)$_2$],[228] [Pd(Se$_2$C$_8$H$_{12}$)(PBu$_3$)$_2$], [Pd(Se$_2$C$_6$H$_8$)(PBu$_3$)$_2$],[227] [Pd(Se$_2$C$_7$H$_{10}$)(PBu$_3$)$_2$],[230] [Ni(mns)(dppp)] (Figure 14),[158] [Ni(bds)(dppf)],[74] and [Pt(Et$_2$CN$_2$bds)(PPh$_3$)$_2$][211] (dppm = 1,1-*bis*(diphenylphosphino)methane; dppp = 1,3-*bis*(diphenylphosphino)propane, dppf = 1,1'-*bis*(diphenylphosphino)ferrocene; Et$_2$CN$_2$bds = 4,5-dicyano-3,6-diethylbenzene-1,2-diselenolato).

Table 5. Selected average bond distances (Å) and angles (°) for the 1,2-diselenolene unit in phosphine-1,2-diselenolato metal complexes.

CCDC code	Complex	M–Se	Se–C	C–C	Se–M–Se	M–Se–C	Se–C–C	λ[a]	η[b]	Ref.
WAQVIT	[Ni(mns)(dppp)]	2.285	1.884	1.349	92.08	102.86	121.01	1.49	4.16	158
FIMSUS	[Ni(bds)(dppf)]	2.293	1.904	1.382	89.42	105.99	118.96	4.96	7.33	74
JAJHEI	[Pd(Se$_2$C$_6$H$_8$)(PBu$_3$)$_2$]	2.407	1.902	1.304	87.07	104.50	121.95	4.54	1.10	227
XAQKAB	[Pd(Se$_2$C$_7$H$_{10}$)(PBu$_3$)$_2$]	2.411	1.886	1.307	86.65	104.60	122.04	3.42	2.40	230
JAJHAE	[Pd(Se$_2$C$_8$H$_{12}$)(PBu$_3$)$_2$]	2.413	1.888	1.344	86.69	105.08	121.41	5.20	5.27	227
HUWYUU	[Pt(Se$_2$C$_7$H$_{10}$)(PEt$_3$)$_2$]	2.416	1.895	1.316	86.77	104.71	121.88	5.48	1.23	228
HUWYOO	[Pt(Se$_2$C$_8$H$_{12}$)(PEt$_3$)$_2$]	2.421	1.897	1.320	86.70	104.75	121.86	4.76	1.97	228
HUWYII	[Pt(Se$_2$C$_8$H$_{12}$)(dppm)]	2.400	1.918	1.288	88.79	102.94	122.64	5.34	1.51	228
XIXSUV	[Pt(Et$_2$CN$_2$bds)(PPh$_3$)$_2$]	2.421	1.903	1.401	87.25	103.75	120.64	5.05	18.78	211

[a] Dihedral angle between the two SeMSe and PMP planes, each defined by two donor atoms within a ligand and the central atom. [b] Average bend angle between the SeMSe and SeCCSe planes of the 1,2-diselenolene ligand.

In all of these complexes the central metal ion (M = Ni, Pd, Pt) shows a square-planar coordination, the dihedral angle λ between the two SeMSe and PMP planes being < 10°. Average M–Se bond lengths found among the existing structural examples range between 2.285 and 2.421 Å.
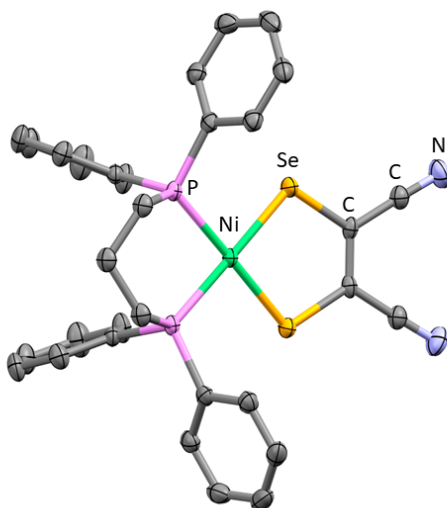
Figure 14. Drawing of the neutral complex [Ni(mns)(dppp)] (CCDC code WAQVIT, ref. 158). Hydrogen atoms were omitted for clarity; thermal ellipsoids drawn at the 50% probability level.

In addition to the two classes of compounds mentioned above, 1,2-diselenolene ligands can be found in mixed-ligand complexes in combination with oxo (Figure 15a) and selenoxo (Figure 15b) ligands[33,217,291] (particularly complexes containing group 4 metal ions, in some cases also in cluster systems; Figure 15c),[292,293,294,295] porphyrines,[209] polyselenides (Figure 15d),[157] dithiocarbamates,[266,296] hydro-*tris*(pyrazolyl)borates,[297] and amidinates.[298] In most cases, these complexes were obtained by means of ligand-exchange reactions.
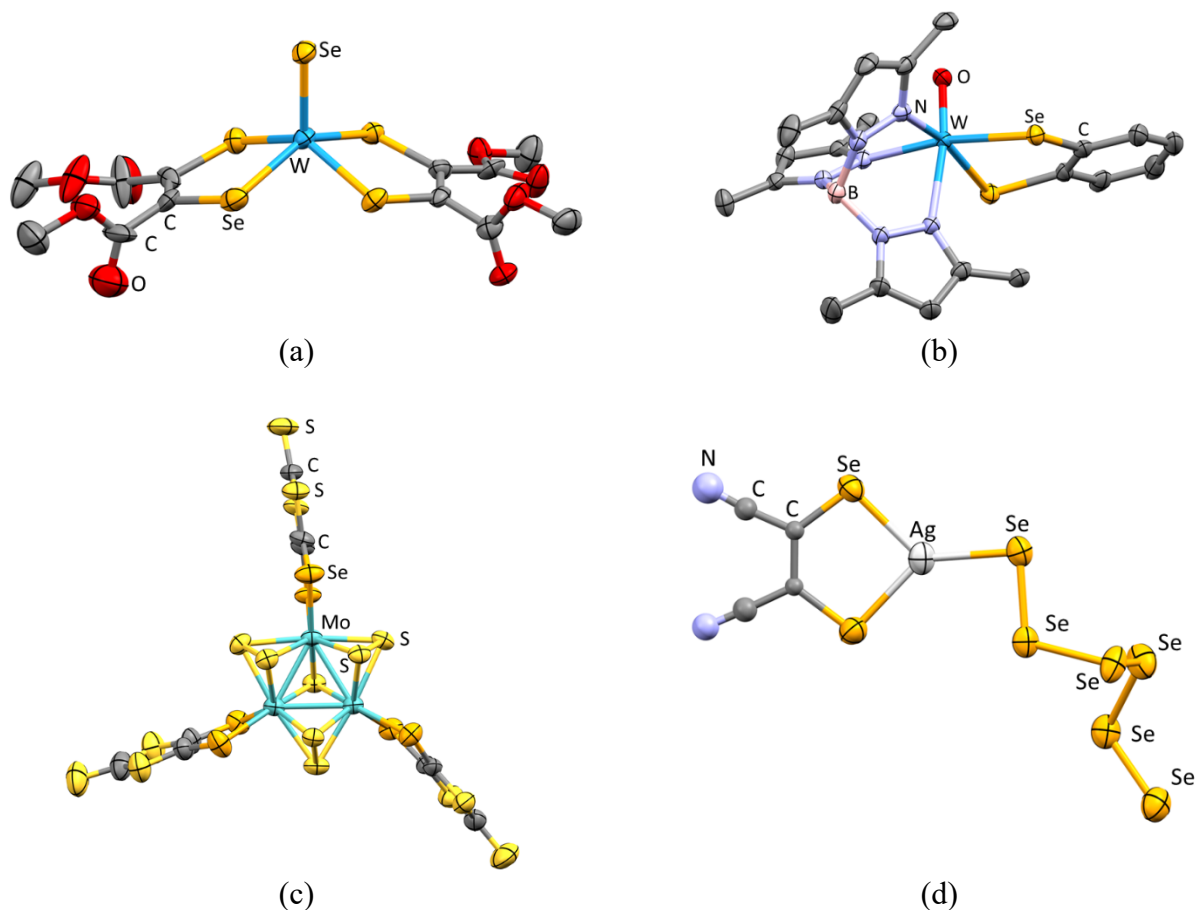
Figure 15. Drawing of a selection of mixed-ligand 1,2-diselenolene complexes: [WSe(Se₂C₂COOMe₂)]²⁻ (a; CCDC code OJIBAL , ref. 33), [WO(bds)(Tp*)] (b; CCDC code ABATEE, ref. 297), [Mo₃S₇(dsit)₃]²⁻ (c; CCDC code GOJDEP, ref. 293), [Ag(mns)Se₆]³⁻ (d; CCDC code NOLXIV, ref. 157); Tp* = hydro*tris*(3,5-dimethylpyrazol-1-yl)borate. Hydrogen atoms were omitted for clarity; thermal ellipsoids drawn at the 50% probability level.

3.1.4. *Mixed-ligand organometallic 1,2-diselenolene metal complexes*

Most mixed-ligand organometallic 1,2-diselenolene complexes belong to the class of *mono*(1,2-diselenolene)arene complexes. These compounds, similarly to their well-known sulphured analogues,[299,300,301,302,303,304,305] feature variously substituted η^5-ciclopentadienyl (Cp) ligands, with

the single exception of $[(\eta^4\text{-}C_4Me_4)Pt(dsit)]$,[306] featuring a η^4-cyclobutadiene (C_4Me_4) derivative ligand. Cyclopentadienyl-1,2-diselenolene metal complexes belong to two classes showing different stoichiometry: (i) $[Cp_2M(Se^\wedge Se)]$ complexes, which are known with early transition metals (such as Ti, Zr, Hf, V, Mo, and W); and (ii) 1:1 $[CpM(Se^\wedge Se)]$ complexes, reported with group 9 and 10 metals (namely Co, Ir, and Ni). In contrast to the analogous complexes featuring 1,2-dithiolene ligands, no examples of complexes of the type $[CpM(Se^\wedge Se)_2]$ are known to date.

Heterometallic arene-1,2-diselenolene clusters[307] and metal complexes of the type $[LCpM(Se^\wedge Se)]$[143,35] are also known (M = Ti, Ir, Re; L = Cl$^-$, PMe$_3$, O^{2-}, N^{t}Bu^{2-}). The first metal complexes belonging to the $[Cp_2M(Se^\wedge Se)]$ class were reported by Rauchfuss and Bolinger in 1982,[136] synthesized through the addition of acetylenes to organotitanium pentaselenides (route i in Scheme 4), thus involving the *in situ* formation of the 1,2-diselenolene ligand (route i in Scheme 21).[147,308] A similar approach (route ii in Scheme 4) was also adopted in the synthesis of $[CpM(Se^\wedge Se)]$ complexes[35] and different related compounds[143,145] (route ii in Scheme 21). In 1984, Gautheron[193,194] reported on the synthesis of similar $[Cp_2M(Se^\wedge Se)]$ complexes featuring arene-1,2-diselenolene ligands (route iii in Scheme 9), by reacting elemental selenium with complexes of the type $[Cp_2MAr_2]$ (route iii in Scheme 21).[39,195] The first example of a 1:1 $[CpM(Se^\wedge Se)]$ complex, namely $[Cp_2Co(Se_2C_2Ph_2)_2]$, was reported in 1985 by Brill and coworkers.[137] This complex was obtained by the reaction of $Cp_2Co(CO)_2$ and diphenylacetylene in a refluxing slurry of selenium in decalin (route iv in Scheme 4 and Scheme 21).[61,138,139,140,142] In 1986 Köpf and Klapötke reported the synthesis of $[Cp_2M(Se^\wedge Se)]$ complexes obtained by reacting Li$_2$bds (see route iv in Scheme 9) with Cp_2MCl_2 complexes (route v in Scheme 21; M = Ti, Zr, Hf, Mo, W).[197] This route, involving alkaline metal 1,2-diselenolates, was also extended to other ligands (see also route i in Scheme 10 and route i in Scheme 13).[205,206,218,219,220] Olk and coworkers developed in 1996s[309] a route for the synthesis of $[Cp_2M(Se^\wedge Se)]$ metal complexes featuring the dsit^{2-} ligand and its isologues starting from their benzoyl-substituted precursors (route iii in Scheme 5; M = Sb, Mo, W, Ti, V).[51,309,310] A similar route, involving cyanoethylseleno-substituted precursors (see route ii in Scheme 7),[311] was successively extended to the related R-thiazds^{2-} ligands (route vi in Scheme 21; M = Mo). Analogously to what mentioned above for different 1,2-diselenolene complexes, $[Cp_2M(R\text{-}thiazds)]$ complexes were also obtained through the reaction of *N*-substituted 1,3-thiazole with lithium diisopropylamide (LDA) followed by reaction with elemental selenium (route vii in Scheme 21; M = Ti).[185,186] Precursors for the *in situ* generation of 1,2-diselenolene ligands in the synthesis of Cp/1,2-diselenolene complexes also include poly-o-phenylenediselenide (route i in Scheme 9 and route viii in Scheme 21),[147,312] 1,2,3-selenadiazoles (route iii in Scheme 14 and route ix in Scheme 21),[221,225,226,135,313] and less usual compounds such as the $[\mu_3\text{-}\eta^1\text{-}CR^1][\mu_3\text{-}\eta^1\text{-}CR^2][CpCO]_3$ clusters [R^1 = Bu, Ph, C$_2$SiMe$_3$, CO$_2$Me;

R^2 = Et, Bu, Ph, C_6D_5, C_2SiMe_3, CO_2Me].[314] Finally, cyclopentadienyl-1,2-diselenolene metal complexes can also be obtained by means of ligand exchange reactions (route x in Scheme 21).[51,315,306]
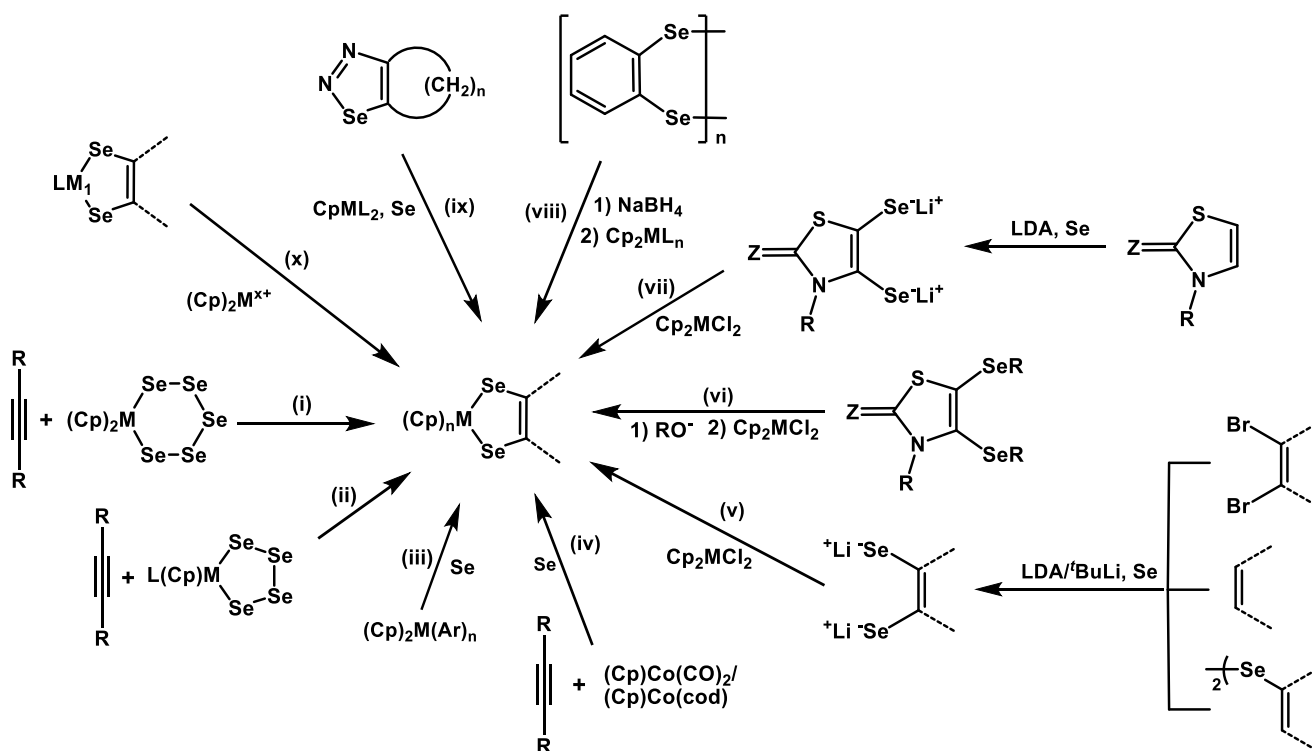
Scheme 21. Synthetic strategies for the synthesis of [$Cp_nM(Se{\wedge}Se)$] metal complexes (n = 1, 2; Z = S, O).

Among 1,2-dithiolene complexes featuring Cp ligand derivatives, a large degree of conformational flexibility was observed, with a possible folding of the MS_2C_2 metallacycle along the S–S hinge (Scheme 22). In particular, in [$Cp_2M(S{\wedge}S)$] complexes a folding angle θ (defined as the angle between the plane passing through the metal ion and the sulphur atoms of the 1,2-dithiolene ligand and the ene-1,2-dithiolate plane)[316] varying between 0 and 50° is typically observed. The θ angle was observed to be strongly dependent on the electron count and the nature of the metal and the ligands. It was observed that while d^0 16–electron [$Cp_2Ti(S{\wedge}S)$] complexes exhibit a strong distortion of the MS_2C_2 metallacycle, d^2 18–electron [$Cp_2Mo(S{\wedge}S)$] complexes are essentially non-folded, and the intermediate d^1 17–electron complexes (either neutral species with M = V or Nb, or cationic ones with M = Mo or W), adopt folded structures with intermediate folding angles between 0 and 35°, depending subtly on the nature of the metal, the ligand and the counter-ion.[311] This behavior was first rationalized by Lauher and Hoffmann[317] on the basis of extended Hückel calculations, more recently confirmed by DFT calculations.[67,316,318,319,320] These calculations showed that the strong folding of the d^0 titanium species found its origin in the overlap stabilization of the empty metallic and occupied 1,2-dithiolene frontier orbitals, of a_1 and b_1 symmetry, respectively, hindering any mixing in the

unfolded C_{2v} conformation ($\theta = 0°$) but affording a net stabilization in the folded C_s conformation ($\theta > 0°$). Similar observations could be extended to [Cp$_2$M(Se^Se)] complexes, the conformation of which was also studied in the past by means of photoelectron spectroscopy.[321]
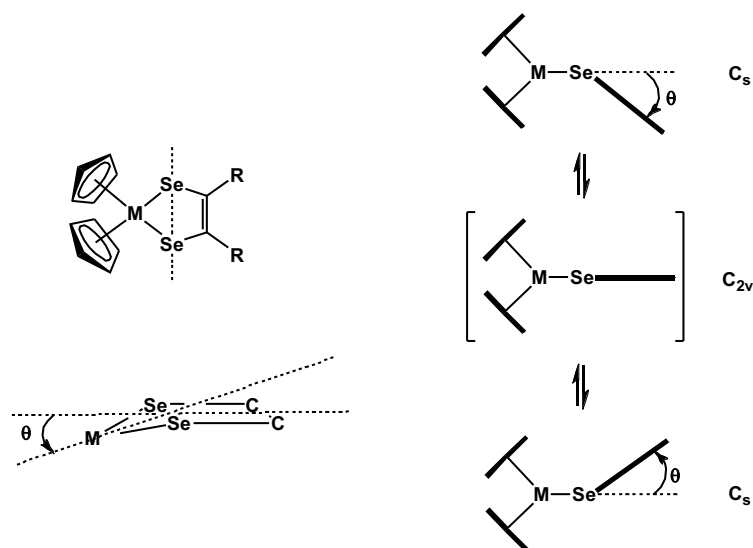
Scheme 22. Folding angle (θ) of the MSe$_2$C$_2$ metallacycle in [Cp$_2$M(Se^Se)] metal complexes.

To date, 23 crystal structures of [Cp$_2$M(Se^Se)] complexes have been deposited at the Cambridge Crystallographic Data Center (Table 6).

Table 6. Selected average bond distances (Å) and angles (°) for the 1,2-diselenolene unit in [Cp$_2$M(Se^Se)] metal complexes.

	Complex	M–Se	Se–C	C–C	Se–M–Se	M–Se–C	Se–C–C	θ^a	λ^b	Ref.
AFUXOP	[Cp$_2$Ti(Me-thiazds)]	2.574	1.879	1.357	85.21	91.21	124.47	48.19	89.11	185
RACZUR	[Cp$_2$Ti(ddds)]	2.544	1.898	1.364	82.46	93.15	121.61	51.30	89.08	322
TUMXAA	[(η^5-MeC$_5$H$_4$)$_2$Ti(dsit)]	2.567	1.890	1.365	83.99	90.72	123.19	52.45	89.22	309
TUMXEE	[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsit)]	2.584	1.884	1.357	83.95	95.68	123.88	40.16	89.27	309
TUMXOO	[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsise)]	2.573	1.850	1.350	84.75	94.79	124.92	39.17	89.40	309
TUMXOO01		2.597	1.886	1.346	83.79	94.63	124.23	42.12	89.36	309
TUMXUU	[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsis)]	2.598	1.885	1.346	82.99	96.23	123.71	39.95	89.73	309
XIKFUT	[Cp$_2$Ti(bds)]	2.555	1.909	1.407	82.16	94.65	120.72	49.96	88.57	147
XIKGAA	[Cp$_2$Ti(dsit)]	2.572	1.881	1.373	84.62	91.31	123.75	49.80	89.50	147
XIKGEE	[Cp$_2$Ti(Se$_2$C$_2$COOMe$_2$)]	2.551	1.890	1.362	82.63	94.43	122.06	47.77	89.83	147
XIKGII	[Cp$_2$Ti(Se$_2$C$_2$COOMeCF$_3$)]	2.561	1.898	1.355	82.41	94.14	122.14	48.41	89.77	147
COMYUY	[(η^5-^{t}BuC$_5$H$_4$)$_2$Zr(bds)]	2.655	1.936	1.395	81.09	90.74	122.07	56.21	88.73	193
MIDLES	[Cp$_2$Mo(Me-thiazds)]	2.598	1.895	1.344	85.38	102.13	125.10	3.84	88.55	311
MIDLIW	[Cp$_2$Mo(Et-thiazds)]	2.601	1.905	1.344	85.27	102.12	124.85	8.26	88.95	311
MIDLUI	[Cp$_2$Mo(Me-thiazds)]$^-$	2.594	1.863	1.374	84.98	102.60	124.82	0.96	89.93	311
MIDMUJ		2.587	1.858	1.381	84.26	100.90	124.20	22.53	89.99	311
MIDMIX	[Cp$_2$Mo(Et-thiazds)]$^-$	2.572	1.852	1.387	85.01	101.36	124.33	18.29	89.15	311
MIDNEU		2.589	1.858	1.390	84.46	101.72	124.18	18.25	89.11	311
POZMIA	[Cp$_2$Mo(dsit)]$^-$	2.561	1.861	1.375	83.68	99.70	123.28	30.90	89.92	310
QAYMOS	[Cp$_2$Mo(dsit)]$^+$	2.559	1.836	1.373	84.74	103.20	124.43	0.00	90.00	67
QAYMEI	[Cp$_2$W(dsit)]	2.571	1.904	1.343	85.00	103.35	123.98	4.53	89.94	67
POZNAT	[Cp$_2$W(dsit)]$^-$	2.553	1.877	1.328	83.88	98.70	123.74	32.37	89.94	310
QAYMUY	[Cp$_2$W(dsit)]$^+$	2.545	1.873	1.362	83.75	100.25	122.91	30.06	89.44	67

[a] Folding angle between the SeMSe and and SeCCSe planes of the diselenolene ligand. [b] Angle between the SeMSe plane and that defined by the Cp centroids and the central metal atom.

Among these structurally characterized complexes, 11 feature [Cp$_2$Ti(Se^Se)] complexes, all showing values of θ ranging between 39.17° in [(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsise)] and 52.45° in [(η^5-MeC$_5$H$_4$)$_2$Ti(dsit)].[309] A single structure of a Zr complex was reported, namely [(η^5-^{t}BuC$_5$H$_4$)$_2$Zr(bds)],[193] showing a folding angle of 56.21°. On the other hand, the 2 structures of neutral [Cp$_2$Mo(Se^Se)] complexes, namely [Cp$_2$Mo(Me-thiazds)] and [Cp$_2$Mo(Et-thiazds)],[311] and that of [Cp$_2$W(dsit)][67] show θ values of 3.84, 8.26, and 4.53°, respectively. When the same or similar complexes are found as monocationic species in combination with counteranions, as in the case of [Cp$_2$W(dsit)](AsF$_6$),[67] or in CT salts, such as [Cp$_2$Mo(R-thiazds)](TCNQ/TCNQF$_4$) (R = Me, Et) or [Cp$_2$M(dist)](TCNQF$_4$) (M = Mo, W; TCNQF$_4$ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane), an increase of θ ranging from 18.29 to 32.37° is observed.[310] The only exceptions to this trend are represented (i) by [Cp$_2$Mo(Me-thiazds)](TCNQ),[311] were the comparatively small θ angle of 0.96° was attributed to a low degree of charge transfer, resulting in a less oxidized complex with a formal charge < 1, and (ii) by [Cp$_2$Mo(dsit)](AsF$_6$), where the planarity of the MS$_2$C$_2$ was attributed to the very low energy barrier (< 0.5 kcal·mol^{-1}) of the folding process for this system.[67] In agreement with what it was observed for the 1,2-dithiolene analogues, larger folding angles are spotted on going from Mo to W, as in the case of the [Cp$_2$M(Me-thiazds)](TCNQF$_4$) couples (θ = 30.90 and 32.37° for M = Mo and W, respectively).[311] As for the effect of the chalcogen donor atom, folding angles are on average 1.75° larger in 1,2-diselenolene complexes as compared to 1,2-dithiolenes.
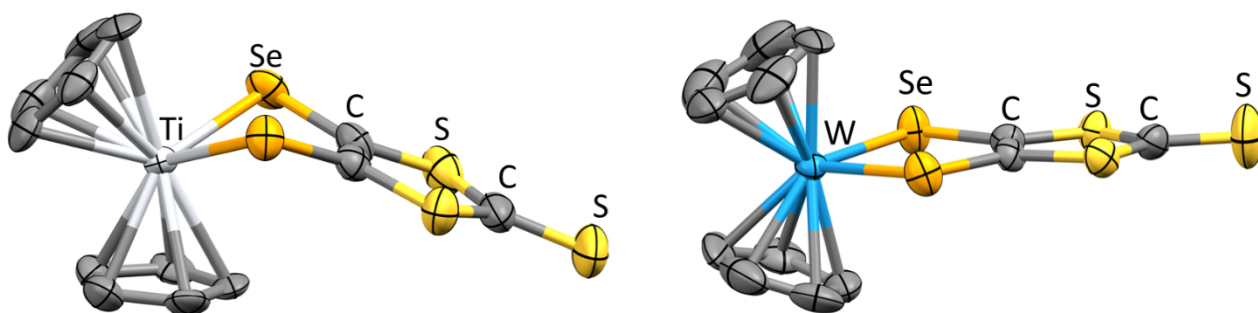
Figure 16. Drawing of [Cp$_2$Ti(dsit)][147] (left; θ = 49.80°, CCDC code XIKGAA) and [Cp$_2$W(dsit)] (right; θ = 4.53°, CCDC code QAYMEI).[67] Hydrogen atoms were omitted for clarity; thermal ellipsoids drawn at the 50% probability level.

Several authors performed variable temperature (VT) NMR studies on [Cp$_2$Ti(Se^Se)] complexes,[135,146,184,196,309] showing that the folding angles θ are associated in solution to an inversion process (Scheme 22). Indeed, the two cyclopentadienyl rings are discernible at low temperatures as two singlets due to the slow exchange between the two folded conformations. Upon raising the temperature, coalescence of the two signals appears due to a rapid inversion process. Determination

of the coalescence temperature T_c allowed to evaluate the activation energy $\Delta G^{\ddagger}$ for the inversion (Table 7), which was observed to range between 42 and > 80 kJ mol^{-1}, and to evolve with the nature of the 1,2-diselenolene ligand (the largest activation energies being associated with the most electron-rich 1,2-diselenolene donors)[147] and the Cp ring (the methylation of the Cp ring resulting in smaller activation energies).[309] This evolution also parallels that of the folding angles, the largest ones being associated with the largest activation energies. A closely similar behavior was observed with the corresponding 1,2-dithiolene complexes, whose activation energies are also very close to those measured in their 1,2-diselenolene analogues.[301,323]

Table 7. VT NMR data for [Cp$_2$M(Se^Se)] metal complexes.

Complex	Solvent	T_c (°C)	$\Delta G^{\ddagger}$ (kJ mol^{-1})	Ref.
[Cp$_2$Ti(Se$_2$C$_2$COOMe$_2$)]	CD$_2$Cl$_2$	− 27	51.5	136
[Cp$_2$Ti(Se$_2$C$_2$COOMeCF$_3$)]	CDCl$_3$	+ 27	54.3	147
[Cp$_2$Ti(bds)]	Toluene-d_8	− 9	57	197
[Cp*$_2$Ti(bds)]	Toluene-d_8	− 28	52	197
[Cp$_2$Ti(dsit)]	CD$_2$Cl$_2$	+ 28	60	309
[(η^5-MeC$_5$H$_4$)$_2$Ti(dsit)]	CD$_2$Cl$_2$	− 12	51	309
[(η^5-MeC$_5$H$_4$)$_2$Ti(dsise)]	CD$_2$Cl$_2$	− 16	50	309
[(η^5-MeC$_5$H$_4$)$_2$Ti(dsitse)]	CD$_2$Cl$_2$	− 14	50	309
[(η^5-MeC$_5$H$_4$)$_2$Ti(dsis)]	CD$_2$Cl$_2$	− 8	52	309
[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsit)]	CD$_2$Cl$_2$	− 59	43	309
[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsise)]	CD$_2$Cl$_2$	− 63	42	309
[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsitse)]	CD$_2$Cl$_2$	− 61	42	309
[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsis)]	CD$_2$Cl$_2$	− 60	43	309
[Cp$_2$Ti(ddds)]	Toluene-d_8	+ 55	67.1	147
[Cp$_2$Ti(Me-thiazds)]	CD$_3$CN	+ 42	58.5	185
[Cp$_2$Mo(bds)]	DMSO-d_6	> + 95	> 80	197
[Cp$_2$W(bds)]	DMSO-d_6	+ 38	68	197

As for the coordination around the central metal ion, which can be described by the angle (λ) between the SeMSe plane and that defined by the cyclopentadienyl centroids and the central metal atoms, an almost unperturbed tetrahedral geometry ($\lambda = 90°$) is found in all known structures, with λ values ranging between 88.55 and 90.00° (Table 6).

Concerning the other metric parameters, average M–Se bond lengths found among the existing structural examples range between 2.544 and 2.654 Å (Table 6). Ti complexes feature the shortest average M–Se bond distances, and the single Zr complex the longest ones. A comparison between neutral and oxidized Mo and W species shows a shortening of the M–Se distance upon oxidation [average Mo–Se distance = 2.598 Å in [Cp$_2$Mo(Me-thiazds)], 2.594 Å in [Cp$_2$Mo(Me-thiazds)](TCNQ), 2.586 Å in [Cp$_2$Mo(Me-thiazds)](TCNQF$_4$), 2.600 Å in [Cp$_2$Mo(Et-thiazds)], 2.572 Å in [Cp$_2$Mo(Et-thiazds)](TCNQ), 2.588 Å in [Cp$_2$Mo(Me-thiazds)](TCNQF$_4$);[311] average W–

Se distance = 2.571 Å in [Cp$_2$W(dsit)], 2.553 Å in [Cp$_2$W(dsit)](TCNQF$_4$)].[67,310,311] The other bond lengths within the metallacycles are quite constant in [Cp$_2$M(Se^Se)] complexes, with average C–S and C–C distances covering a range of 0.100 (1.836–1.936 Å) and 0.079 Å (1.328–1.407 Å), respectively. The Se–M–Se ligand bite angle varies between 81.09 and 95.78°.

On passing to [CpM(Se^Se)] complexes, 4 out of the 9 structures known (Table 8) are represented by dimeric systems held together by the formation of additional M–Se bonds (Figure 17).

Table 8. Selected average bond distances (Å) and angles (°) for the 1,2-diselenolene unit in [CpM(Se^Se)] metal complexes.

CCDC code	Complex	M–Se	Se–C	C–C	Se–M–Se	M–Se–C	Se–C–C	θ [a]	λ [b]	Ref.
AMIGOT	[CpCo(Se$_2$C$_2$Py$_2$)]$_2$	2.342	1.909	1.354	89.18	101.59	120.34	24.86	56.68	300
AMIHEK	[CpCo(Se$_2$C$_2$HCOOEt)]$_2$	2.360	1.895	1.338	90.52	99.99	122.11	22.38	55.51	300
QARZOY	[Cp*Ir(Se$_2$C$_2$(COOMe)$_2$)]	2.351	1.882	1.339	89.22	103.96	121.41	1.31	89.44	145
QASBAN	[Cp*Ir(Se$_2$C$_2$HCOOMe)]$_2$	2.456	1.935	1.362	88.31	102.51	121.71	13.16	56.81	145
QERGAW	[CpNi(ddds)]	2.240	1.888	1.348	93.35	102.84	120.40	2.37	88.97	315
QERGIE	[CpNi(bds)]	2.244	1.882	1.393	94.44	102.23	120.33	6.03	88.57	315
RAMQIG	[CpNi(dsit)]	2.250	1.867	1.359	95.78	99.96	122.00	4.84	88.23	51
RUYBES	[CpCo(bds)]$_2$	2.350	1.921	1.382	90.66	102.03	120.67	19.07	55.49	312
FAJFAB	[CpCo(Se$_2$C$_2$HPh)]	2.229	1.876	1.334	92.29	103.71	120.09	2.76	89.24	324

[a] Folding angle between the SeMSe and and SeCCSe planes of the diselenolene ligand. [b] Angle between the SeMSe plane and that defined by the cyclopentadienyl centroids.

These 4 structures all feature group 9 metals (Co and Ir), and the tendency of these systems to self-dimerization is due to the coordinatively unsaturation of the 16-electron metal ions in monomers.[312] The dimeric structures of [CpCo(Se$_2$C$_2$Py$_2$)]$_2$, [CpCo(Se$_2$C$_2$HCOOEt)]$_2$,[300] [Cp*Ir(Se$_2$C$_2$HCOOMe)]$_2$,[145] and [CpCo(bds)]$_2$ (Figure 17)[312] are all perfectly symmetric and lie on a crystallographic inversion center, the M$_2$Se$_2$ system being essentially planar. The MSe$_2$C$_2$ ring is bent around the Se–Se vector by 13.16–24.85°, and the dihedral angle (λ) between the Se–M–Se and cyclopentaldienyl amounts to 55.49–56.81°.
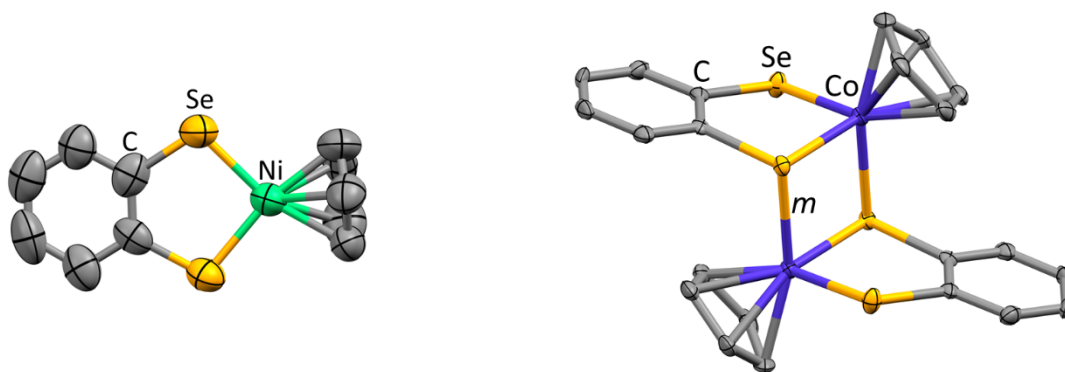

Figure 17. Drawing of the [CpNi(bds)] monomer (left, CCDC code QERGIE, ref. 315) and [CpCo(bds)]$_2$ dimer (right, CCDC code RUYBES, ref. 312, m = 2.371 Å). Hydrogen atoms were omitted for clarity; thermal ellipsoids drawn at the 50% probability level.

The 5 structures of monomeric [CpM(Se^Se)] complexes, namely [Cp*Ir(Se$_2$C$_2$HCOOMe)],[145] [CpNi(ddds)], [CpNi(bds)] (Figure 17),[315] [CpCo(Se$_2$C$_2$HPh)],[324] and [CpNi(dsit)],[51] show moderate distortion of the metallacycle (average θ = 1.31–6.03°, Table 8). The SeMSe plane is essentially perpendicular to the cyclopentadienyl ring (dihedral angle λ between the two = 85.39–89.24°, Table 8), the central metal ion featuring a two–legged piano stool geometry. A comparison between [Cp*Ir(Se$_2$C$_2$HCOOEt)]$_2$ and [Cp*Ir(Se$_2$C$_2$HCOOMe)] shows that M–Se bond lengths in the monomer are shorter than those of the dimer,[145] because the π-donating effect of Se atoms in the monomer is stronger than those of the coordinatively saturated dimer.

Another class of organometallic 1,2-diselenolene complexes features alkyl (Me, Bu) or aryl (Ph) ancillary R ligands in combination with p-block metals. The first complex of this class ever reported, [Bi(CH$_3$)(bds)],[325] was obtained by reacting Li$_2$bds with CH$_3$BiBr$_2$. Since then, several complexes of the type [M(R)$_2$(Se^Se)], all featuring Ge or Sn as the metal ion, were prepared starting from analogous lithium salts,[155,202,203,204,206,207,293] from 1,3-diselenole-3-ones (see route v in Scheme 3)[155,326,327] or cyanoethylseleno-substituted precursors,[327] or through ligand exchange reactions.[196,264,265,266] The only Sb complex of this type, [Sb(Ph)(dsit)], was obtained from dsit(COPh)$_2$ (route iii in Scheme 5) and dichlorophenylstibine.[51] Finally, two [Si(L)(bds)$_2$] complexes (L = dimethylaminophenyl, morpholinomethyl) were obtained through the reaction of 1,2-benzenediselonol (route v in Scheme 9) with the corresponding trihydridosilane precursors.[201]

In addition to the two classes of compounds mentioned above, 1,2-diselenolene ligands can be found in mixed-ligand complexes in combination with organic ligands as varied as alkenes,[33] $tris$(1-cyclohepta-2,4,6-trienyl)phosphane,[328] and carbon monoxide,[136,329] often involving more exotic synthetic pathways (Figure 18).
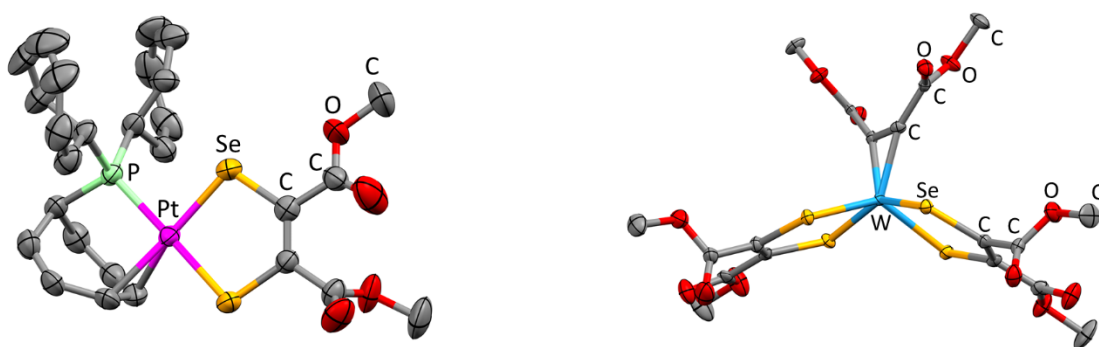
Figure 18. Drawings of [Pt(P(C$_7$H$_7$)$_3$)(Se$_2$C$_2$COOMe$_2$)] (left; CCDC code MEZZOG, ref. 328) and [W(DMAD)(Se$_2$C$_2$COOMe$_2$)$_2$] (right; CCDC code OJIBEP, ref. 33); P(C$_7$H$_7$)$_3$ = $tris$(1-cyclohepta-2,4,6-trienyl)phosphane. Hydrogen atoms were omitted for clarity; thermal ellipsoids drawn at the 50% probability level.

It is worth noting that 1,2-diselenolene systems are also found in organometallic iron clusters of the type [Fe$_2$(CO)$_6$(Se^Se)], as those first described in the 1980s by Mayr and Pannell[330] and subsequently extensively studied by Mathur,[331,332,333,334,335,336,337,338,339,340,341,342,343,344,345,346,347,348,349,350] the description of which is beyond the scope of this review, since in these compounds the 1,2-diselenolene ligand displays a bridging rather than chelating coordination mode, resulting in different electronic structure and properties.

3.2. Properties and applications

The physical-chemical properties of metal complexes displaying 1,2-diselenolene ligands have been subject to extended investigations over the past decades. The interest of the researchers has been particularly focused on the electrochemical and optical properties of the title complexes in solution, and on their electrical and magnetic properties in the solid state, often showing rationalizable structure-property relationships which can be exploited for their fine-tuning. In the following sections, the properties and applications, as well as the peculiar reactivity, of 1,2-diselenolene metal complexes will be reviewed.

3.2.1. Electrochemical properties

A peculiar property of metal *bis*(1,2-dichalcogenolene) complexes is their rich electrochemistry, testified by their ability to assume different molecular charges, reversibly accessible by chemical or electrochemical means. In particular, most square-planar *bis*(1,2-dichalcogenolene) metal complexes belong to a three- (Scheme 23) or, rarely, four-membered electron-transfer series.
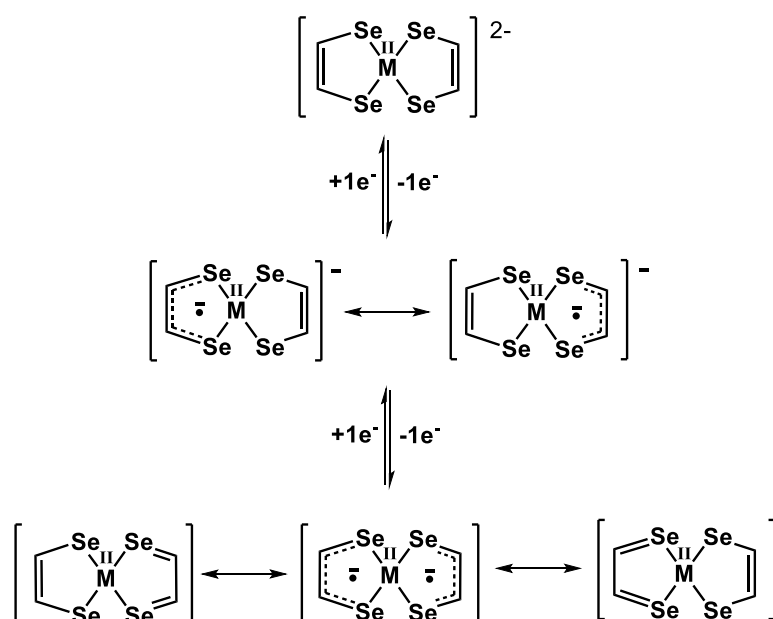
Scheme 23. Redox electron-transfer series in *bis*(1,2-diselenolene) complexes of d^8 metal ions.

Over the past 50 years, there has been a debate on the electronic structure of these complexes, the assignment of the charge to the ligands and the central metal ion, and the *innocence* of 1,2-dichalcogenolene species. The seminal works by Wieghardt, Solomon and coworkers[240,241,351,352,353] on different *bis*(1,2-dithiolene) complexes, combining an experimental and theoretical approach, shed some light on this matter. These authors inferred that in most complexes the redox processes are ligand-based, due to the fact that the molecular orbitals involved are predominantly localized on the ligands, particularly in complexes featuring metal ions such as Pd^{II} or Au^{III}, where the high effective nuclear charge of the metal causes their nd orbitals ($n = 4$ and 5, respectively) to lie at very low energies compared to those of the ligand π-donor orbitals, thus preventing the metal-ligand mixing of the resulting frontier-molecular orbitals in the complex. The metal-ligand mixing in the latter orbitals is slightly larger in the case of Pt^{II} or Ni^{II}, and yet more pronounced in the case of cobalt, where the oxidation state of the metal ion and the nature of the redox processes cannot be unambiguously assigned. These conclusions were recently extended to heteroleptic push-pull *bis*(1,2-dithiolene) Pd complexes.[243] On the other hand, in 1,2-dithiolene copper complexes some of the redox processes are metal-centered. More in general, when metal-centered and ligand-centered molecular orbitals lie at different energies, the related redox processes can be assigned to the metal or the ligand without uncertainty. Thus, redox properties are strongly dependent on the nature of the central metal ion, and the term *noninnocent*, rather than to the ligand itself, is applied properly when it is referred to a particular combination of the metal and the ligand. These considerations have recently been extended to *bis*(1,2-diselenolene) complexes.[242] In fact, the electronic structure and electrochemical properties of 1,2-diselenolene ligands and complexes have been recently the subject of a series of theoretical investigations,[56,59,72,354,355,356] prompted in part by their potential applications as electrocatalysts (see section 3.2.5).[55,56,72]

The redox potentials of a selection of homoleptic *bis*(1,2-diselenolene) complexes are summarized in Table 9. Electrochemical data provide fundamental information for the understanding of the unique physical and chemical properties of these systems and are indispensable for the design of complexes featuring properties of interest, such as superconductors. Moreover, the spectral properties of *bis*(1,2-diselenolene) complexes are related to their redox properties (see section 3.2.2).

41

Table 9. Redox potentials for selected homoleptic *bis*(1,2-diselenolene) metal complexes.

Complex	Redox Potential (V) [a,b]				Reference electrode	Solvent	Ref.
	1/0	0/–1	–1/–2	–2/–3			
[Ni(tds)$_2$]$^{2-}$		0.89	–0.17		SCE	CH$_2$Cl$_2$	32
		0.90	–0.06		SCE	CH$_2$Cl$_2$	148
[Ni(tds)$_2$]$^{-}$		0.89 (ir)	–0.17		SCE	CH$_2$Cl$_2$	3
		0.84 (ir)	–0.16		SCE	CH$_3$CN	263
[Ni(Se$_2$c$_2$HMe)$_2$]$^{-}$		–0.04	–0.74		SCE	CH$_2$Cl$_2$	148
[Ni(dmeds)$_2$]$^{-}$		–0.02	–0.88		SCE	CH$_2$Cl$_2$	148
[Ni(mns)$_2$]$^{2-}$			0.310 (0.265)		Ag/AgCl	CH$_3$CN	160
[Ni(dsit)$_2$]$^{2-}$			–0.47 (0.089)		Ag/Ag$^+$	CH$_3$CN	170
		0.250 (qr)	–0.138		SCE	DMF/CH$_3$CN 3:2	173
			–0.170		SCE	CH$_3$CN	173
			-0.095		SCE	DMF	173
		0.385 (ir)	–0.070	–0.300 (ir)	SCE	DMF	262,357
		0.240 (ir)	–0.160	0.00 (ir)	SCE	Acetone	262
		–0.050 (ir)	–0.250	–0.260 (ir)	SCE	CH$_3$CN	262
[Ni(dsit)$_2$]$^{-}$			–0.47 (0.089)		Ag/Ag$^+$	CH$_3$CN	170
[Ni(dsis)$_2$]$^{2-}$		0.230 (ir)	–0.150	–0.300 (ir)	SCE	DMF	262,357
		–0.130 (ir)	–0.320	–0.400 (ir)	SCE	CH$_3$CN	262
[Ni(dsis)$_2$]$^{-}$		0.097 (ir)	–0.12		SCE	DMF/CH$_3$CN 3:2	168
[Ni(dsise)$_2$]$^{2-}$		0.350 (ir)	–0.050	–0.220 (ir)	SCE	DMF	262,357
		0.250 (ir)	–0.120	0.060 (ir)	SCE	Acetone	262
		–0.070 (ir)	–0.220	–0.320 (ir)	SCE	CH$_3$CN	262
			–0.123		SCE	DMF/CH$_3$CN 3:2	259
[Ni(bds)$_2$]$^{-}$			–0.47		SCE		191,192
[Ni(pds)$_2$]$^{2-}$			–0.12 (–0.165)		Ag/AgCl	CH$_3$CN	254
			–0.16 (–0.205)		Ag/AgCl	CH$_3$CN	254
			–0.03 (–0.075)		Ag/AgCl	CH$_3$OH	254
[Ni(ddds)$_2$]$^{-}$		–0.23 (0.113, ir)	–0.97 (–0.627)		Ag/AgNO$_3$	CH$_3$CN	273
	0.71 (0.665, ir)	0.16 (0.115)	–0.60 (–0.645)		Ag/AgCl	PhCN	256
[Ni(Me-thiazds)$_2$]$^{2-}$		0.21 (qr)	–0.24		SCE	CH$_3$CN	60
[Pd(dsit)$_2$]$^{2-}$			–0.34 (0.219, ir)		Ag/Ag$^+$	CH$_3$CN	170
			–0.03		SCE	CH$_3$CN	173
			–0.0 (–0.045, ir)		Ag/AgCl	CH$_3$CN	359
		0.250 (ir)	0.125	0.130 (ir)	SCE	DMF	262,357
		0.055 (ir)	0.0	–0.080 (ir)	SCE	Acetone	262
[Pd(dsis)$_2$]$^{2-}$		0.200 (ir)	0.065	0.030 (ir)	SCE	DMF	262,357
[Pd(dsise)$_2$]$^{2-}$		0.230 (ir)	0.150	0.100 (ir)	SCE	DMF	262,357
		0.115 (ir)	0.055	–0.025 (ir)	SCE	Acetone	262
[Pd(Me-thiazds)$_2$]$^{2-}$		0.25 (qr)	–0.03		SCE	CH$_3$CN	60
		0.17 (qr)	–0.12		SCE	CH$_2$Cl$_2$	60
[Pt(tds)$_2$]$^{-}$		0.74	–0.13		SCE	CH$_3$CN	263
[Pt(mns)$_2$]$^{2-}$			0.272 (0.227)		Ag/AgCl	CH$_3$CN	160
[Pt(dsit)$_2$]$^{2-}$		0.355 (ir)	–0.130	0.090 (ir)	SCE	DMF	262,357
		0.225 (ir)	–0.210	–0.45 (ir)	SCE	Acetone	262
[Pt(dsise)$_2$]$^{2-}$		0.280 (ir)	–0.095		SCE	DMF	262,357
		0.200 (ir)	–0.195	0.600 (ir)	SCE	Acetone	262
[Cu(tds)$_2$]$^{-}$			–0.42		SCE	CH$_2$Cl$_2$	3
		0.94 (ir)	–0.42		SCE	CH$_3$CN	263
[Cu(bds)$_2$]$^{-}$			–0.75		SCE		192
[Cu(dsis)$_2$]$^{2-}$			–0.8 (ir)	–0.15	SCE	CH$_3$CN	71
[Cu(pds)$_2$]$^{-}$			–0.54 (–0.585)		Ag/AgCl	CH$_3$CN	252,255
[Au(tds)$_2$]$^{-}$		1.04 (ir)	–1.10		SCE	CH$_3$CN	263
[Au(dsis)$_2$]$^{-}$		0.34 (ir)	–0.70		SCE	DMF	45
[Au(Et-thiazds)$_2$]$^{-}$		0.52 (ir)	–0.89 (ir)		SCE	CH$_2$Cl$_2$	41
[Au(L)$_2$]$^{-}$ [c]	0.88	0.44	–1.07 (ir)		SCE	CH$_2$Cl$_2$	41
[Co(bds)$_2$]$^{-}$			–0.92		SCE		192
			–1.04 (0.733, ir)		Fc/Fc$^+$	CH$_3$CN	55
			–1.04 (0.733, ir)		Fc/Fc$^+$	CH$_3$CN/H$_2$O 1:1	55
[Zn(Me-thiazds)$_2$]$^{2-}$			0.13 (ir)		SCE	CH$_3$CN	60
[Fe(dsis)$_2$]$^{-}$	+0.29 (ir)	+0.14 (ir)	–0.43		SCE	DMF	260

[a] Numbers in parentheses are vs. SCE, converted by using the following conversion factors: $E_{1/2}$(SCE) = $E_{1/2}$(Ag/AgCl) –0.045 V; $E_{1/2}$(SCE) = $E_{1/2}$(Ag/Ag$^+$) +0.559 V; $E_{1/2}$(SCE) = $E_{1/2}$(Fc/Fc$^+$) +0.307 V; $E_{1/2}$(SCE) = $E_{1/2}$(Ag/AgNO$_3$) +0.343 V; see refs.358 and 360.
[b] ir = irreversible process; qr = quasireversible process. [c] L = *N*-ethyl-1,3-thiazoline-2-one-4,5-diselenolate.

The stability of these complexes in their mono- or dianionic forms is attested by the reversibility of the [M(Se^Se)$_2$]$^{-/2-}$ redox process shown by most complexes, irrespective of the nature of the Se^Se
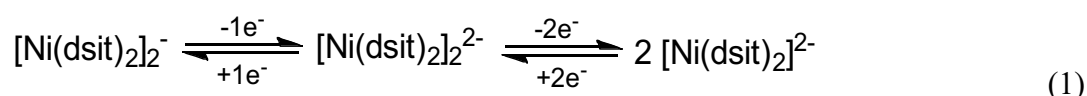
ligand and metal ion. In many cases, compounds featuring the *bis*(1,2-diselenolene) metal complexes in these different oxidation states could be isolated, by using oxidizing/reducing agents (see section 3.1.1) or through complete or partial electrochemical oxidation.[70,71,262,266,276,359] Some salts containing 1,2-diselenolene complexes featuring fractional charges (NIOS salts) were also prepared,[70,71,260,262,266,276] the crystal structures of some of which have been discussed above. Species in more reduced states are observed to be less stable, the corresponding $[M(Se^\wedge Se)_2]^{2-/3-}$ reduction being irreversible for all complexes but $[Cu(dsis)_2]^{2-}$.[71] The same consideration can be drawn for the oxidized species, the $[M(Se^\wedge Se)_2]^{0/-}$ process being irreversible for all complexes but for $[Pt(tds)_2]^-$, whose neutral $[Pt(tds)_2]$ form could also be isolated.[263] In the case of $[Au(L)_2]^-$ (L = N-ethyl-1,3-thiazoline-2-one-4,5-diselenolate) and $[Ni(ddds)_2]^-$, the oxidation to cationic complexes was observed electrochemically.[41,256]

In complexes featuring disubstituted ethylene-1,2-diselenolato ligands $R_2C_2Se_2^{2-}$, the ease of oxidation parallels the electron-donating and withdrawing ability of the substituent groups R, decreasing in the order Me > CF$_3$ > CN, as highlighted in the case of nickel complexes,[3,32,148,160,263] and in agreement with the trend observed for 1,2-dithiolene analogues.[360] On the other hand, in complexes featuring the dsit^{2-} ligand and its analogues the redox potential of the $[M(Se^\wedge Se)_2]^{-/2-}$ couple increases in the order dsis^{2-} < dsit^{2-} < dsise^{2-}.[262,357] As far as the role of the central metal ion is concerned, within group 10 metal complexes the stability of the monoanionic species towards reduction increases in the order Pd < Ni < Pt.[262,357]

In general, 1,2-diselenolene complexes of group 10 metal ions tend to exhibit higher potentials for the $[M(Se^\wedge Se)_2]^{-/2-}$ redox process than the corresponding $[M(S^\wedge S)_2]^{-/2-}$ 1,2-dithiolene species (see for example the following potentials $E_{1/2}$ for selected redox isologous couples (E = S, Se): $[Ni(Me-thiazdt)_2]^{2-}/[Ni(Me-thiazds)_2]^{2-}$, –0.29/–0.24 V; $[Pd(Me-thiazdt)_2]^{2-}/[Pd(Me-thiazds)_2]^{2-}$, –0.11/–0.03 V);[60] $[Ni(dmit)_2]^{2-}/[Ni(dsit)_2]^{2-}$, –0.125/–0.070 V; $[Pd(dmit)_2]^{2-}/[Pd(dsit)_2]^{2-}$, 0.060/0.125 V; $[Pt(dmit)_2]^{2-}/[Pt(dsit)_2]^{2-}$, –0.195/–0.130 V; $[Ni(dmise)_2]^{2-}/[Ni(dsise)_2]^{2-}$, –0.075/–0.050 V; $[Pd(dmise)_2]^{2-}/[Pd(dsise)_2]^{2-}$, 0.100/0.150 V; $[Pt(dmise)_2]^{2-}/[Pt(dsise)_2]^{2-}$, –0.160/ –0.095 V;[262,357] $[Ni(bdt)_2]^-/[Ni(bds)_2]^-$, –0.55/–0.47 V;[192] $[Ni(mnt)_2]^{2-}/[Ni(mns)_2]^{2-}$, 0.271/0.310 V vs Ag/AgCl; $[Pt(mnt)_2]^{2-}/[Pt(mns)_2]^{2-}$, 0.259/0.272 V vs Ag/AgCl;[160] $[Pt(tfd)_2]^-/[Pt(tds)_2]^-$, –0.27/–0.13 V;[263] $[Ni(dddt)_2]^-/[Ni(ddds)_2]^-$,–0.71/–0.60 V vs Ag/AgCl;[256] all potentials vs SCE if not specified otherwise). The only exception is possibly represented by the reduction potentials of $[Ni(tfd)_2]^-$ and $[Ni(tds)_2]^-$ ($E_{1/2}$ = –0.12 and –0.16 V vs SCE, respectively).[263] This testifies for a more oxidizing nature of 1,2-diselenolene as compared to 1,2-dithiolene metal complexes, which is in agreement with the stabilization of the HOMO calculated at DFT level.[62,242] An opposite trend was observed for complexes of group 9 and 11 metal ions, reflecting the relative stability of their occupied frontier

molecular orbitals due to a lower contribution of the metal to their composition, as inferred by DFT calculations[55,242] (see for example, the following potentials $E_{1/2}$ for selected $[M(E^\wedge E)_2]^{-/2-}$ redox couples (E = S, Se): $[Cu(tfd)_2]^-/[Cu(tds)_2]^-$,–0.01/–0.42 V;[263] $[Co(bdt)_2]^-/[Co(bds)_2]^-$, –0.88/–0.92 V; $[Cu(bdt)_2]^-/[Cu(bds)_2]^-$, –0.64/–0.75 V;[192] $[Au(dsit)]^{2-}/[Au(dsis)]^{2-}$, –0.62/–0.70 V;[45] $[Cu(pdt)_2]^-$ /$[Cu(pds)_2]^-$, –0.33/–0.54 V vs Ag/AgCl;[255] all potentials vs SCE if not specified otherwise).

The analysis of the redox behavior of the dimer $(Bu_4N)_2[Ni(dsit)_2]_2$[272] indicates that the metal complex keeps its dimeric form when partially reduced and undergoes dissociation into monomers when fully reduced according to Eq. 1, as previously suggested for related 1,2-dithiolene species.[360]

$$[Ni(dsit)_2]_2^- \underset{+1e^-}{\overset{-1e^-}{\rightleftharpoons}} [Ni(dsit)_2]_2^{2-} \underset{+2e^-}{\overset{-2e^-}{\rightleftharpoons}} 2\,[Ni(dsit)_2]^{2-}$$

(1)

Accordingly, dimeric systems can be electrochemically synthesized through the oxidation of the corresponding monomers, as in the case of $[Ni(ddds)_2]_2$.[68]

The few electrochemical reports on *tris*(1,2-diselenolene) complexes, limited to group 5 metal ions (Table 10), suggest that the stability of monoanionic species as compared to dianions increases along the series Mo < W < V (as also recently elucidated by DFT calculations),[355] and that it is higher for 1,2-diselenolene as compared to 1,2-dithiolene complexes (see for example, the following potentials $E_{1/2}$ vs SCE for selected $[M(E^\wedge E)_3]^{-/2-}$ redox couples (E = S, Se): $[V(tfd)_3]^-/[V(tds)_3]^-$, 0.08/–0.07 V; $[Mo(tfd)_3]^{2-}/[Mo(tds)_3]^{2-}$, 0.25/0.22 V; $[W(tfd)_3]^{2-}/[W(tds)_3]^{2-}$, 0.12/0.16 V;[3] $[W(dsit)_3]^{2-}$ /$[W(dsis)_3]^{2-}$, 0.05/–0.04 V).[70]

Table 10. Redox potentials for selected homoleptic *tris*(1,2-diselenolene) metal complexes.

Complex	Redox Potential (V)[a]			Reference electrode	Solvent	Ref.
	0/–1	–1/–2	–2/–3			
$[V(tds)_3]^-$		–0.07	–1.05	SCE	CH_2Cl_2	3,32
$[Mo(tds)_3]^{2-}$	0.78	0.22	–1.56	SCE	CH_2Cl_2	3
$[W(tds)_3]^{2-}$	0.70	0.16		SCE	CH_2Cl_2	3
$[W(dsis)_3]^{2-}$	0.04 (ir)	–0.03 (ir)		SCE	CH_2Cl_2	70

[a] ir = irreversible process

Heteroleptic $[M(S^\wedge S)(Se^\wedge Se)]^{x-}$complexes (x = 0–2; Table 11) show redox potentials intermediate between those of the corresponding homoleptic complexes, thus suggesting that the electrochemical properties of the mixed-ligand systems can be tuned by the ligand combination (see for example, the following $E_{1/2}$ reduction potentials for selected $[Ni(S^\wedge S)_2]^-$ complexes: $[Ni(mnt)_2]^-$, –0.13 V; $[Ni(dmit)_2]^-$, –0.49 V;[273] $[Ni(edo)_2]^-$: –1.55 V vs Ag/AgNO₃).[278]

Table 11. Redox potentials for selected heteroleptic [M(S^S)(Se^Se)]$^{x-}$ metal complexes.

Complex	Redox Potential (V) [a]			Reference electrode	Solvent	Ref.
	1/0	0/–1	–1/–2			
[Ni(dddse)(mnt)]$^-$		0.12 (ir)	–0.59	Ag/AgNO$_3$	CH$_3$CN	273
[Ni(dddse)(dmit)]$^-$		0.14 (ir)	–0.72	Ag/AgNO$_3$	CH$_3$CN	273
[Ni(ddds)(edo)]	–0.08 (ir)	–0.72	–1.46	Ag/AgNO$_3$	PhCN	278
[Ni(dmit)(dsit)]$^{2-}$			–0.050	SCE	DMF	276
[Ni(Me$_2$pipdt)(dsit)]	0.610 (ir)	–0.505	–0.966	Ag/AgCl	DMF	279
[Ni(Bz$_2$pipdt)(dsit)]	0.86 (ir)	–0.39	–0.84	Ag/AgCl	DMF	54
[Pd(Bz$_2$pipdt)(dsit)]	0.69 (ir)	–0.41	–0.91	Ag/AgCl	DMF	54
[Pd(Bz$_2$pipdt)(dsit)]	0.65 (ir)	–0.49	–1.04	Ag/AgCl	DMF	54

[a] ir = irreversible process

Dimine-diselenolate complexes [M(N^N)(Se^Se)] show the ability to assume different molecular charges (Table 12), and other mixed-ligand systems whose redox properties were studied also include clusters[234,235,292,293,307,295] and other polynuclear complexes of the type {tto[M(dsit)]$_2$},[2–282,283,284] and complexes featuring mono- or bi-dentate phosphines.[211] Of particular relevance is the recent cyclic voltammetry investigation on the complex [Ni(bds)(dppf)][74] and coordination polymers [M(L)]$_n$ (M = Ni, Co; L = benzene-1,2,4,5-tetraselenolate)[73] as catalysts for the production of dihydrogen through the electrochemical reduction of protons and water, respectively.

Table 12. Redox potentials for selected diimine-diselenolate metal complexes [Pt(N^N)(Se^Se)].

Complex	Redox Potential (V) [a]				Reference electrode	Solvent	Ref.
	2/1	1/0	0/–1	–1/–2			
[Pt(bipy)(bds)]	0.10 (ir)	–0.21 (ir)	–1.78		Fc/Fc$^+$	PhCN	58
[Pt(bipy)(Me-dset)]		0.044 (qr)	–1.607	–2.245	Fc/Fc$^+$	DMSO	63
[Pt(phen)(Me-dset)]		–0.027 (qr)	–1.620		Fc/Fc$^+$	DMSO	63
[Pt(Et-pa)(dsit)]		0.68 (ir)			SCE	DMF	289
[Pt(Pr^i-pa)(dsit)]		0.60 (ir)			SCE	DMF	289
[Pt(bipy)(dsit)]		0.59 (ir)			SCE	DMF	289

[a] ir = irreversible process; qr = quasireversible process.

Among organometallic mixed-ligand 1,2-diselenolene complexes, those featuring Cp ligand derivatives were studied for their electrochemical properties.[304] An analysis of the redox potentials for these systems (Table 13) shows that all 1:1 [CpCo(Se^Se)] complexes, usually isolated in the neutral state, feature reversible reduction processes corresponding to the [CpCo(Se^Se)]$^{0/-}$ couple, and assigned to the Co$^{III/II}$ reduction.

Table 13. Redox potentials for selected [Cp$_n$M(Se^Se)] metal complexes (n = 1, 2).

Complex	Redox Potential (V)[a,b]			Reference electrode	Solvent	Ref.
	2/1	1/0	0/–1			
[CpNi(dsit)]		0.32 (0.627)	–0.74 (–0.433)	Fc/Fc$^+$	CH$_2$Cl$_2$	315
		0.28 (0.587)	–0.72 (–0.413)	Fc/Fc$^+$	CH$_2$Cl$_2$	51
[CpNi(bds)]		0.30 (0.067)	–1.04 (–0.733)	Fc/Fc$^+$	CH$_2$Cl$_2$	315
[CpNi(ddds)]		0.03 (0.337)	–1.07 (–0.763)	Fc/Fc$^+$	CH$_2$Cl$_2$	315
[CpCo(Se$_2$C$_2$Ph$_2$)]			–1.08 (–0.521)	Ag/Ag$^+$	CH$_3$CN	61,140,361
			–1.12 (–0.813)	Fc/Fc$^+$	DMF	135
[CpCo(Se$_2$C$_2$HPh)]			–1.09 (–0.531)	Ag/Ag$^+$	CH$_3$CN	61,140
			–1.08 (–0.773)	Fc/Fc$^+$	CH$_3$CN	135
			–1.14 (–0.833)	Fc/Fc$^+$	DMF	135
[(η^4-C$_4$Me$_4$)Co(Se$_2$C$_2$HPh)]			–1.40 (–1.093)	Fc/Fc$^+$	DMF	135
[CpCo(Se$_2$C$_2$(COOMe$_2$)]			–0.85 (–0.291)	Ag/Ag$^+$	CH$_3$CN	61
[CpCo(Se$_2$C$_8$H$_{12}$)]			–0.652	SCE	CH$_3$CN/CH$_3$OH 3:1	221
			–1.24 (–0.933)	Fc/Fc$^+$	CH$_3$CN	135
[CpCo(Se$_2$C$_8$H$_{10}$)]			–0.830	SCE	CH$_3$CN/CH$_3$OH 3:1	221
			–1.18 (–0.873)	Fc/Fc$^+$	CH$_3$CN	135
			–1.20 (–0.893)	Fc/Fc$^+$	DMF	135
[CpCo(Se$_2$C$_8$H$_8$)]			–0.815	SCE	CH$_3$CN/CH$_3$OH 3:1	135
			–1.15 (–0.843)	Fc/Fc$^+$	CH$_3$CN	135
[(η^4-C$_4$Me$_4$)Co(Se$_2$C$_8$H$_{12}$)]			–1.52 (–1.213)	Fc/Fc$^+$	CH$_3$CN	135
[(η^4-C$_4$Me$_4$)Co(Se$_2$C$_8$H$_{10}$)]			–1.46 (–1.153)	Fc/Fc$^+$	CH$_3$CN	135
			–1.47 (–1.163)	Fc/Fc$^+$	DMF	135
[(η^4-C$_4$Me$_4$)Co(Se$_2$C$_8$H$_8$)]			–1.40 (–1.093)	Fc/Fc$^+$	CH$_3$CN	135
			–1.43 (–1.123)	Fc/Fc$^+$	DMF	135
[(η^4-C$_4$Me$_4$)Pt(dsit)]		0.26 (0.567, ir)	–1.85 (–1543 ir)	Fc/Fc$^+$	CH$_2$Cl$_2$	306
[Cp$_2$Ti(Me-thiazds)]		0.78 (ir)	–0.86	SCE	CH$_2$Cl$_2$	185
[Cp$_2$Ti(Se$_2$C$_2$(COOMe)$_2$)]		0.55 (1.109)	–1.20 (–0.641)	Ag/Ag$^+$	CH$_3$CN	136
		057 (0.877, ir)	–1.32 (–1.013)	Fc/Fc$^+$	CH$_2$CH$_2$	147
[Cp$_2$Ti(Se$_2$C$_2$COOMeCF$_3$)]		0.70 (1.007, ir)	–1.36 (–1.053)	Fc/Fc$^+$	CH$_2$CH$_2$	147
[Cp$_2$Ti(dsit)]		0.51 (0.817, ir)	–1.21 (–0.086)	Fc/Fc$^+$	CH$_2$CH$_2$	147
			–0.62 (–0.665)	Ag/AgCl	CH$_2$CH$_2$	309
[(η^5-MeC$_5$H$_4$)$_2$Ti(dsit)]			–0.68 (–0.725)	Ag/AgCl	CH$_2$CH$_2$	309
[(η^5-MeC$_5$H$_4$)$_2$Ti(dsise)]			–0.64 (–0.685)	Ag/AgCl	CH$_2$CH$_2$	309
[(η^5-MeC$_5$H$_4$)$_2$Ti(dsitse)]			–0.66 (–0.705)	Ag/AgCl	CH$_2$CH$_2$	309
[(η^5-MeC$_5$H$_4$)$_2$Ti(dsis)]			–0.69 (–0.735)	Ag/AgCl	CH$_2$CH$_2$	309
[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsit)]			–0.87 (–0.915)	Ag/AgCl	CH$_2$CH$_2$	309
[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$Ti(dsise)]			–0.86 (–0.905)	Ag/AgCl	CH$_2$CH$_2$	309
[Cp$_2$Ti(bds)]		0.27 (0.577, ir)	–1.44 (–0.556)	Fc/Fc$^+$	CH$_2$CH$_2$	147
[Cp$_2$Ti(ddds)]		0.21 (0.517, ir)	–1.48 (–1.163)	Fc/Fc$^+$	CH$_2$CH$_2$	147
[(η^5-C$_5$(CH$_3$)$_4$C$_2$H$_5$)$_2$V(dsis)]			–0.89 (–0.935)	Ag/AgCl	CH$_2$CH$_2$	309
[(η^5-MeC$_5$H$_4$)$_2$V(dsise)]		0.54 (0.495)	–0.79 (–0.835)	Ag/AgCl	CH$_2$CH$_2$	309
[(η^5-MeC$_5$H$_4$)$_2$V(dsis)]		0.52 (0.475)	–0.84 (–0.885)	Ag/AgCl	CH$_2$CH$_2$	309
[Cp$_2$Mo(Me-thiazds)]	0.82	0.26		SCE	CH$_2$CH$_2$	311
[Cp$_2$Mo(Et-thiazds)]	0.82	0.26		SCE	CH$_2$CH$_2$	311
[Cp$_2$Mo(dsit)]	1.03	0.42		SCE	CH$_2$CH$_2$	311

[a] Numbers in parentheses are vs. SCE, converted by using the following conversion factors: $E_{1/2}$(SCE) = $E_{1/2}$(Ag/AgCl) –0.045 V; $E_{1/2}$(SCE) = $E_{1/2}$(Ag/Ag$^+$) +0.559 V; $E_{1/2}$(SCE) = $E_{1/2}$(Fc/Fc$^+$) +0.307 V; see ref. 360. [a] ir = irreversible process; qr = quasireversible process.

Electron-withdrawing substituents at the 1,2-diselenolene or cyclopentadienyl ligand shift the potential of this reduction to less negative values, while electron-donating substituents induce the opposite effect.[61,135] The effects of the substituents are independent of each other, and therefore additive. The change brought about by the methylation of the arene ring is particularly intense.[61] Compared to their sulphured analogues, [CpCo(Se^Se)] complexes tend to show more positive reduction potentials, suggesting that the central metal ion should be more positively charged when coordinated by 1,2-diselenolene ligands as compared to 1,2-dithiolene ligands (see for example, the following reduction potentials $E_{1/2}$ for selected [CpCo(S^S)]^0 complexes: [CpCo(S$_2$C$_8$H$_{12}$)], –1.37 V vs Fc/Fc$^+$;[135] [CpCo(S$_2$C$_2$Ph$_2$)], –1.16 V vs Ag/Ag$^+$; [CpCo(S$_2$C$_2$HPh$_2$)], –1.17 V vs Ag/Ag$^+$;

[Cp$_2$Ti(S$_2$C$_2$(COOMe)$_2$)], –0.91 V vs Ag/Ag$^+$).[61,140] The possibility of a photochemical reduction in the presence of triethanolamine as electron donor was also reported for [CpCo(Se$_2$C$_2$Ph$_2$)].[361]

[CpNi(Se^Se)] complexes also feature a reversible oxidation in addition to the reduction. Noteworthy is the large electrochemical window of stability of these neutral radical species, the difference between the oxidation and reduction potentials ranging between 1.00 and 1.34 V.[299] The redox potentials of these metal complexes were found to be close to those of the corresponding 1,2-dithiolene complexes,[315] indicating a moderate if not negligible dependence on the nature of the chalcogen donor atom (see for example, the following reduction potentials $E_{1/2}$ for selected [CpNi(S^S)]^0 complexes: [CpNi(dddt)], –1.06 V vs Fc/Fc$^+$; [CpNi(bdt)], –1.00 V vs vs Fc/Fc$^+$; [CpNi(dmit)], –0.72 V vs Fc/Fc$^+$).[315] Neutral [Cp$_2$Ti(Se^Se)] complexes also feature a reversible reduction corresponding to the Ti$^{IV/III}$ couple, whose potential shows the same dependence on the electron-withdrawing/-donating properties of the ligands as discussed for [CpCo(Se^Se)] complexes.[147,185] A 1,2-diselenolene-centred oxidation was reported for [Cp$_2$Ti(Me-thiazds)] and [Cp$_2$Ti(dsit)] complexes, whose irreversibility was proposed to be a consequence of the decoordination of the oxidised ligand form the complex.[185]

3.2.2. Optical properties

Notwithstanding the amount of literature on the linear and nonlinear optical properties and related applications of *bis*(1,2-dithiolene) metal complexes, there is a substantial lack of studies on the optical properties of 1,2-diselenolene analogues. One of the most striking features of homoleptic *bis*(1,2-dithiolene) metal complexes (particularly square-planar complexes featuring d^8 metal ions) is in fact their intense molecular absorption in the Visible-Near Infrared (Vis-NIR) region, whose wavelength depends on the nature of the ligand, the metal ion, the global charge of the complex (electrochromism) and the solvent (solvatochromism).[17,23,24,362,363] Notably, the NIR absorption of some *bis*(1,2-dichalcogenolene) metal complexes allowed for their employment as constituents of a heat ray shielding composition recently patented by Mitsubishi Materials Corporation.[364]

In neutral complexes this absorption is assigned to the monoelectronic π–π* transition between the HOMO and the LUMO, while in monoanionic radical complexes, the SOMO-1→SOMO excitation is involved.[241,365,366] In all cases, the involved molecular orbitals are delocalized on the ligands, with the latest having a contribution from the metal also (Figure 19).[240,367,368,369]

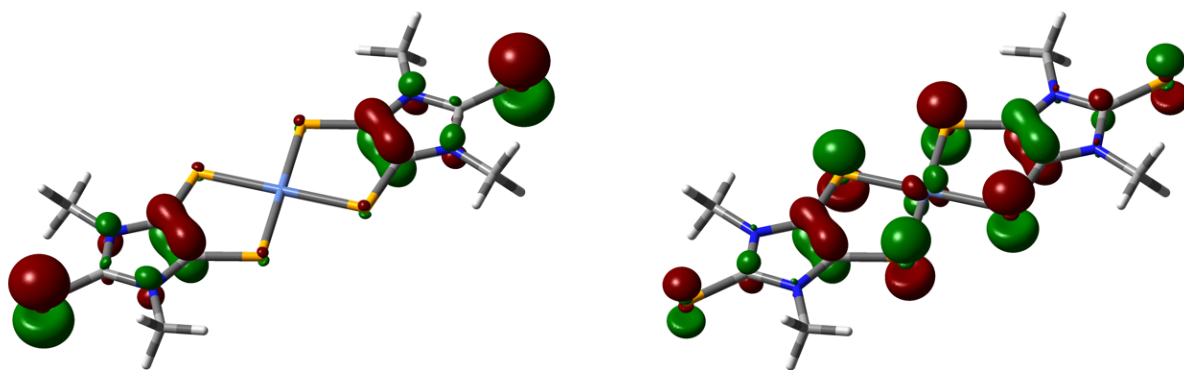**Figure 19.** Kohn-Sham HOMO (left) and LUMO (right) isosurfaces calculated for [Ni(Me$_2$simds)$_2$] at DFT level (mPW1PW functional, pVDZ basis set for C, H, N, S, Se; CRENBL BS/ECP for Ni). Cutoff value = 0.05 |e|.[62]

The Vis-NIR absorption spectral features were described for less than twenty *bis*(1,2-diselenolene) complexes (Table 14), almost all featuring group 10 metal ions.

Table 14. NIR spectral data for *bis*(1,2-diselenolene) metal complexes.

Complex	λ_{max} (nm)	ε (M^{-1} cm^{-1})	Solvent	Ref.
[Ni(Se$_2$C$_2$HMe)$_2$]$^-$	900	2860	CH$_2$Cl$_2$	148
[Ni(Se$_2$C$_2$Me$_2$)$_2$]$^-$	920	7558	CH$_2$Cl$_2$	148
[Ni(bds)$_2$]$^-$	965	3200	/	191, 269
[Ni(pds)$_2$]$^{2-}$	795	4900	CH$_3$CN	254
	797	1900	CH$_3$CN	254
	798	3600	CH$_3$OH	254
[Ni(pds)$_2$]$^-$	793	4900	CH$_3$CN	254
	746	1900	CHCl$_3$	173
[Ni(dsit)$_2$]$^-$	740	21900	CHCl$_3$	173
	1067	/	Acetone	258
[Ni(dsis)$_2$]$^-$	1350	/	Acetone	370
	925	/	Acetone	258
[Ni(Me-thiazds)$_2$]$^-$	1187	22300	CH$_2$Cl$_2$	60
[Ni(Me$_2$timds)$_2$]$^-$	1398	/	CH$_2$Cl$_2$	62
[Ni(Me$_2$timds)$_2$]	1097	/	CH$_2$Cl$_2$	62
[Ni(Me$_2$simds)$_2$]$^-$	1399	/	CH$_2$Cl$_2$	62
[Pd(Me-thiazds)$_2$]$^-$	1512	29135	CH$_2$Cl$_2$	60
[Pt(Me$_2$timds)$_2$]$^-$	1389	/	CH$_2$Cl$_2$	62
[Pt(Me$_2$timds)$_2$]	1054	/	CH$_2$Cl$_2$	62
[Pt(Me$_2$simds)$_2$]$^-$	1363	/	CH$_2$Cl$_2$	62
[Co(bds)$_2$]$^-$	799	1100	/	269
[Cu(pds)$_2$]$^-$	921	105	CH$_3$CN	252, 255

The few data available show λ_{max} values ranging between 724 and 1512, and seem to confirm the electrochromism observed for *bis*(1,2-dithiolene) metal complexes, the Vis-NIR absorption being bathochromically shifted for the monoanionic complexes as compared to the corresponding neutral species (Figure 20).[62]
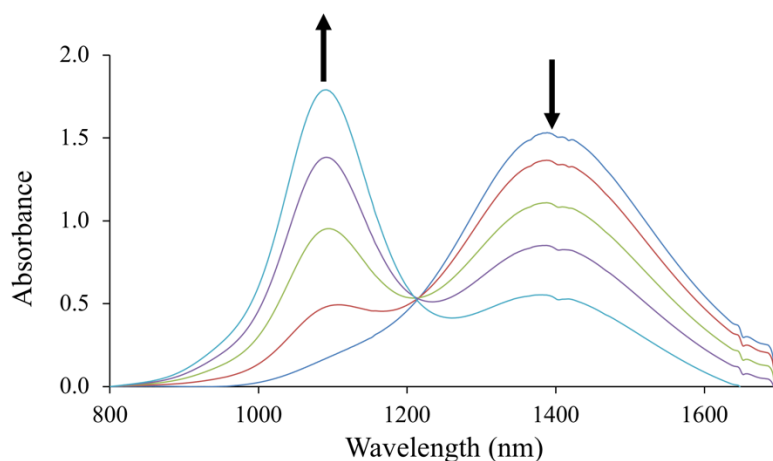
Figure 20. Spectrophotometric titration of $(Et_4N)[Ni(Me_2timds)_2]$ ($\lambda_{max} = 1398$ nm) with diiodine to give $[Ni(Me_2timds)_2]$ ($\lambda_{max} = 1097$ nm) in CH_2Cl_2 solution. Adapted from ref. 62.

Moreover, the Vis-NIR absorption in *bis*(1,2-diselenolene) metal complexes appears in most cases to be hypsochromically shifted and less intense as compared to their sulphured congeners (for example: $[Ni(Me_2timdt)_2]^-$, $\lambda_{max} = 1438$; $[Ni(Me_2timds)_2]^-$, $\lambda_{max} = 1398$ in CH_2Cl_2; $[Ni(Me_2simdt)_2]^-$, $\lambda_{max} = 1428$; $[Ni(Me_2simds)_2]^-$, $\lambda_{max} = 1399$ in CH_2Cl_2; $[Pt(Me_2simdt)_2]^-$, $\lambda_{max} = 1412$; $[Pt(Me_2simds)_2]^-$, $\lambda_{max} = 1363$ in CH_2Cl_2;[62] $[Ni(Me\text{-thiazdt})_2]^-$, $\lambda_{max} = 1284$; $[Ni(Me\text{-thiazds})_2]^-$, $\lambda_{max} = 1187$ in CH_2Cl_2; $[Pd(Me\text{-thiazdt})_2]^-$, $\lambda_{max} = 1556$; $[Pd(Me\text{-thiazds})_2]^-$, $\lambda_{max} = 1512$ in CH_2Cl_2).[60] This can be attributed to a stabilization of the HOMO induced by the introduction of selenium, and possibly to the lesser contribution of the singlet diradical character to the description of the ground state of the neutral species.[62]

In addition to the Vis-NIR absorption, 1,2-dithiolene metal complexes are also well known for their nonlinear optical (NLO) properties. In particular, homoleptic centrosymmetric complexes can be exploited for their third-order NLO properties in fields such as optical limiting.[363] On the other hand, heteroleptic and mixed-ligand complexes, usually non-centrosymmetric, can show second-order nonlinear optical (SONLO) properties.[362] Of particular interest are those complexes where the two ligands have opposite donor/acceptor behavior, the so-called push-pull systems.[243] In these species, the HOMO is mainly localized on the ligand with the larger electron-acceptor character, while the LUMO is centered on the ligand with the larger electron-donor character, so that the peculiar low-energy transition possesses an intramolecular CT nature, resulting in high first hyperpolarizability (β) values. Although a series of computational studies indicate homoleptic *bis*(1,2-diselenolene) complexes as potential candidates for nonlinear optics applications, with calculated second hyperpolarizability values (γ) in some cases larger than those of *bis*(1,2-dithiolene) complexes,[65,66,244] their NLO properties have not been studied experimentally yet. On the other hand, few SONLO

studies have been conducted on heteroleptic $[M(S^\wedge S)(Se^\wedge Se)]^{x-}$ complexes belonging to the series $[M(Bz_2pipdt)(dsit)]$ (M = Ni, Pd, Pt), whose second-order polarizabilities [estimated through the Electric-Field-Induced Second Harmonic (EFISH) generation technique] were not observed to vary significantly when compared to their sulphured $[M(Bz_2pipdt)(dmit)]$ analogues.[54] The excited-state dynamics of these systems were also studied in order to investigate their possible applications to photonics.[280] Similar conclusions about the scarce influence of the chalcogen atom in the SONLO properties of mixed-ligand complexes were drawn through DFT calculations on the related class of dimmine-dichalcogenolato complexes, but unlike their sulphured analogues the NLO properties of $[M(N^\wedge N)(Se^\wedge Se)]$ systems were not studied experimentally.[63] On the other hand, a recent study reports also for this class of compounds an investigation of their excited-state lifetimes,[64] and some of these systems have been studied for their luminescent properties, showing a NIR emission upon excitation at wavelengths matching those of their solvatochromic absorption in the Vis region (Figure 21), much like their sulphured analogues.[58]
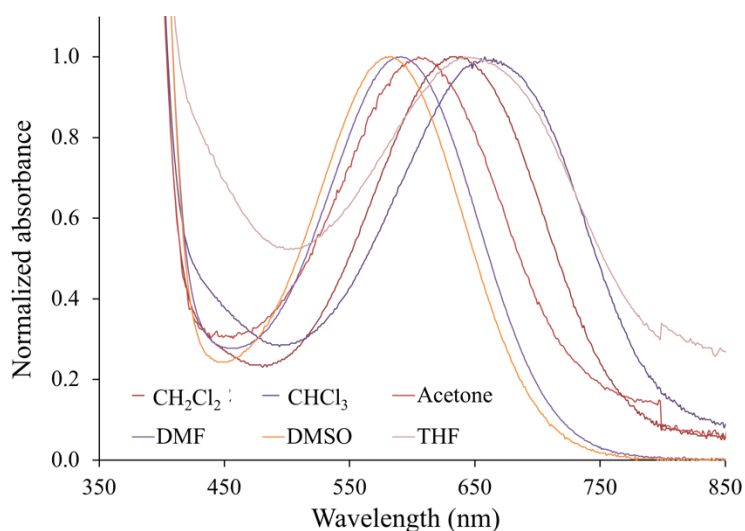

Figure 21. Normalized absorption spectra in the UV-Vis region (350-850 nm) recorded for [Pt(bipy)(Me-dset)] in selected solvents. Adapted from ref. 63.

Vis-NIR luminescence has also been reported for mixed-ligand complexes featuring mono- or bi-dentate phosphines.[53,228]

Absorptions in the NIR region were reported since the late 1980s also in *mono*(1,2-dichalcogenolene)-arene complexes (Table 15), although the molar extinction coefficients ε calculated for these bands are lower than those of *bis*(1,2-diselenolene) metal complexes.[140,221,315]

Table 15. Vis-NIR spectral data for *mono*(1,2-diselenolene)-arene metal complexes.

Complex	λ_{max} (nm)	ε (M^{-1} cm^{-1})	Solvent	Ref.
[CpCo(Se$_2$C$_8$H$_{12}$)]	827	920	Hexane	221
	823	400	Pentane	135
[Cp*Co(Se$_2$C$_8$H$_{12}$)]	763	370	Pentane	135
[CpCo(Se$_2$C$_8$H$_{10}$)]	830	460	Hexane	221
	830	460	Pentane	135
[Cp*Co(Se$_2$C$_8$H$_{10}$)]	773	850	Pentane	135
[CpCo(Se$_2$C$_8$H$_8$)]	841	370	Hexane	221
	841	370	Pentane	135
[Cp*Co(Se$_2$C$_8$H$_8$)]	782	330	Pentane	135
[CpCo(Se$_2$C$_2$HPh)]	812	1060	CH$_3$CN	140
	809	170	Pentane	135
[CpCo(Se$_2$C$_2$Ph$_2$)]	812	1050	CH$_3$CN	140
	819	230	Pentane	135
[Cp*Co(Se$_2$C$_2$Ph$_2$)]	757	450	Pentane	135
[CpNi(ddds)]	1000	3600	CH$_2$Cl$_2$	315
[CpNi(dsit)]	948	3200	CH$_2$Cl$_2$	315
[CpNi(bds)]	718	2800	CH$_2$Cl$_2$	315

These absorptions were attributed to ligand-to-metal charge transfer (LMCT) processes,[299] and in [CpM(Se^Se)] complexes they were observed to fall at longer and shorter wavelengths for the Co and Ni complexes, respectively, with respect to their sulphured analogues (see for example the following data for [CpM(S^S)] complexes: [CpCo(S$_2$C$_2$Ph$_2$)], λ_{max} = 750 in CH$_3$CN; [CpCo(S$_2$C$_2$HPh)], λ_{max} = 748 in CH$_3$CN;[140] [CpNi(dddt)], λ_{max} = 1012 in CH$_2$Cl$_2$; [CpNi(dmit)], λ_{max} = 967 in CH$_2$Cl$_2$; [CpNi(bdt)] λ_{max} = 722 in CH$_2$Cl$_2$).[315] The absorption energy shows a strong dependence on the permethylation of the cyclopentadienyl ring.[135]

3.2.3. Electrical properties

Square-planar transition *bis*(1,2-dithiolene) metal complexes have been widely used in the preparation of molecular conductors.[16] In some cases, these complexes can form solid-state stacks or bidimensional networks of partially oxidized species that are responsible for metallic[371,372] or even superconducting properties, as in the case of various complexes featuring the dmit^{2-} ligand in combination with a group 10 metal ion.[373,374,375] Anionic complexes act as simple counterions in CT salts where the electron transport properties are assured by electron donor species. In principle, the selenium analogues of such complexes would be better suited for the formation of extended molecular networks suitable for the arising of superconducting properties, because of the increased van der Waals radius and greater polarizability of selenium, allowing a larger extent of soft-soft Se⋯Se interactions.[263] The electrical properties of coordination compounds featuring [M(dsit)$_2$]$^{x-}$ complexes and other isologues of [M(dmit)$_2$]$^{x-}$ were thus studied starting since the 1980s,[164,165] but all showed a semiconducting or even insulating behavior (Table 16), although in a few cases they showed larger

room-temperature conductivities than those reported for the corresponding 1,2-dithiolene metal complexes.[257,271]

Table 16. Electrical properties of coordination compounds featuring *bis*(1,2-diselenolene) metal complexes.

Compound	σ_{RT} (S cm^{-1})	E_a (eV)	Ref.
(Me$_4$N)[Ni(dsit)$_2$]$_2$	36	0.11	175
(Me$_4$P)[Ni(dsit)$_2$]$_2$	19	0.13	175
(Et$_4$N)$_2$[Ni(dsit)$_2$]$_2$	5·10^{-5}	0.61	175
[Ni(dmf)$_6$][Ni(dsit)$_2$]$_2$	1.2	0.035	43
(Me$_4$N)[Ni(dsise)$_2$]	3.5·10^{-3}	/	357
(Me$_4$N)$_{0.5}$[Ni(dsise)$_2$]	12	0.06	262, 357
(Bu$_4$N)$_2$[Ni(dsis)$_2$]	5.0·10^{-8}	/	71
(Bu$_4$N)[Ni(dsis)$_2$]	2.0·10^{-4}	/	71
(Bu$_4$N)$_{0.25}$[Ni(dsis)$_2$]	0.21	0.075	71
(Me$_4$N)$_{0.33}$[Ni(dsis)$_2$]	0.056	0.056	71
(Me$_4$N)$_{0.5}$[Ni(dsis)$_2$]	1	/	357
(TMTSF)$_2$[Ni(tds)$_2$]	20		46, 270
(Et$_4$N)[Ni(tds)$_2$]	2.6·10^{-8}	/	267
(Bu$_4$N)[Ni(tds)$_2$]	2.1·10^{-8}	/	267
Li[Ni(tds)$_2$]	5.2·10^{-5}	/	267
Na[Ni(tds)$_2$]	7.0·10^{-6}	/	267
K[Ni(tds)$_2$]	8.8·10^{-6}	/	267
Rb[Ni(tds)$_2$]	4.1·10^{-6}	/	267
(NH$_4$)[Ni(tds)$_2$]	2.6·10^{-6}	/	267
Cs[Ni(tds)$_2$]	3.5·10^{-6}	/	267
(Et$_4$N)$_2$[Ni(tds)$_2$]$_2$	1.2·10^{-8}	/	267
Na$_2$[Ni(pds)$_2$]$_2$	1.7·10^{-4}	0.2754	254
[Ni(L)$_2$]^a	2.8	0.014	69
[(C$_6$H$_{13}$)$_4$N][Ni(L)$_2$]^a	< 10^{-10}	/	69
(Me$_4$N)$_{0.5}$[Pd(dsise)$_2$]	0.12	/	357
(Me$_4$N)[Pd(dsis)$_2$]	50	0.08	271
(Me$_4$N)$_{0.5}$[Pd(dsis)$_2$]	5.6·10^{-2}	/	357
(Me$_4$N)$_{0.5}$[Pt(dsise)$_2$]	3.3·10^{-2}	/	357
(Me$_4$N)$_{0.5}$[Pt(dsis)$_2$]	3.3·10^{-3}	/	357
[TMTSF]$_2$[Pt(tds)$_2$]	65	/	46, 270
(epy)$_2$[Cu(dsis)$_2$]	1.2·10^{-7}	0.37	71, 257
(Me$_4$N)$_2$[Cu(dsis)$_2$]	7.1·10^{-7}	0.25	71, 257
(Me$_4$N)[Cu(dsis)$_2$]	6.9·10^{-7}	0.22	71
(TTF)$_{0.4}$[Cu(dsis)$_2$]	1.4·10^{-5}	0.76	71
(TMTSF)$_2$[Cu(tds)$_2$]	63.2	0.05	270
(DT-TTF)$_4$[Cu(pds)$_2$]$_3$	0.1	/	50
(Bu$_4$N)[Au(dsis)$_2$]	4.9·10^{-8}	/	45
[Au(dsis)$_2$]	6.3·10^{-4}	0.16	45
(TTF)$_{0.3}$[Au(dsis)$_2$]	3.2·10^{-3}	0.12	45
[Fe(Cp)$_2$]$_{0.2}$[Au(dsis)$_2$]	0.16	0.068	45
(TTF)$_2$[Au(pds)$_2$]$_2$	1.0·10^{-4}	0.245	44
(TTF)$_3$[Au(pds)$_2$]$_2$	1.0·10^{-2}	0.24	44
(DT-TTF)$_4$[Au(pds)$_2$]$_3$	2	0.095	50, 253
[AuSe$_4$(=O)$_2$]^b	0.18	0.06	41
[AuSe$_4$(=S)$_2$]^c	40	0.05	41
(Me$_4$N)[Fe(dsis)$_2$]	5.9·10^{-8}	/	260
(TTF)$_{0.28}$[Fe(dsis)$_2$]	4.0·10^{-5}	/	260
[Fe(Cp*)$_2$]$_{0.7}$[Fe(dsis)$_2$]	1.5·10^{-6}	/	260
(Bu$_4$N)$_{0.05}$[Fe(dsis)$_2$]	1.9·10^{-5}	/	260

^{a} L = diethylthiotetrathiafulvalenyldiselenolate. ^{b} Se$_4$(=O)$_2$ = two units of the ligand N-ethyl-1,3-thiazoline-2-one-4,5-diselenolate. ^{c} Se$_4$(=S)$_2$ = two units of the ligand N-ethyl-1,3-thiazoline-2-thione-4,5-diselenolate, Et-thiazds.

Complexes featuring the tds^{2-} ligand were also studied for their electrical properties,[376] and the compounds (TMTSF)$_2$[Ni(tds)$_2$] and (TMTSF)$_2$[Pd(tds)$_2$] showed an unprecedented phase transition near room temperature (T_c *ca*. 275 and 245 K for M = Ni and Pt, respectively) with an abrupt increase

in conductivity, representing the first example of a structural transition in which the low temperature state is more conductive that the high temperature state.[46,267,270,377]

A third class of complexes studied for their conductive properties features the pds^{2-} ligand, but also these complexes were found to be semiconductors.[44,254] The occurrence of phase transitions was observed for these complexes as well, $(DT\text{-}TTF)_4[Au(pds)_2]_3$ (DT-TTF = dithiophenotetrathiafulvalene) undergoing an unusual sequence of phase transitions.[50,253]

Only in neutral complexes $[Ni(L_2)]$,[69] $[AuSe_4(=O)_2]$, and $[AuSe_4(=S)_2]$[41] [L = diethylthiotetrathiafulvalenyldiselenolate; $Se_4(=O)_2$ = two ligand units of N-ethyl-1,3-thiazoline-2-one-4,5-diselenolate; $Se_4(=S)_2$ = two ligand units of Et-thiazds, N-ethyl-1,3-thiazoline-2-thione-4,5-diselenolate] the predicted increase in conductivity with respect to their sulphured analogues was observed, amounting to about two orders of magnitude and showing a strongly anisotropic nature of this chemical pressure effect in the case of $[AuSe_4(=O)_2]$.
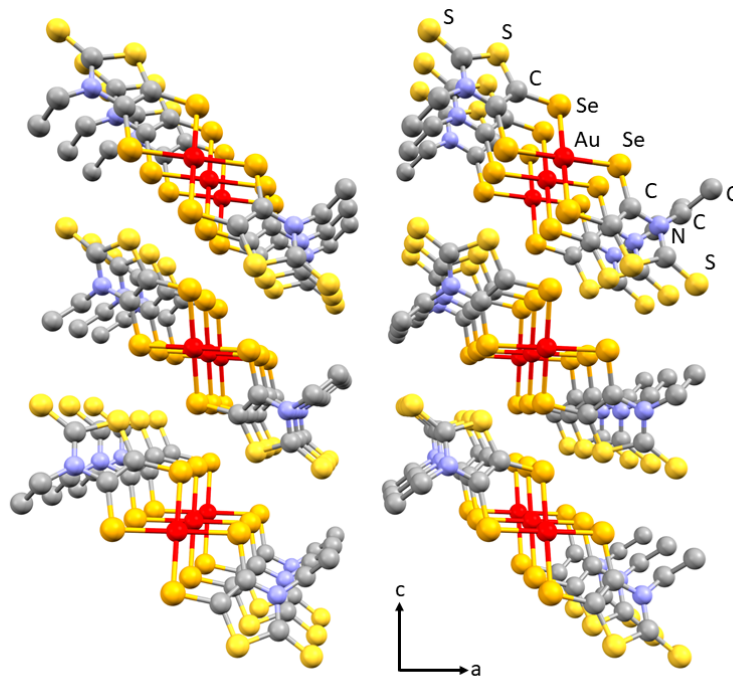
Figure 22. View of the packing of $[AuSe_4(=S)_2]$ along b (CCDC code HEZPIN, ref. 41). Hydrogen atoms were omitted for clarity.

In many cases, oxidized or partially oxidized complexes were observed to show larger conductivities as compared to the corresponding monoanionic or dianionic species,[45,69,71,260,357] due to the formation of ligand-ligand interactions through selenium⋯selenium contacts in the crystals. These interactions result in the formation of more effective electron conduction pathways that in turn lead to increased conductivities. The same conclusions were drawn for different 1,2-diselenolene metal complexes studied for their electrical properties, such as the *tris*(1,2-diselenolene) complex $[W(dsis)_3]^{x-}$ (x = −2, −0.6, −0.5, −0.1),[70] the heteroleptic complex $[Ni(dmit)(dsit)]^{x-}$ (x = −2, −0.7, −0.3),[276] the

[Pt(dsis)(N$_2$-chelate)]·I$_x$ systems (N$_2$-chelate = 2,2'-bipyridine, *N*-alkyl-2-methylpyridien-2-carbamide; alkyl = Et and ^{i}Pr; x = 2, 6.8, 6.4, 5.4, 0),[289] and the [Cu$_4$(dsis)$_3$]$^{x-}$ clusters (x = –2, –0.5, –0.16).[234,235]

The electric properties of 1,2-diselenolene metal complexes render them promising candidates as semiconducting materials for field-effect transistors.[42] Moreover, copper coordination polymers featuring the dsedt^{2-} tetradentate ligand (dsedt^{2-} = 1,2-selenoethene-1,2-dithiolate) feature promising thermoelectric properties with potential applications in energy harvesting, local cooling or heating, and thermal sensing.[189] Besides, the conductive properties of two-dimensional copper conjugated coordination polymers based on benzenehexaselenolate were also investigated and compared with those of the corresponding sulphured systems, showing intrinsic metallic characteristics and one of the highest electrical conductivity values ever reported for coordination polymers measured on pressed pellet;[213] on the other hand, the related cobalt system featuring 2,3,6,7,10,11-triphenylenehexa(selenolate) only showed a semiconductive behaviour.[213] Similar coordination polymers featuring tetra- or hexa-dentate selenolate ligands systems were the subject of recent computational studies aimed at predicting their potential conductive properties based on structure-property relationships.[378,379,380,381]

3.2.4. Magnetic properties

The magnetic properties of 1,2-diselenolene metal complexes were the subject of intense studies, and as already mentioned electron paramagnetic resonance (EPR) measurements were often used in the past to assess the electronic structure of these systems.[3,32,49,71,168,173,191,192,217,134,256,259,262,263,281,292,295,297,299,303,309,361,382,383] The solid-state magnetic properties of *bis*(1,2-diselenolene) metal complexes were also studied,[44,269,384,385,386] and as it was observed previously for relevant 1,2-dithiolene metal complexes,[16] the most common magnetic behavior is antiferromagnetism, often in the form of antiferromagnetic spin coupling of unpaired electrons on adjacent complex molecules due to the presence of dimeric structures,[267] as in the case of [Ni(ddds)$_2$]$_2$,[68] [Ni(dmf)$_2$][Ni(dsit)$_2$]$_2$,[69] [Fe(Cp*)$_2$]$_2$[Ni(dsit)$_2$]$_2$ (Figure 23a),[249] or Na$_2$[Ni(pds)$_2$]$_2$.[254] Other mechanisms include antiferromagnetic interactions in stacks between neighboring neutral complexes, as for *bis*(diethylthiotetrathiafulvalenyldiselenolate)nickel,[69] or donor-acceptor couples in electron-transfer salts, as in [Cr(Cp*)$_2$][Ni(tds)$_2$] (Figure 23b).[248] Magnetic coupling between complex molecules belonging to different anion chains was reported, arising via superexchange interactions mediated by cations, as in the cases of (TMTSF)$_2$[M(tds)$_2$] (M = Ni, Pt).[270]
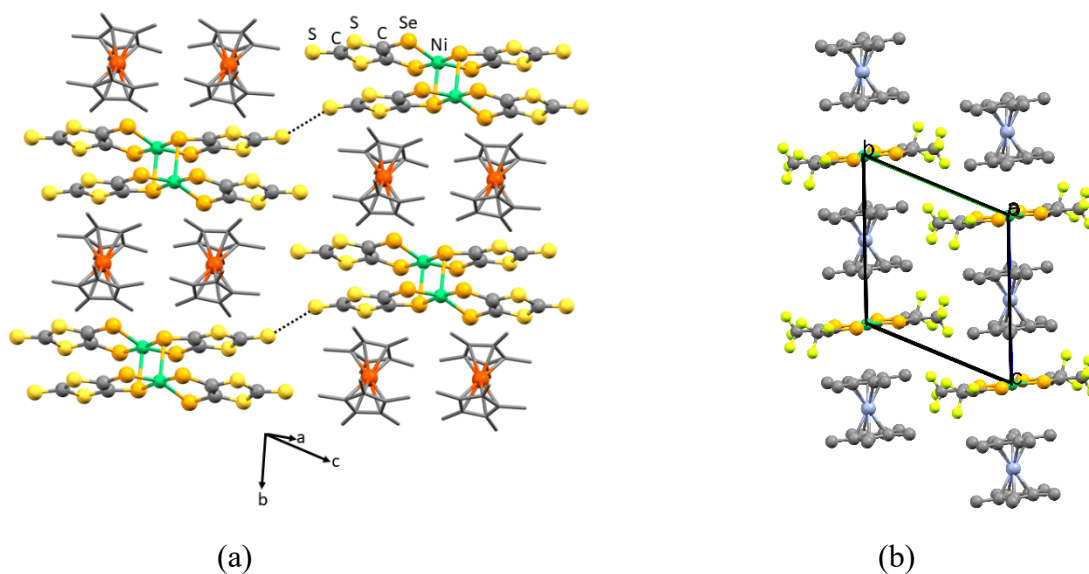
(a)   (b)

Figure 23. (a) View of the packing of [Fe(Cp*)$_2$]$_2$[Ni(dsit)$_2$]$_2$ (CCDC code JIMCOY, ref. 249), showing a dimeric complex structure. (b) Packing diagram of [Cr(Cp*)$_2$][Ni(tds)$_2$] (CCDC code COHROH, ref. 248), showing the donor-acceptor stacks in the *bc* plane. Hydrogen atoms were omitted for clarity.

Antiferromagnetic interactions were also observed for some *mono*(1,2-diselenolene)-arene complexes, including (C)[Cp$_2$Mo(R-thiazds)] (C = TCNQ, TCNQF$_4$)[311] and (TCNQF$_4$)[Cp$_2$M(dsit)] (M = Mo, W),[310] where the complex molecules form chains of dimers with a head-to-tail organization (Figure 24a), and [CpNi(dsit)], where a three-dimensional set of intermolecular interactions is present in the crystal structure (Figure 24b).[51]

(a)   (b)
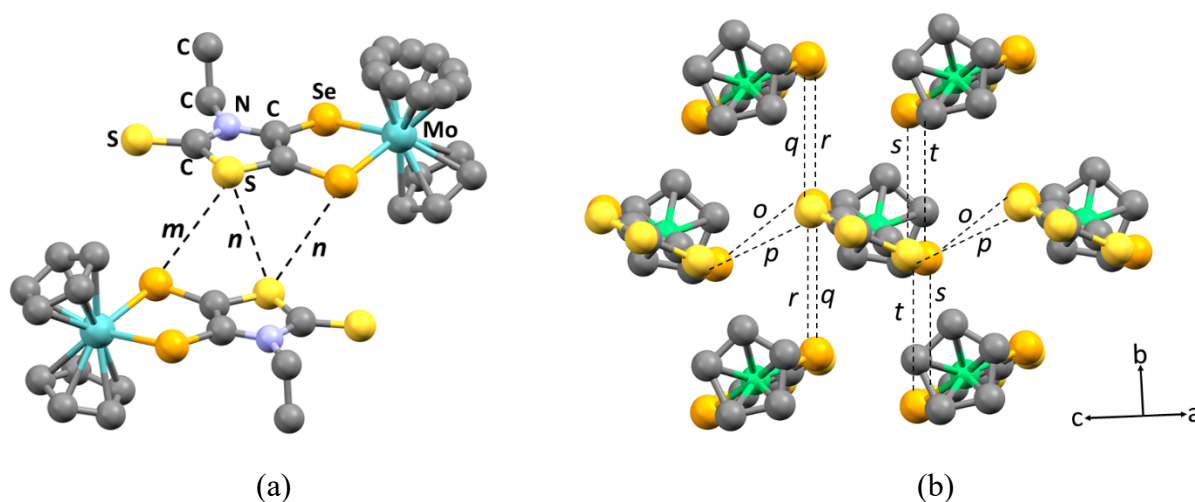
Figure 24. (a) S···S and Se···Se interactions within the complex dimers in [TCNQ][Cp$_2$Mo(Et-thiazds)] (CCDC code MIDMIX, ref. 311, *m* = 3.715 Å, *n* = 3.565 Å). (b) View of one (*a,b*) layer in [CpNi(dsit)] (CCDC code RAMQIG, ref. 51), with intralayer interactions *o* (Se···Se = 3.634 Å) and *p* (S···S = 3.854 Å) running along *a* and interactions *q* (Se···S = 4.079 Å), *r* (Se···S = 4.342 Å), *s* (Se···S = 3.911 Å), and *t* (Se···S = 4.104 Å) running along *b*. Hydrogen atoms were omitted for clarity.

55

Analogously to their sulphured analogues, very few 1,2-diselenolene metal complexes exhibit unusual or remarkable magnetic behaviors. Short-range order ferromagnetic interactions were reported for some charge-transfer salts, including $[M_1(Cp^*)_2][M_2(tds)_2]$ (M_1 = Fe, Mn; M_2 = Ni, Pt)[47,247,248] and $[Fe(Cp^*)_2][Ni(bds)_2]$,[52] were they arise from donor-acceptor interactions (Figure 25a), or $(Me_4N)[Ni(ddds)_2]$ (R = Me),[68] were they are due to interactions between neighboring complex anions (Figure 25b).

| (a) | (b) |
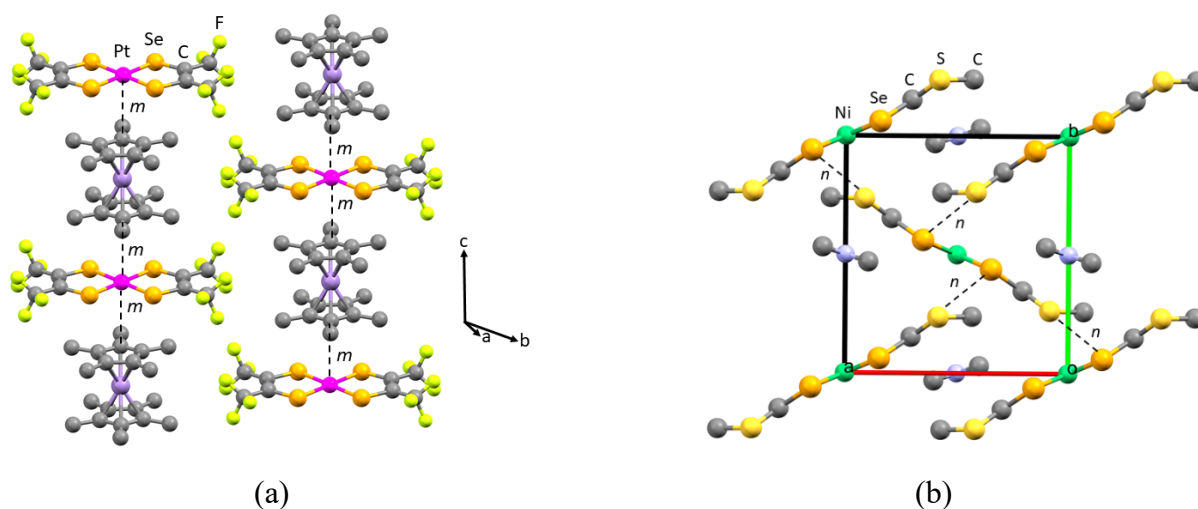
Figure 25. (a) View of the packing of $[Mn(Cp^*)_2][Pt(tds)_2]$ (CCDC code COHRIB, ref. 47), showing the intrachain donor-acceptor contacts (m = 3.883). (b) Crystal packing $(Me_4N)[Ni(ddds)_2]$ (CCDC code SUHQOB, ref. 68) projected onto the *ab*-plane (n = 3.781 Å). Hydrogen atoms were omitted for clarity.

Another noteworthy example is represented by $(TTF)[Cu(tds)_2]_2$, which shows a spin-Peierls transition at 6 K.[387] Finally, $[Cp_2W(dsit)](AsF_6)$ behaves as a spin-ladder system. In its crystal packing, the folded molecular geometry of the complex molecules (see section 3.1.4) leads to their association into inversion-related dimers, which in turn interact with each other giving rise to a ladderlike organization.[67]
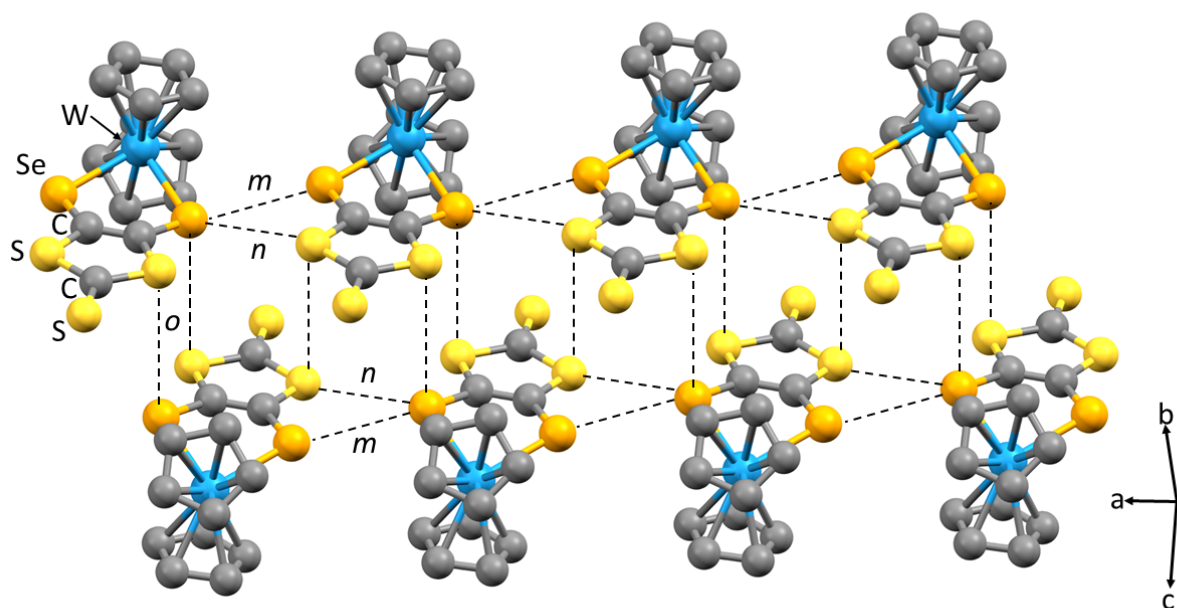
Figure 26. View of the ladder-type organization of complex molecules in [Cp$_2$W(dsit)](AsF$_6$) (CCDC code QAYMUY, ref. 67; m = 3.812 Å, n = 3.496 Å, n = 3.716 Å). Hydrogen atoms were omitted for clarity.

The phase-transitions often observed in coordination compounds featuring *bis*(1,2-diselenolene) metal complexes[253,270,388] render them suitable materials for magnetic devices with potential applications as thermal sensors or switching units.[50] Moreover, very recently the spin-lattice relaxation in homoleptic *bis-* and *tris*(1,2-diselenolene) metal complexes was studied in view of their possible applications in the development of molecular spin-based qbits, the smallest unit of a quantum information system.[57] It is also worth mentioning that the abovementioned cobalt metal organic framework based on the 2,3,6,7,10,11-triphenylenehexa(selenolate) ligand showed glassy magnetic properties in addition to its semiconductive behavior.[213]

3.2.5. Reactivity

As compared to the body of structural or electrochemical data, very few reports have been published on the chemical reactivity of *bis*(1,2-diselenolene) metal complexes. Although most of these complexes are stable towards strong acids or bases, they undergo ligand-exchange or ligand-substitution reactions such as those described in Sections 3.1.2 and 3.1.3 for the synthesis of heteroleptic and mixed-ligand complexes (Scheme 18). The use of zinc complexes featuring dsit^{2-} and its isologues for the synthesis of protected forms of the corresponding ligands was mentioned above (Scheme 5 and Scheme 7 in Section 2), as well as the possibility of employing them in metal-exchange reactions (Scheme 17).

In analogy to their 1,2-dithiolene analogues, the salts of [Zn(dsit)$_2$]$^{2-}$,[389,390] [Zn(dsis)$_2$]$^{2-}$[182,391] and other Zn complexes[180] were used as precursors to organic compounds, representing shelf-stable equivalents of less handy 1,2-diselenolates. For example, [Zn(dsit)$_2$]$^{2-}$ was employed as an intermediate for the synthesis of organoselenium heterocycles (routes i and ii in Scheme 24)[392,393,394] and thiacrown compounds (route iii in Scheme 24).[395]
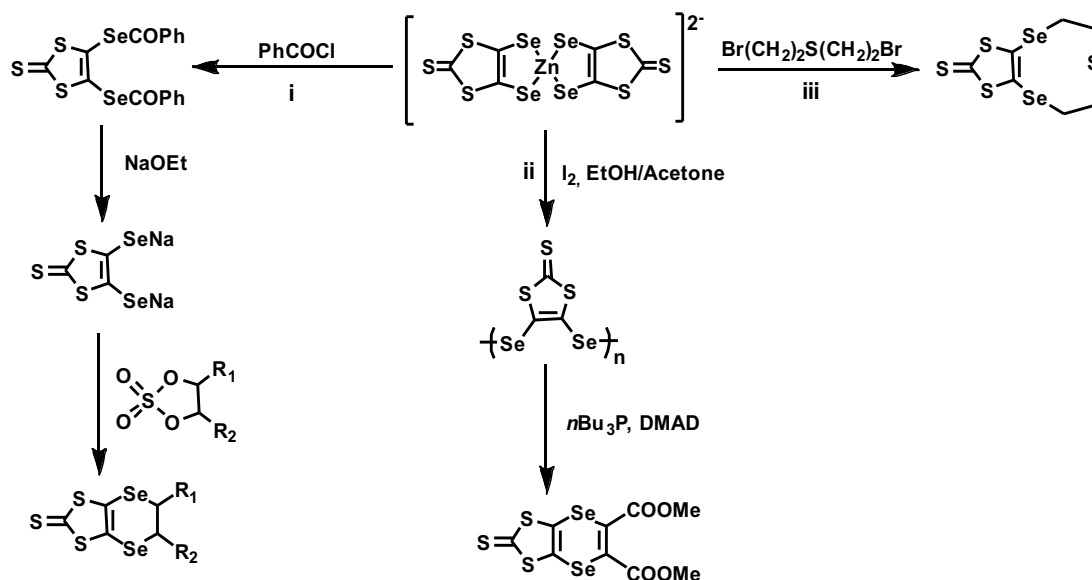
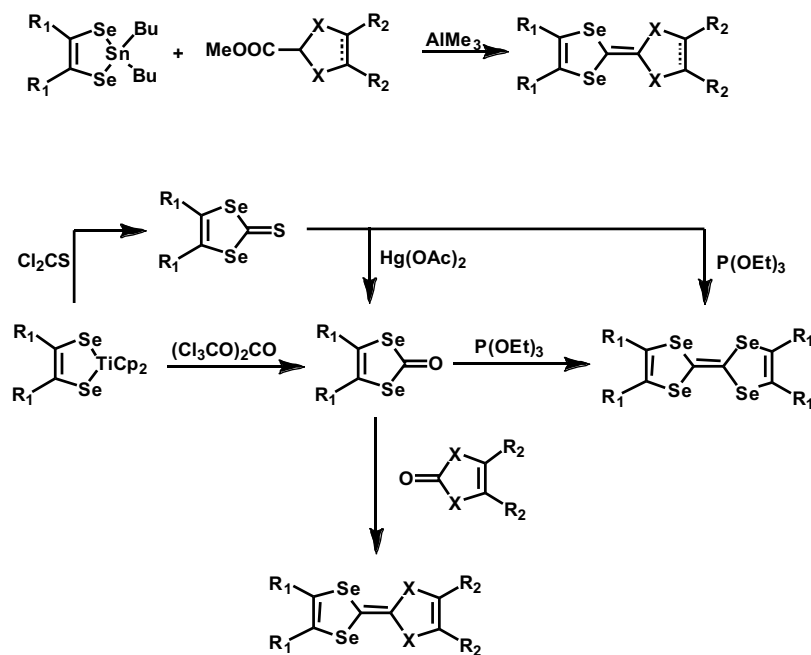**Scheme 24.** Synthetic routes for the preparation of organoselenium species form [Zn(dsit)$_2$]$^{2-}$.

On the other hand, (TBA)$_2$[M(bds)$_2$] (M = Ni, Zn) and the related complexes sporting naphthalene-2,3-diselenolate ligands were used as precursors for recently patented semiconductive naphthalene diimide derivatives.[396]

However, the most common synthetic application is the use of *bis*(1,2-diselenolene) metal complexes as intermediates for the synthesis of tetrathiafulvalene derivatives, which in turn are precursors of organic conductors and superconductors (Scheme 25).[397,398,399]
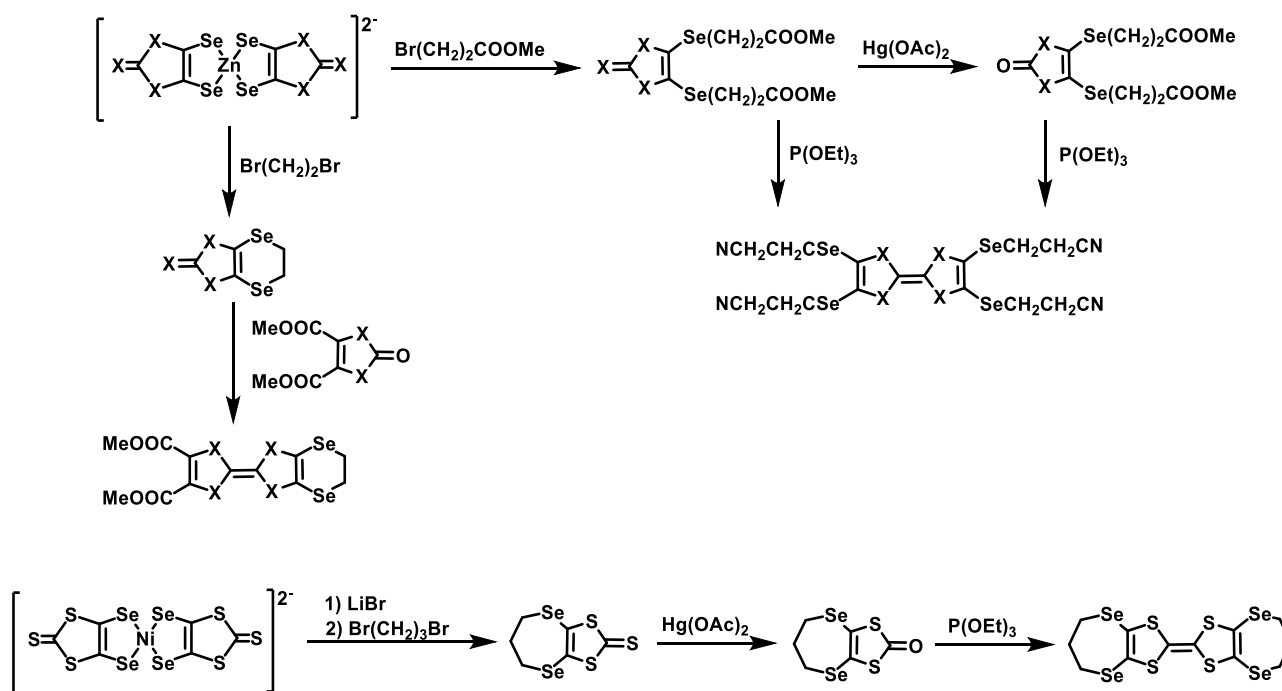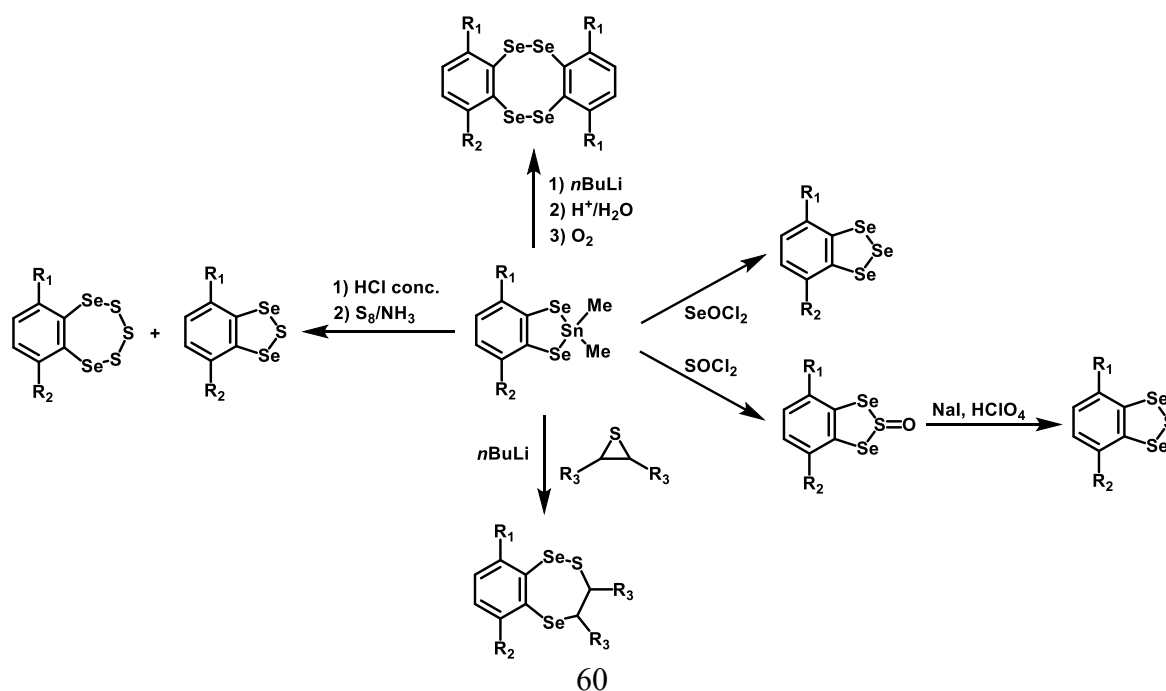
Scheme 25. Examples of synthetic routes for the preparation of TTF derivatives from [Zn(dsit)$_2$]$^{2-}$ or [Zn(dsis)$_2$]$^{2-}$ (top) and [Ni(dsit)$_2$]$^{2-}$ (bottom; X = S, Se).

The preparation of TTF derivatives was also achieved by starting from organometallic mixed-ligand 1,2-diselenolene metal complexes, more reactive than *bis*(1,2-diselenolene) metal complexes. This application was extended both to diorganotin 1,2-diselenolates and [CpM(Se^Se)] metal complexes. The former can undergo Me$_3$Al-promoted reactions with a variety of esters (Scheme 26, top),[155,326,327,400,401,402] while the latter can be converted by reaction with triphosgene or thiophosgene into the corresponding ketones or thioketones, respectively, which in turn undergo coupling reactions[218,219,220,308,313,403,404,405,406] to give the organic donors (Scheme 26, bottom).

Scheme 26. Synthetic strategy for the preparation of TTF derivatives from diorganotin 1,2-selenolates (top) and [CpM(Se^Se)] metal complexes (bottom; X = S, Se).

The aforementioned organotin selenolates, and in particular benzodiselenostannoles, were used by the group of Ogawa and Sato as precursors for the synthesis of a variety of organic cyclic polychalcogenides,[202,203,204,206,207,407,408,409] which represent a class of interest because of their chemical, physical, and biological properties. Some of these compounds were patented as electrochromic elements applicable to recording or displaying devices as electrophotographic receptors (Scheme 27).[410]

Scheme 27. Synthetic routes for the preparation of organic cyclic polychalcogenides from benzodiselenostannoles.

[SnMe₂(dsit)] was also reported as a ligand-transfer reagent toward other metals, such as gold(I) and gold(III) (Scheme 28).[266,411]
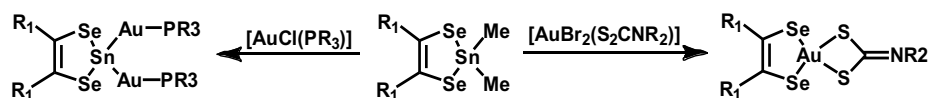

Scheme 28. Metal-transfer reactions involving [SnMe₂(dsit)].

[CpM(Se^Se)] complexes can undergo ligand- and metal-exchange reactions, the displacement of the 1,2-diselenolene ligand from the complex being particularly investigated to afford selenium derivatives otherwise not easily synthesized. In the case of [Cp₂M(Se^Se)] complexes (M = Ti, Zr), alcoholysis can provide 1,2-diselenolate salts that can subsequently undergo complexation (routes i and vi in Scheme 29).[136] Isolation of the 1,2-diselenolate salts is not mandatory and metal complexes can be directly reacted with a variety of metal chlorides,[136,196,264] with concomitant regeneration of the metallocene dichloride (routes ii-v and vii in Scheme 29).
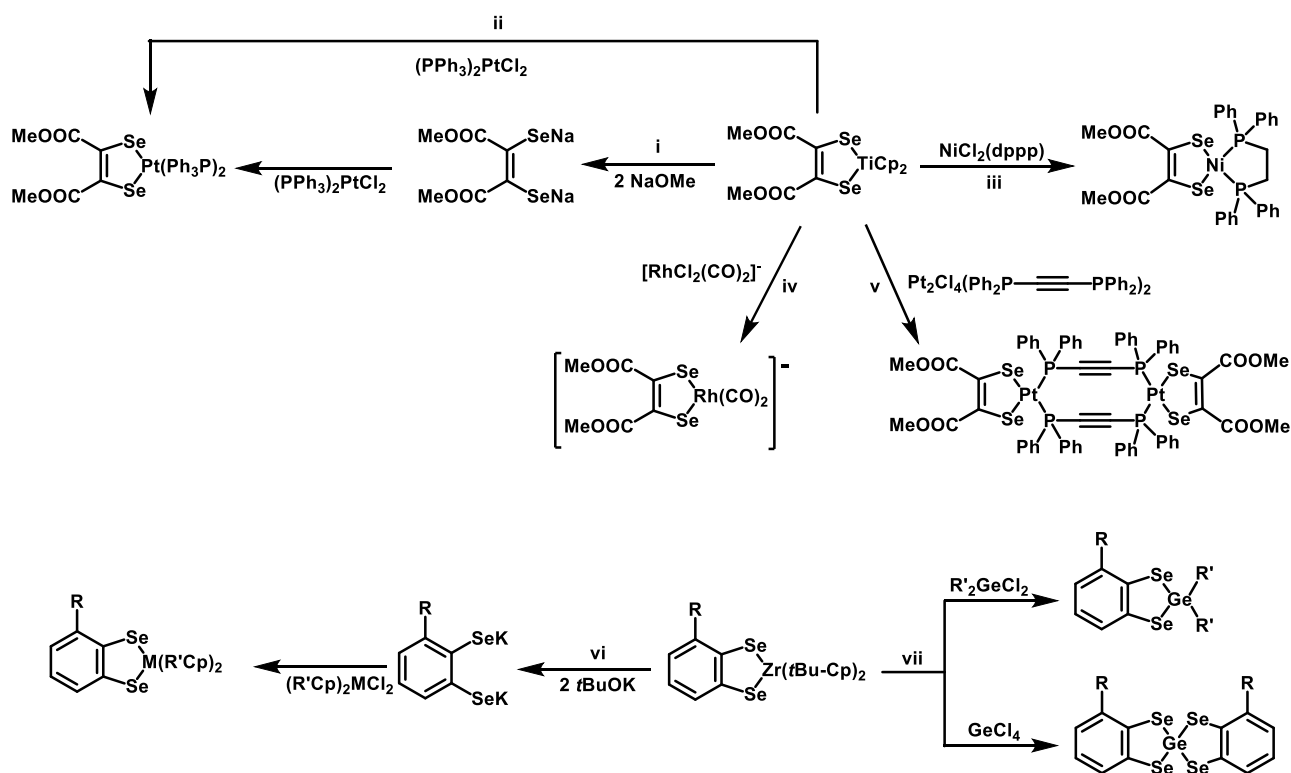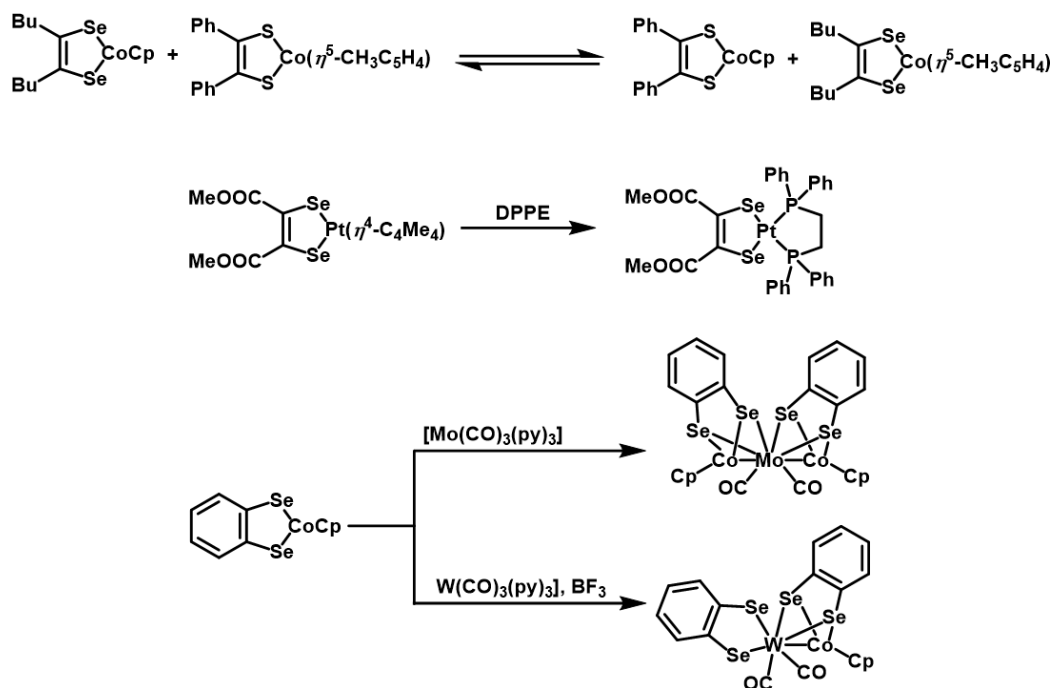

Scheme 29. Ligand- and metal-exchange reactions in [Cp₂M(Se^Se)] metal complexes (M = Ti, Hf).

Moreover, [(*t*-BuCp)$_2$Zr(bds)] was used as a precursor of benzene-1,2-diselenolate derivatives[195,412,413] or benzodiselenoheterocycles,[414] obtained through electrophilic cleavage of the complex (routes i and ii in Scheme Scheme 30), while [Cp$_2$Ti(Et-thiazds)] was recently observed to be a precursor for the corresponding diselenine (route iii in Scheme 30),[186] also obtained from (Et$_4$N)$_2$[Zn(Et-thiazds)$_2$] through electrocrystallization (route iv in Scheme 30), both compounds showing a different behavior with respect to the corresponding 1,2-dithiolene complexes.[415]
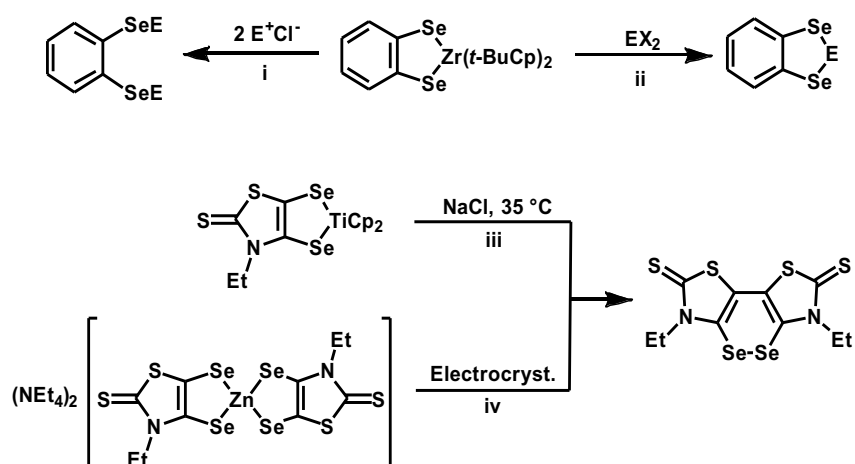
Scheme 30. Synthetic strategy for the preparation of benzene-1,2-diselenolate derivatives and benzodiselenoheterocycles from [(*t*-BuCp)$_2$Zr(bds)] (X = Cl, Br; E = CH$_2$, CH$_2$CH$_2$, PPh, CH$_2$CO, and different electrophile groups), and diselenines from [Cp$_2$Ti(Et-thiazds)] and (Et$_4$N)$_2$[Zn(Et-thiazds)$_2$].

[CpM(Se^Se)] (M = Co, Pt, Mo, W) and related complexes were used for ligand-exchange reactions and as ligand delivery systems as well (Scheme 31),[306,307,314] and some studies suggest that this kind of reactions proceed through a Se$_3$-chelate intermediate.[225]

Scheme 31. Ligand- and metal-exchange reactions in [CpM(Se^Se)] metal complexes (M = Co, Pt).

[CpM(Se^Se)] complexes could also be converted into their sulphured analogues through chalcogen exchange when reacted with elemental sulphur (Scheme 32).[138,226]
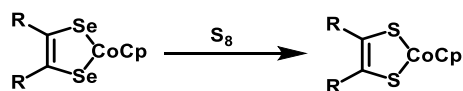
Scheme 32. Chalcogen-exchange reactions in [CpM(Se^Se)] metal complexes.

[CpCo(Se$_2$C$_2$Ph$_2$)] was observed to form alkylidene-bridged adducts with ethyldiazoacetate or diazomethane (Scheme 33),[416,417] and the formation of adducts with tributylphosphine was also reported.[140]
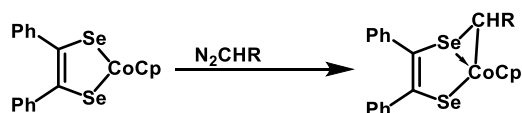
Scheme 33. Formation of alkylidene adducts with [CpCo(Se$_2$C$_2$Ph$_2$)].

Given the presence of 1,2-dithiolene ligands in the active sites of metalloenzymes throughout the entire kingdom of life,[418] the relevant complexes have been employed as low molecular weight

analogues of these centers in order to study and/or reproduce the enzymatic activities.[29] In some cases the selenated analogues were also studied: this is the case of $(PPh_4)[WO_2(bds)_2]$,[291] since the corresponding 1,2-dithiolene species $(PPh_4)[WO_2(bdt)_2]$ closely resembles the structure of the aldehyde ferredoxin oxidoreductase cofactor in hyperthermophilic organisms.[419] In order to clarify the role of tungsten ions in thermally stable enzymes, the oxidation of benzoin with these model complexes was studied at extreme temperatures (above 100 °C), showing similar rate constants for the sulphured and selenated systems.[291] The oxygen-atom transfer reactions of Mo-1,2-diselenolene biomimetic complexes were also the object of recent computational studies.[76,420]

Also bioinspired was the recent study of nickel and cobalt 1,2-diselenolene polymers (Scheme 34) for the reduction of water and production of molecular hydrogen (hydrogen evolution reactions, HER). The biological counterparts of these systems are [NiFeSe] hydrogenases, a subclass of [NiFe] hydrogenases with a selenocysteine replacing a cysteine residue, which usually display higher activities and O_2 tolerance than their sulphur-only analogues. Encouraged by this enhanced activity upon replacement of sulphur with selenium, the authors extended a previously reported study on analogue 1,2-dithiolene polymers,[421,422,423] showing that the cobalt 1,2-selenolate polymers display an improvement in the overpotential compared to the 1,2-dithiolate polymers in electrocatalytic activity.[73]
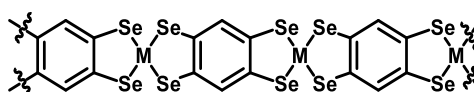
Scheme 34. Metal 1,2-diselenolate polymers used as electrocatalysts for H_2 evolution (M = Ni, Co).

After these reports, $(nBu_4N)[Co(bds)_2]$ was investigated as a molecular analogue of the aforementioned polymers, also showing electrocatalytic HER activity,[55] and the potential application of *bis*(1,2-diselenolene) nickel complexes for the reduction of H^+ to H_2 was the subject of computational studies.[72]

The same [NiFeSe] hydrogenases inspired the study of [Ni(bds)(dppf)], which acts as a highly efficient oxygen-tolerant molecular catalyst for electrochemical reduction of protons, with superior catalytic activities as compared to its sulphured analogue.[74]

As mentioned in the introduction, the possibility to extend the reactivity towards olefins reported for 1,2-dithiolene complexes[424] to their 1,2-diselenolene analogues was investigated in recent computational studies,[56,75] suggesting the effectiveness of solid-state extended lattices based on 1,2-diselenolene nickel complexes as potential heterogeneous catalysts for olefin purification.

On a closing note, [Au(pds)$_2$]$^-$ was tested along with a series of 1,2-dithiolene complexes as π-guest for a Pd-based nanocage in a metal-directed supramolecular synthetic approach, in order to test the molecular recognition properties of the host and the tuning of the properties of the guests, with the final aim of developing polyfunctional supramolecular nanovessels with applications as sensors or nanoreactors.[425]

4. Conclusions and perspectives

We have reported the research progress over the past decades on 1,2-diselenolene complexes, a class of coordination compounds belonging to the larger family of 1,2-dichalcogenolenes. Notwithstanding the general interest toward the sulphured members of this family of compounds (1,2-dithiolene complexes) displayed by the scientific community over the past 60 years, it is immediately clear from an analysis of the available literature that in comparison only a limited number of research groups have investigated the chemistry of 1,2-diselenolene complexes. This is partly due to the synthetic difficulties encountered in the preparation of 1,2-diselenolene ligands and their metal complexes, but also to the fact that earlier reports did not evidence significant differences between the properties of 1,2-diselenolene and their sulphured analogues. Despite that, over the past years more and more papers have indicated that the subtle differences introduced by the substitution of sulphur with selenium on the electronic structure of 1,2-dichalcogenolene complexes can exert a pivotal role in the fine-tuning of their electrochemical, optical, electrical, and magnetic properties. More importantly, recent experimental and theoretical studies by different research groups have indicated that in some cases 1,2-diselenolene complexes represent better candidates than 1,2-dithiolenes for some of their most promising and recently developed catalytic applications, such as hydrogen evolution reactions (HER), olefin purification or biomimetic oxo-transfer. Based on these findings, a renewed interest on the chemistry of 1,2-diselenolene metal complexes is to be expected in the near future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

References

[1]   Dithiolene Chemistry: Synthesis, Properties, and Applications (Ed.: E. I. Stiefel), Wiley, Hoboken, 2004.
[2]   Dithiolenes and non-innocent redox-active ligands: COST Action D35 Conference 2009, Coord. Chem. Rev. 254 (2010) 12–13.
[3]   A. Davison, E. T. Shawl, Inorg. Chem. (1970) 1820–1825.
[4]   M. Arca, M. C. Aragoni, A. Pintus, "1,2-dichalcogenolene ligands and related metal complexes", in Handbook of chalcogen chemistry, (Eds.: F. A. Devillanova, W. -W. du Mont), RSC Publishing, Cambridge, UK, 2013.
[5]   P. Tavarès, M. M. Kubicki, P. Meunier, B. Gautheron, Trans. Met. Chem. 17 (1992) 220–223.
[6]   W. A. Flomer, J. W. Kolis, Inorg. Chem. 28 (1989) 2513–2517.
[7]   D. M. Smith, L. C. Roof, M. A. Ansari, J. M. McConnachie, J. C. Bollinger, M. A. Pell, R. J. Salm, J. A. Ibers, Inorg. Chem. 35 (1996) 4999–5006.
[8]   J. A. McCleverty, D. G. Orchard, J. Chem. Soc. A (1970) 3315-3318.
[9]   D. Coucouvanis, D. Swenson, N. C. Baenziger, R. Pedelty, M. L. Caffery, S. Kanodia, Inorg. Chem. 28 (1989) 2829–2836.
[10]   W. H. Mills, R. E. D. Clarck, J. Chem. Soc. (1936) 175–181.
[11]   R. E. D. Clarck, Analyst 60 (1936) 242–245.
[12]   R. E. D. Clarck, Analyst 62 (1937) 661–663.
[13]   G. N. Schrauzer, V. P. Mayweg, J. Am. Chem. Soc. 84 (1962) 3321.
[14]   H. B. Gray, R. Williams, I. Beranl, E. Billig, J. Am. Chem. Soc. 84 (1962) 3596–3597.
[15]   R. Kato, Chem. Rev. 104 (2004) 5319–5346.
[16]   N. Robertson, L. Cronin, Coord. Chem. Rev. 227 (2002) 93–123.
[17]   C. Faulmann, P. Cassoux, Prog. Inorg. Chem. 52 (2004) 399–490.
[18]   A. Kobayashi, E. Fujiwara, H. Kobayashi, Chem. Rev. 104 (2004) 5243–5264.
[19]   J. Y. Cho, B. Domercq, S. C. Jones, J. Yu, X. Zhang, Z. An, M. Bishop, S. Barlow, S. R. Marder, B. Kippelen, J. Mater. Chem.17 (2007) 2642–2647.
[20]   Y. Qi, T. Sajoto, S. BArlow, E. -G. Kim, J. -L, Bredas, S. R. Marder, A. Kahn, J. Am. Chem. Soc. 131 (2009) 12530–12531.
[21]   J. Fabian, H. Nakazumi, M. Matsuoka, Chem. Rev.92 (1992) 1197–1226.
[22]   U. T. Mueller-Westerhoff, D. I. Yoon, K. Plourde, Mol. Cryst. Liq. Cryst. 183 (1990) 291–302.
[23]   U. T. Mueller-Westerhoff, B. Vance, D. I. Yoon, Tetrahedron 47 (1991) 909–932.
[24]   K. L. Marshall, G. Painter, K. Lotito, A. G. Noto, P. Chang, Mol. Cryst. Liq. Cryst.454 (2006) 449–481.
[25]   A. -M. Giroud-Godquin, P. M. Maitlis, Angew. Chem. Int. Ed. 30 (1991) 375–402.
[26]   C. S. Winter, S. N. Oliver, R. J. Manning, J. D. Rush, C. A. S. Hill, A. E. Underhill, J. Mater. Chem. 2 (1992) 443–447.
[27]   R. H. Holm, P. Kennepohl, E. I. Solomon, Chem.Rev. 96 (1996) 2239 –2314.
[28]   S. Leimkuhler, Biol. Chem. 398 (2017) 1009–1026.
[29]   F. J. Hine, A. J. Taylor and C. D. Garner, Coord. Chem. Rev. 254 (2010) 1570–1579.
[30]   Comprehensive Coordination Chemistry II, (Eds.: J. M. Tunney, J. McMaster, C. D. Garner, J. A. McCleverty, T. J. Meyer), vol. 8, Elsevier–Pergamon (2004) Oxford.
[31]   R. S. Pilato, E. I. Stiefel, in Bioinorganic Catalysis, Eds. J. Reedijik, Marcel Dekker (1998) New York.
[32]   A. Davison, E. T. Shawl, Chem. Commun. (1967) 670.
[33]   W. -H. Chiu, Q. -F. Zhang, I. D. Williams, W. -H. Leung, Organometallics 29 (2010) 2631–2633.
[34]   D. M. Giolando, T. B. Rauchfuss, A. L. Rheingold, Inorg. Chem., 26 (1987) 1636–1638.
[35]   G. -X. Jin, M. Herberhold, A. L. Reingold, New. J. Chem. (1998) 1035–1036.
[36]   T. Klapötke, H. Köpf, P. Gowik, Polyhedron, 6 (1987) 1923–1924.
[37]   H. Köpf, T. Klapötke, J. Chem. Soc., Chem. Commun. (1986) 1192–1193.

[38] R. D. McCullough, J. A. Belot, J. Seth, A. L. Rheingold, G. P. A. Yap, D. O. Cowan, J. Mater. Chem. 5 (1995) 1581–1587.

[39] P. Meunier, B. Gautheron, A. Mazouz, J. Organomet. Chem. 320 (1987) C39–C43.

[40] M. S. Thomas, J. Darkwa, E. Y. Osei-Twum, L. A. Lotorja Jr., Polyhedron 18 (1999) 2803–2810.

[41] G. Yzambart, N. Bellec, G. Nasser, O. Jeannin, T. Roisnel, M. Formigué, P. Auban-Senzier, J. Iñiguez, E. Canadell, D. Lorcy, J. Am. Chem. Soc. 134 (2012) 17138–17148.

[42] G. C. Papavassiliou, G. C. Anyfantis, B. R. Steele, A. Terzis, C. P. Raptopoulou, G. Tatakis, G. Chaidogiannos, N. Glezos, Y. Weng, H. Yoshino, K. Murata, Z. Naturforsch., 62b (2007) 679–684.

[43] S. Curreli, P. Deplano, M. L. Mercuri, L. Pilia, A. Serpe, F. Bigoli, M. A. Pellinghelli, E. Coronado, C. J. Gómez-García, E. Canadell, J. Solid State Chem. 168 (2002) 653–660.

[44] J. Morgado, I. C. Santos, L. F. Veiros, C. Rodrigues, R. T. Henriques, M. T. Duarte, L. Alcácer, M. Almeida, J. Mater. Chem. 11 (2001) 2108.

[45] G. Matsubayashi, A. Yokozawa, J, Chem. Soc. Dalton Trans. (1990) 3535–3539.

[46] W. B. Heuer, B. M. Hoffman, J. Chem. Soc., Chem. Commun. (1986) 174–175.

[47] S. Rabaça, B. J. C. Vieira, R. Meira, I. C. Santos, L. C. J. Pereira, M. T. Duarte, V. da Gama, Eur. J. Inorg. Chem. (2008) 3839–3851.

[48] E. Coronado, J. C. Dias, M. Carmen Giménez-Lopez, C. Giménez-Saiz, C. J. Gómez-García, J. Molec.Struct. 890 (2008) 215–220.

[49] P. Grosshans, P, Adkine, H. Sidorenkova, M. Nomura, M. Formigué, M. Geoffroy, J. Phys. Chem. A 112 (2008) 4067–4073.

[50] J. C. Dias, X. Ribas, J. Morgado, J. Seiça, E. B. Lopes, I. C. Santos, R. T. Henriques, M. Almeida, K. Wurst, P. Foury-Leylekian, E. Canadell, J. Vidal-Gancedo, J. Veciana, C. Rovira, J. Mater. Chem. 15 (2005) 3187–3199.

[51] M. Formigué, N. Avarvari, Dalton Trans. (2005) 1365–1371.

[52] W. E. Broderick, J. A. Thompson, M. R. Godfrey, M. Sabat, B. N. Hoffman, J. Am. Chem. Soc. 111 (1989) 7656–7657.

[53] K. Rofe, P. Douglas, C. P. Morley, C. A. Webster, J. G. Picherau, Inorg. Chem. 48 (2009) 4549–4556.

[54] D. Espa, L. Pilia, L. Marchiò, M. Pizzotti, N. Robertson, F. Tessore, M. L. Mercuri, A. Serpa, P. Deplano, Dalton Trans. 41 (2012) 12106–12113.

[55] C. A. Downes, J. W. Yoo, N. M. Orchanian, R. Haiges, S. C. Marinescu, Chem. Commun. 53 (2017) 7306–7309.

[56] R. K. Raju, D. N. Sredojevic, S. Moncho, E. N. Brothers, Inorg. Chem. 55 (2016) 10182–10191.

[57] M. S. Fataftah, M. D. Krzyaniak, B. Vlaisavljevich, M. R. Wasielewski, J. M. Zadrozny, D. E. Freeddman, Chem. Sci. 10 (2019) 6707–6714.

[58] S. M. Dibrov, R. E. Bachman, Inorg. Chim. Acta 357 (2004) 1198–1204.

[59] E. A. C. Bushnell, R. J. Boyd, Int. J. Quantum Chem. 116 (2016) 369–376.

[60] S. Eid, M. Formigué, T. Roisnel, D. Lorcy, Inorg. Chem. 46 (2007) 10647–10654.

[61] H. Ushijima, M. Kajitani, K. Shimizu, G. P. Satô, T. Akiyama, A. Sugimori, J. Electroanal. Chem. 303 (1991) 199–209.

[62] C. Deiana, M. C. Aragoni, F. Isaia, V. Lippolis, A. Pintus, A. M. Z. Slawin, J. D. Woollins, M. Arca, New J. Chem. 40 (2016) 8206–8210.

[63] A. Pintus, M. C. Aragoni, F. Isaia, V. Lippolis, D. Lorcy, A. M. Z. Slawin, J. D. Woollins, M. Arca, Eur. J. Inorg. Chem. (2015) 5163–5170.

[64] J. Yang, D. K. Kersi, L. J. Giles, B. W. Stein, C. Feng, C. R. Tichnell, D. A. Shultz, M. L. Kirk, Inorg. Chem. 53 (2014) 4791–4793.

[65] H. Fukui, H. Nagai, R. Kishi, T. Minami, H. Takahashi, T. Kubo, M. Nakano, Synth. Met. 159 (2009) 2416–2418.

[66] H. Fukui, R. Kishi, T. Minami, H. Nagai, H. Takahashi, T. Kubo, K. Kamada, K. Ohta, B. Champagne, E. Botek, M. Nakano, J. Phys. Chem. A 112 (2008) 8423–8429.

[67] B. Domercq, C. Coulon, M. Formigué, Inorg. Chem. 40 (2001) 371–378.

[68] H. Fujiwara, E. Ojima, H. Kobayashi, T. Courcet, I. Malfant, P. Cassoux, Eur. J. Inorg. Chem. (1998) 1631–1639.

[69] K. Ueda, Y. Kamata, M. Iwamatsu, T. Sugimoto, H. Fujita, J. Mater. Chem. 9 (1999) 2979–2983.

[70] K. Douki, G. Matsubayashi, Inorg. Chim. Acta 230 (1995) 235–239.

[71] G. Matsubayashi, A. Yokozawa, J. Chem. Soc. Dalton Trans. (1990) 3013–3019.

[72] B. T. A. Boychuk, E. A. C. Bushnell, Can. J. Chem. 96 (2018) 51–57.

[73] C. A. Downes, S. C. Marinescu, ACS Catal. 7 (2017) 848–854.

[74] Z. -H. Pan, Y. -W. Tao, Q. -F. He, Q. -Y. Wu, L. -P. Cheng, Z. -H. Wei, J. -H. Wu, J. -Q. Lin, D. Sun, Q. -C. Zhang, D. Tian, G. -G. Luo, Chem. Eur. J. 24 (2018) 8275–8280.

[75] D. N. Sredojevic, S. Moncho, R. K. Raju, M. R. Belić, E. N. Brothers, J. Phys. Chem. C 122 (2018) 22424–22434.
[76] E. A. C. Bushnell, Can. J. Chem. 94 (2016) 1127–1132.
[77] R. Eisenberg, H. B. Gray, Inorg. Chem. 50 (2011) 9741–9751.
[78] A. E. Pullen, R. -M. Olk, Coord. Chem. Rev. 188 (1999) 211–262.
[79] X. -Y. Yu, G. -X. Jin, N. -H. Hu, L. -H. Weng, Organometallics 21 (2002) 5540–5548.
[80] X. -F. Hou, X. -C. Wang, J. -Q. Wang, G. -X. Jin, J. Organomet. Chem. 689 (2004) 2228–2235.
[81] S. Lu, G. -X. Jin, S. Eibl, M. Herberhold, Y. Xin, Organometallics 21 (2002) 2533–2535.
[82] J. -Q. Wang, S. Cai, G. -X. Jin, L. -H. Weng, M. Herberhold, Chem. Eur. J. 11 (2005) 7342–7350.
[83] G. -X. Jin, J. -Q. Wang, C. Zhang, L. -H. Weng, M. Herberhold, Angew. Chem., Int. Ed. 44 (2005) 259–262.
[84] J. -Q. Wang, L. -H. Weng, G. -X. Jin, J. Organomet. Chem. 690 (2005) 249–252.
[85] S. Cai, G. -X. Jin, Organometallics 24 (2005) 5280–5286.
[86] S. Cai, Y. Lin, G. -X. Jin, J. Chem. Soc., Dalton Trans. (2006) 912–918.
[87] X. -F. Hou, S. Liu, H. Wang, Y. -Q. Chen, G. -X. Jin, J. Chem. Soc., Dalton Trans. (2006) 5231–5239.
[88] J. -Q. Wang, M. Herberhold, G. -X. Jin, Organometallics 25 (2006) 5308–3514.
[89] J. -S. Zhang, Y. -J. Lin, G. -X. Jin, J. Organomet. Chem. 694 (2009) 2069–2074.
[90] W. -G. Jin, Y. -F. Han, G. -X. Jin, Organometallics 27 (2008) 6035–6038.
[91] X. -Q. Xiao, Y. -J. Lin, G. -X. Jin, J. Chem. Soc., Dalton Trans. (2008) 2615–2619.
[92] G. -L. Wang, Y. -J. Lin, O. Balcque, H. Berke, G. -X. Jin, Inorg. Chem. 47 (2008) 2940–2942.
[93] S. Cai, G. -X. Jin, Organometallics 26 (2007) 5442–5445.
[94] S. Liu, J. -Q. Wang, L. -H. Weng, G. -X. Jin, J. Chem. Soc., Dalton Trans. (2007) 3792–3797.
[95] X. Wang, S. Liu, L. -H. Weng, G. -X. Jin, Chem. Eur. J. 13 (2007) 188–195.
[96] S. Cai, X. Hou, L. -H. Weng, G. -X. Jin, J. Organomet. Chem., 690 (2005) 910–915.
[97] S. Cai, J. -Q. Wang. G. -X. Jin, Organometallics, 24 (2005) 4226–4231.
[98] S. Liu, G. -X. Jin, Dalton Trans. (2007) 949–954.
[99] Y. -Q. Chen, J. -Q. Wang, G. -X. Jin, J. Organomet. Chem. 692 (2007) 5190–5194.
[100] S. Liu, J. Zhang, X. Wang, G. -X. Jin, Dalton Trans. (2006) 5225–5230.
[101] W. -G. Jia, Y. -F. Han, G. -X. Jin, Organometallics 27 (2008) 6035–6038.
[102] Y. -Q. Chen, J. Zhang, S. Cai, X. -F. Hou, H. Schumann, G. -X. Jin, Dalton Trans. (2007) 749–758.
[103] J. -S. Zhang, G. -X. Jin, J. Organomet. Chem. 692 (2007) 3944–3948.
[104] J. -Q. Wang, X. Hou, L. Weng, G. -X. Jin, Organometallics 24 (2005) 826–830.
[105] G. -X. Jin, J. -Q. Wang, Dalton Trans. (2006) 86–90.
[106] S. Cai, X. -F. Hou, Q. -Y. Chen, G. -X. Jin, Dalton Trans. (2006) 3736–3741.
[107] J. -S. Zhang, Y. -J. Lin, G. -X. Jin, Dalton Trans. (2009) 111–118.
[108] M. Herberhold, G. -X. Jin, H. Yan, W. Milius, B. Wrackmeyer, J. Organomet. Chem. 587 (1999) 252–257.
[109] M. Herberhold, W. Milius, G. -X. Jin, W. Kremnitz, B. Wrackmeyer, Z. Anorg. Allg. Chem., 632 (2006) 2031–2036.
[110] M. Herberold, G. -X. Jin, H. Yan, W. Milius, B. Wrackmeyer, Eur. J. Inorg. Chem. (1999) 873–875.
[111] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, J. Organomet. Chem. 604 (2000) 170–177.
[112] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, Chem. Eur. J. 8 (2002) 388–395.
[113] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, Dalton Trans. (2001) 1782–1789.
[114] B. Wrackmeyer, Z. G. Hernandez, R. Kempe, M. Herberhold, Eur. J. Inorg. Chem. (2007) 239–246.
[115] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, Z. Anorg. Allg. Chem. 626 (2000) 1627–1633.
[116] M. Herberhold, H. Yan, W. Milius, B. Wrackmeyer, Organometallics 19 (2000) 2489–2494.
[117] B. Wrackmeyer, Z. García Hernández, R. Kempe, M. Herberhold, Appl. Organomet. Chem. 21 (2007) 108–116.
[118] B. Wrackmeyer, E. V. Klimkina, W. Milius, Appl. Organomet. Chem. 24 (2010) 25–32.
[119] B. Wrackmeyer, Z. García Hernández, R. Kempe, M. Herberhold, Z. Anorg. Allg. Chem. 633 (2007) 851–857.
[120] B. -H. Xu, D. -H. Wu, Y. -Z. Li, H. Yan, Organometallics 26 (2007) 4344–4349.
[121] B. -H. Xu, J. -C. Tao, Y. -Z. Li, S. -H. Li, H. Yan, Organometallics, 27 (2008) 334–340.
[122] B. -H. Xu, X. -Q. Peng, Y. -Z. Li, H. Yan, Chem. Eur. J. 14 (2008) 9347–9356.
[123] H. Ye, W. Bai, M. Wie, Y. Li, H. Yan, Eur. J. Inorg. Chem. (2011) 2763–2768.
[124] J. Hu, J. Wen, D. Wu, R. Zhang, G. Liu, Q. Jiang, Y. Li, H. Yan, Organometallics 30 (2011) 298–304.
[125] D. -H. Wu, C. -H. Wu, Y. -Z. Li, D. -D. Guo, X. -M. Wang, H. Yan, J. Chem. Soc., Dalton Trans. (2009) 285–290.
[126] W. Zhong, X. Liu, H. Zhu, J. Zhao, H. Liu, ACS Omega 4 (2019) 12719–12726.
[127] G. -X. Jin, Coord. Chem. Rev. 248 (2004) 587–602.
[128] J. -Q. Wang, L. -H. Weng, G. -X. Jin, Rev. Inorg. Chem. 27 (2005) 55–66.
[129] C. G. Screttas, B. R. Steele, G. -X. Jin in Perspectives in Organometallic Chemistry, (Edss.: C. G. Screttas, B. R. Steele), RSC Cambridge Press (2004) 47–61.

[130]   X. Meng, F. Wang, G. -X. Jin, Coord. Chem. Rev. 254 (2010) 1260–1272.
[131]   S. Liu, Y. -F. Han, G. -X. Jin, Chem. Soc. Rev. 36 (2007) 1543–1560.
[132]   Z. -J. Yao, W. Deng, Coord. Chem. Rev. 309 (2016) 21–35.
[133]   W. -B. Yu, P. -F. Cui, W. -X. Gao, G. -X. Jin, Coord. Chem. Rev. 350 (2017) 300–319.
[134]   R. M. Olk, W. Dietzsch, R. Kirmse, J. Stach, E. Hoyer, Inorg. Chim. Acta 128 (1987) 251–259.
[135]   C. P. Morley, R. R. Vaughan,. J. Chem. Soc. Dalton Trans. (1993) 703–707.
[136]   C. M. Bolinger, T. B. Rauchfuss, Inorg. Chem. 21 (1982) 3947–3954.
[137]   E. J. Miller, S. J. Landon, T. B. Brill, Organometallics 4 (1985) 533–538.
[138]   M. Kajitani, M. Ito, N. Kobayashi, T. Akiyama, A. Sugimori, Chem. Lett. (1986) 1537–1540.
[139]   M. Kajitani, R. Ochiai, N. Kobayashi, T. Akiyama, A. Sugimori, Chem. Lett. (1987) 245–248.
[140]   M. Kajitani, R. Ochiai, K. Dohki, N. Kobayashi, T. Akiyama, A. Sugimori, Bull. Chem. Soc. Jpn. 62 (1989) 3266–3271.
[141]   M. A. Ansari, C. H. Mahler, J. A. Ibers, Inorg. Chem. 28 (1989) 2669–2674.
[142]   M. R. J. Dorrity, J. F. Malone, C. P. Morley, R. R. Vaughan, Phosporus, Sulfur, and Silicon 68 (1992) 37–43.
[143]   M. Herberhold, G. -X. Jin, W. Milius, Z. Anorg. Allg. Chem. 620 (1994) 1295–1300.
[144]   C. C. McLauchlan, J. A. Ibers, Acta Cryst. A (1999) 30–32.
[145]   S. Nagao, H. Seino, T. Okada, Y. Mizobe, M. Hidai, J. Chem. Soc. Dalton Trans. (2000) 3546–3553.
[146]   S. Ford, M. R. Lewtas, C. P. Morley, M. Di Vaira, Eur. J. Inorg. Chem. (2000) 933–938.
[147]   O. Jeannin, M. Nomura, M. Formigué, J. Organomet. Chem. 692 (2007) 4113–4118.
[148]   F. Wudl, E. T. Zellers, S. D. Cox, Inorg. Chem., 24 (1985) 2864–2866.
[149]   L. Henriksen, Acta Chem. Scand. 21 (1967) 1981–1983.
[150]   F. Wudl, D. Nalewajek, J. Chem. Soc., Chem. Commun. (1980) 866.
[151]   L. -Y. Chiang, T. O. Poehler, A. N. Bloch, D. O. Cowan, J. Chem. Soc., Chem. Commun. (1980) 866–867.
[152]   A. MOradpour, V. Peyrussan, J. Johansen, K. Bechgaard, J. Org. Chem. 48 (1983) 388–389.
[153]   K. Bechgaard, D. O. Cowan, A. N. Bloch, J. Org. Chem. 40 (1975) 746–749.
[154]   J. Morgado, I. C. Santos, M. T. Duarte, L. Alcácer, M. Almeida, Chem. Commun. (1996) 1837–1838.
[155]   J. Yamada, S. Satoki, S. MIshima, N. Akashi, K. Takahashi, N. Masuda, Y. Nishimoto, S. Takasaki, H. Anzai, J. Org. Chem. 61 (1996) 3987–3995.
[156]   H. Poleschner, E. Fanghänel, J. Prakt. Chem. 324 (1982) 691–694.
[157]   D. M. Smith, T. E. Albrecht-Schmitt, J. Ibers, Angew. Chem. Int. Ed. 37 (1998) 1089–1091.
[158]   C. C. McLauchlan, J. A. Ibers, Inorg. Chem. 39 (2000) 1046–1048.
[159]   C. C. McLauchlan, J. A. Ibers, Inorg. Chem. 40 (2001) 18109–1815.
[160]   C. C. McLauchlan, S. D. Robowski, J. A. Ibers, Inorg. Chem. 40 (2001) 1372–1375.
[161]   C. Bianchini, C. Mealli, A. Meli, M. Sabat, J. Chem. Soc., Chem. Comun. (1984) 1647–1648.
[162]   C. Bianchini, C. Mealli, ,A. Meli, M. Sabat, P. Zanello, J. Am. Chem. Soc. 109 (1987) 185–198.
[163]   L. W. Mire, D. S. Marynick, Inorg. Chem. 39 (2000) 5970–5975.
[164]   G. C. Papavassiliou, Mol. Cryst. Liq. Cryst. 86 (1982) 159–162.
[165]   G. C. Papavassiliou, Z. Naturforsch. 37b (1982) 825–827.
[166]   G. Matsubayashi, K. Akiba, T. Tanaka, J. Chem. Soc. Dalton Trans. (1990) 115–119.
[167]   R. -M. Olk, W. Dietzsch, E. Hoyer, Synth. React. Inorg. Met. -Org. Chem. 14 (1984) 915–919.
[168]   R. -M. Olk, W. Dietzsch, J. Mattusch, J. Stach, C. Nieke, E. Hoyer, Z. Anorg. Allg. Chem. 544 (1987) 199–208.
[169]   P. J. Nigrey, Synth. React. Inorg. Met. -Org. Chem. 16 (1986) 1351–1355.
[170]   P. J. Nigrey, Synth. Met. 27 (1988) B365–B371.
[171]   E. M. Engler, V. V. Patel, J. org. Chem. 40 (1975) 387–389.
[172]   R. -M. Olk, A. Röhr, B. Olk, E. Hoyer, Z. Chem. 28 (1988) 304–305.
[173]   R. -M. Olk, A. Röhr, J. Sieler, K. Köhler, R. Kirmse, W. Dietzsch, E. Hoyer, B. Olk, Z. Anorg. Allg. Chem. 577 (1989) 206–216.
[174]   R. -M. Olk, B. Olk, W. Dietzsch, E. Hoyer, Z. Chem. 29 (1989) 250–251.
[175]   A. M. Kini, M. A. Beno, S. Budz, H. H. Wang, J. M. Williams , Mat. Res. Soc. Symp. Proc. 173 (1990) 177–188.
[176]   R. -M. Olk, B. Olk. J. Rohlof, E. Hoyer, Z. Chem. 30 (1990) 445–446.
[177]   B. Olk, R. -M. Olk, Z. Anorg. Allg. Chem. 600 (1991) 89–93.
[178]   B. Olk, R. -M. Olk, J. Sieler, E. Hoyer, Synth. Met. 43–43 (1991) 2585–2588.
[179]   H. Poleschner, R. Radeglia, J. Fuchs, J. Organomet. Chem. 427 (1992) 213–230.
[180]   G. C. Papavassiliou, V. C. Kakoussis, D. J. Lagouvardos, Z. Naturforsch. 46b (1991) 1269–1271.
[181]   J. Becher, J. Lau, P. Leriche, P. Mørk, N. Svenstrup, J. Chem. Soc., Chem. Commun. (1994) 2715–2716.
[182]   M. Kodani, K. Takimiya, Y. Aso, T. Otsubo, T. Nakayashiki, Y. Misaki, Synthesis 11 (2001) 1614–1618.
[183]   K. Takimiya, K. Yamane, Y. Aso, T. Otsubo, Mol. Cryst. Liq. Cryst. 379 (2002) 65–70.
[184]   S. Eid, M. Formiguè, T. Roisnel, D. Lorcy, Inorg. Chem. 46 (2007) 10647–10654.

[185]   S. Eid, T. Roisnel, D. Lorcy, J. Organomet. Chem. 693 (2008) 2755–2760.
[186]   Y. Le Gal, T. Roisnel, F, Barrière, T. Mori, D. Lorcy, New J. Chem. 45 (2021) 8971–8977.
[187]   C. Deiana, M. C. Aragoni, F. Isaia, V. Lippolis, A. Pintus, A. M. Z. Slawin, J. D. Woollins, M. Arca, New J. Chem. 40 (2016) 8206–8210.
[188]   N. Svenstrup, K. M. Rasmussen, T. K. Hansen, J. Becher, Synhtesis 8 (1994) 809–812.
[189]   Y. Cui, J. Yan, Y. Sun, Y. Zou, Y. Sun, W. Xu, D. Zhu, Sci. Bull. 63 (2018) 814–816.
[190]   D. J. Sandaman, J. C. Stark, L. A. Acampora, P. Gagne, Organomet. 2 (1983) 549–551.
[191]   D. J. Sandman, J. C. Stark, L. A. Acampora, L. A. Samuelson, G. W. Allen, Mol. Cryst. Liq. Cryst. 107 (1984) 1–17.
[192]   D. J. Sandman, G. W. Allen, L. A. Acampora, J. C. Stark, S. Jansen, M. T. Jones, G. J. Ashwell, B. M. Foxman, Inorg. Chem. 26 (1987) 1664–1669.
[193]   B. Gautheron, G. Tainturier, S. Pouly, Organometallics 3 (1984) 1495–1499.
[194]   P. Granger, B. Gautheron, G. Tainturier, S. Pouy, Org. Msgn. Res. 22 (1984) 701–704.
[195]   J. Bodiguel, P. Meunier, B. Gautheron, Appl. Organomet. Chem. 5 (1991) 479–486.
[196]   C. Legrand, P. Meunier, J. L. Petersen, P. Tavares, J. Bodiguel, B. Gautheron, G. Dousse, Organometallics 14 (1995) 162–169.
[197]   H. Köpf, T. Klapötke, J. Organomet. Chem. 310 (1986) 303–309.
[198]   K. Lerstrup, M. Lee, F. M. Wiygul, T. J. Kistenmacher, D. O. Cowan, J. Chem. Soc. Chem. Commun. (1983) 294–295.
[199]   G. Wittig, F. Bickelhaupt, Chem. Ber. 91 (1958) 883–894.
[200]   A. Krief, L. Defrère, Tetrahedron Lett. 40 (1999) 6571–6575.
[201]   B. Theis, S. Metz, C. Burschka, R. Bertermann, S. Maisch, R. Tacke, Chem. Eur. J. 15 (2009) 7329–7338.
[202]   S. Ogawa, T. Kikuchi, A. Sasaki, S. Chida, R. Sato, Tetrahedron Lett. 35 (1994) 5469–5472.
[203]   S. Ogawa, T. Kikuchi, S. Niizuma, R. Sato, J. Chem. Soc., Chem. Commun. (1994) 1593–1594.
[204]   S. Ogawa, T. Ohmiya, T. Kikuchi, A. Kawaguchi, S. Sato, A. Sai, N. Ohyama, Y. Kawai, S. Niizuma, S. Nakajo, T. Kimura, R. Sato, J. Organomet. Chem. 611 (2000) 136–145.
[205]   S. Ogawa, S. Yoshimura, N. Nagahora, Y. Kawai, Y. Mikata, R. Sato, Chem. Commun. (2002) 1918–1919.
[206]   N. Nagahora, S. Ogawa, S. Yoshimura, Y. Kawai, R. Sato, Bull. Chem. Soc. Jpn. 76 (2003) 1043–1054.
[207]   A. Alam, S. Ogawa, H. Muraoka, M. Kon-no, S. Nakajo, R. Sato, Eur. J. Inorg. Chem. (2007) 6097–6105.
[208]   T. Kimura, A. Yomogita, T. Matsutani, T. Suzuki, L. Tanaka, Y. Kawai, Y. Takaguchi, T. Wakahara, T. Akasaka, J. Org. Chem. 69 (2004) 4716–4723.
[209]   T. Kimura, K. Amano, T. Namauo, Phosphorus, Sulfur, and Silicon 186 (2011) 1234–1237.
[210]   T. Kimura, T. Nakahodo, H. Fujihara, E. Suzuki, Inorg. Chem. 53 (2014) 4411–4417.
[211]   T. Kimura, T. Nakahodo, H. Fujihara, Heteroatom Chem. (2018) 1–9.
[212]   D. L. Turner, T. P. Vaid, J. Org. Chem. 77 (2012) 9397–9400.
[213]   Y. Cui, J. Yan, Z. Chen, J. Zhang, Y. Zou, Y. Sun, W. Xu, D. Zhu, Adv. Sci. 6 (2019) 1802235.
[214]   Y. Cui, J. Yan, Z. Chen, W. Xing, C. Ye, X. Li, Y. Zou, Y. Sun, C. Liu, W. Xu, D. Zhu, iScience 23 (2020) 100812.
[215]   G. C. Papavassiliou, S. Y. Yiannopoulos, J. S. Zambounis, K. Kobayashi, K. Umemoto, Chem. Lett. (1987) 1279–1282.
[216]   U. Drutkowski, B. Wenzel, P. Strauch, Inorg. Chem. Commun. 1 (1998) 449–451.
[217]   U. Drutkowski, B. Wenzel, D. Tews, P. Strauch, Z. Anorg. Allg. Chem. 627 (2001) 1888–1894.
[218]   R. Kato, H. Kobayashi, A. Kobayashi, Synth. Met. 41–43 (1991) 2093–2096.
[219]   Y. Okano, H. Sawa, S. Aonuma, R. Kato, Chem. Lett. (1993) 1851–1993.
[220]   Y. Okano, H. Sawa, S. Aonuma, R. Kato, Synth. Met. 70 (1995) 1161–1162.
[221]   C. P. Morley, R. R. Vaughan, B. J. Wheatley, J. Organomet. Chem. 353 (1988) C39–C41.
[222]   H. Meier, E. Voigt, Tetrahedron 28 (1972) 187–198.
[223]   H. Meier, T. Echter, H. Petersen, Angew. Chem. Int. Ed. Engl. 17 (1978) 942–943.
[224]   H. Petersen, H. Meier, Chem. Ber. 113 (1980) 2383–2397.
[225]   C. P. Morley, R. R. Vaughan, J. Organomet. Chem. 444 (1993) 219–222.
[226]   M. R. J. Dorrity, A. Lavery, J. F. Malone, C. P. Morley, R. R. Vaughan, Heteroatom Chem. 3 (1992) 87–91.
[227]   S. Ford, C. P. Morley, M. Di Vaira, Inorg. Chem. 43 (2004) 7101–7110.
[228]   C. P. Morley, C. A. Webster, P. Douglas, K. Rofe, M. Di Vaira, Dalton Trans. 39 (2010) 3177–3189.
[229]   S. Ford, P. K. Khanna, C. P. Morley, M. Di Vaira, Dalton Trans. (1999) 791–794.
[230]   S. Ford, C. P. Morley, M. Di Vaira, New J. Chem. 23 (1999) 801–813.
[231]   I. Lalezari, A. Shafiee, Tetrahedron Lett. 58 (1969) 5105–5106.
[232]   T. L. Gilchrist, P. G. Mente, C. W. Rees, J. Chem. Soc. Perkin Trans. (1972) 2165–2170.
[233]   X. Ribas, J. C. Dias, J. Morgado, K. Wurst, M. Almeida, T. Parella, J. Veciana, C. Rovira, Angew. Chem. Int. Ed., 43 (2004) 4049–4052.

[234] G. Matsubayashi, Phosphorus Sulphur Silicon 67 (1992) 339–344.
[235] A. Yokozawa, G. Matsubayashi, Inorg. Chim. Acta. 186 (1991) 165–169.
[236] B. Olk, R. -M. Olk, E. Hoyer, Z. Chem. 29 (1989) 64–65.
[237] W. Dietzsch, R. -M. Olk, E. Hoyer, W. Meiler, W. Robien, Magn. Res. Chem. 26 (1988) 653–657.
[238] V. Bachler, G. Olbrich, F. Neese, K. Wieghardt, Inorg. Chem. 41 (2002) 4179–4193.
[239] L. Serrano-Andrés, A. Avramopoulos, J. Li, P. Labéguerie, D. Bégue, V. Kellö, M. G. Papadopoulos, J. Chem. Phys. 131 (2009) 134312-1–134312-11.
[240] K. Ray, T. Weyhermüller, F. Neese, K. Wieghardt, Inorg. Chem. 44 (2005) 5345–5360.
[241] S. Kokatam, K. Ray, J. Pap, E. Bill, W. E. Geiger, R. J. LeSuer, P. H. Rieger, T. Weyhermüller, F. Neese, K. Wieghardt, Inorg. Chem. 46 (2007) 110–1111.
[242] G. Bruno, M. Almeida, F. Artizzu, J. C. Dias, M. L. Mercuri, L. Pilia, C. Rovira, X. Ribas, A. Serpe, P. Deplano, Dalton Trans. 39 (2010) 4566–4574.
[243] M. C. Aragoni, C. Caltagirone, V. Lippolis, E. Podda, A. M. Z. Slawin, J. D. Woollins, A. Pintus, M. Arca, Inorg. Chem. 59 (2020) 17385−17401.
[244] H. Fukui, Y. Shigeta, M. Nakano, J. Phys. Chem. A 115 (2011) 1117–1124.
[245] C. G. Pierpont, R. Eisenberg, J. Chem. Soc. (1971) 2285–2289.
[246] F. de Assis, Z. H. Chohan, R. A. Howie, A. Khan, J. N. Low, G. M. Spencer, J. L. Wardell, S. M. S. V. Wardell, Polyhedron 18 (1999) 3533–3544.
[247] S. Rabaça, R. Meira, L. C. J. Pereira, M. T. Duarte, J. J. Novoa, V. Gama, Inorg. Chim. Acta 326 (2001) 89–100.
[248] V. Da Gama, S. Rabaça, C. Ramos, D. Belo, I. C. Santos, M. T. Duarte, Mol. Cryst. Liq. Cryst. 335 (1999) 81–90.
[249] S. Rabaça, I. C. Santos, M. T. Duarte, V. Gama, Inorg. Chem. Acta 360 (2007) 3855–3860.
[250] M. del Carmen Giménez-López, M. Clemente-León, C. Giménez-Saiz, Dalton Trans. 47 (2018) 10453–10462.
[251] J. C. Dias, A. Soriano-Portillo, M. Clemente-Léon, C. Giménez-Saiz, J. R. Galán-Mascarós, C. J. Gómez-García, E. Coronado, Inorg. Chim. Acta 360 (2007) 3843–3847.
[252] X. Ribas, J. Dias, J. Morgado, K. Wurst, M. Almeida, J. Veciana, C. Rovira, CrystEngComm 4 (2002) 564–567.
[253] J. C. Dias, J. Morgado, H. Alves, E. B. Lopes, I. C. Santos, M. T. Duarte, R. T. Henriques, M. Almeida, X. Ribas, C. Rovira, J. Veciana, Polyhedron 22 (2003) 2447–2452.
[254] X. Ribas, J. C. Dias, J. Morgado, K. Wurst, I. C. Santos, M. Almeida, J. Vidal-Gancedo, J. Veciana, C. Rovira, Inorg. Chem. 43 (2004) 3631–3641.
[255] X. Ribas, J. C. Dias, J. Morgado, K. Wurst, E. Molins, E. Ruiz, M. Almeida, J. Veciana, C. Rovira, Chem. Eur. J. 10 (2004) 1691–1704.
[256] H. Fujiwara, E. Arai, H. Kobayashi, Chem. Commun. (1997) 837–838.
[257] G. Matsubayashi, A. Yokozawa, Chem. Lett. (1990) 355–358.
[258] G. C. Papavassiliou, V. C. Kakoussis, D. J. Lagouvardos, G. A. Mousdis, Mol. Cryst. Liq. Cryst. 181 (1990) 171–184.
[259] R. -M. Olk, B. Olk, J. Rohloff, J. Reinhold, J. Sieler, K. Trübenbach, R. Kirmse, E. Hoyer, Z. Anorg. Allg. Chem. 609 (1992) 103–116.
[260] S. Tanaka, G. Matsubayashi, J. Chem. Soc. Dalton Trans. (1992) 2837–2843.
[261] G. Matsubayashi, A. Yokozawa, Inorg. Chim. Acta 208 (1993) 95–97.
[262] R. -M. Olk, R. Kirmse, E. Hoyer, Z. Anorg. Allg. Chem. 620 (1994) 90–100.
[263] W. B. Heuer, A. E. True, P. N. Swepston, B. M. Hoffman, Inorg. Chem. 27 (1988) 1474–1482.
[264] P. Tavarès, P. Meunier, B. Gautheron, Phosphorus, Sulfur and Silicon 55 (1991) 249–253.
[265] P. Tavarès, P. Meunier, M. M. Kubicki, B. Gautheron, Heteroatom Chem. 4 (1993) 383–392.
[266] E. Cerrada, M. Laguna, Can. J. Chem. 76 (1998) 1033–1037.
[267] N. J. Harris, A. E. Underhill, J. Chem. Soc., Dalton Trans. (1987) 1683–1685.
[268] C. L. Beswick, J. Schulman, E. I. Stiefel, Progr. Inorg. Chem. 52 (2004) 55–110.
[269] D. J. Sandman, J. C. Stark, G. Allen, L. A. Acampora, Mol. Cryst. Liq. Cryst. 120 (1985) 405–412.
[270] W. B. Heuer, P. J. Squattrito, B. M. Hoffman, J. A. Ibers, J. Am. Chem. Soc. 110 (1988) 792–803.
[271] C. Faulmann, J. -P. Legros, P. Cassoux, J. Cornelissen, L. Brossard, M. Inokuchi, H. Tajima, M. Tokumoto, J. Chem. Soc. Dalton Trans. (1994) 249–254.
[272] J. P. Cornelissen, J. G. Haasnoot, J, Reedijk, C. Faulmann, J. -P. Legros, P. Cassoux, P. J. Nigrey, Inorg. Chim. Acta 202 (1992) 131–139.
[273] R. Kato, Y. Kashimura, H. Sawa, Y. Okano, Chem. Lett. (1997) 921–922.
[274] X. Ribas, D. Maspoch, J. Dias, J. Morgado, M. Almeida, K. Wurst, G. Vaughan, J. Veciana, C. Rovira, CrystEngComm 6 (2004) 589–592.
[275] M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, J. Phys. Chem. A 113 (2009) 5806–5812.
[276] G. Matsubayashi, S. Tanaka, A. Yokozawa, J. Chem. Soc. Dalton Trans. (1992) 1827–1830.

[277] Y. Kashimura, Y. Okano, J. -I. Yamaura, R. Kato, Synth. Met. 103 (1999) 2123–2124.
[278] E. Watanabe, M. Fujiwara, J. -I. Yamaura, R. Kato, J. Mater. Chem. 11 (2001) 2131–2141.
[279] F. Bigoli. C. -T. Chen, W. -C. Wu, P. Deplano, M. L. Mercuri, M. A. Pellinghelli, L. Pilia, G. Pintus, A. Serpe, E. F. Trogu, Chem. Commun. (2001) 2246–2247.
[280] F. Frei, A. Rondi, D. Espa, M. L. Mercuri, L. Pilia, A. Serpe, A. Odeh, F. Van Mourik, M. Chergui, T. Feurer, P. Deplano, A. Vlček Jr., A. Cannizzo, Dalton Trans. 43 (2014) 17666–17676.
[281] R. Kirmse, S. Saluschke, S. Ritter, W. Dietzsch, Z. Anorg. Allg. Chem. 619 (1993) 576–582.
[282] A. E. Pullen, K. A. Abboud, J. R. Reynolds, J. Piotraschke, S. Zeltner, R. M. Olk, E. Hoyer, H. L. Liu, D. B. Tanner, Synth. Met. 86 (1997) 1791–1793.
[283] A. E. Pullen, S. Zeltner, R. M. Olk, E. Hoyer, K. A. Abboud, J. R. Reynolds, Inorg. Chem. 36 (1997) 4163–4171.
[284] A. E. Pullen, S. Zeltner, R. M. Olk, E. Hoyer, K. A. Abboud, J. R. Reynolds, Inorg. Chem. 35 (1996) 4420–4426.
[285] J. A. Zuleta, M. S. Burberry, R. Eisenberg, Coord. Chem. Rev. 97 (1990) 47–64.
[286] W. Paw, S. D. Cummings, M. A. Mansour, W. B. Connick, D. K. Geiger, R. Eisenberg., Coord. Chem. Rev. 171 (1998) 125–150.
[287] M. Hissler, J. E. McGarrah, W. B. Connick, D. K. Geiger, S. D. Cummings, R. Eisenberg, Coord. Chem. Rev. 208 (2000) 115–137.
[288] C. A. Mitsopoulou, Coord. Chem. Rev. 254 (2010) 1448–1456.
[289] G. Matsubayashi, Y. Hiroshige, Inorg. Chim. Acta 183 (1991) 173–177.
[290] C. P. Morley, C. D. Jones, C. A. Webster, M. Di Vaira, Phosphorus, Sufur, and Silicon 180 (2005) 801–813.
[291] H. Oku, N. Ueyama, A. Nakamura, Chem. Lett. (1996) 1131–1132.
[292] A. L. Gushchin, R. Llusar, C. Vicent, P. A. Abramov, C. J. Gómez-Garcia, Eur. J. Inorg. Chem. (2013) 2615–2622.
[293] R. Llusar, S. Triguero, V. Polo, C. Vicent, C. J. Gómez-García, O. Jeannin, M. Formigué, Inorg. Chem. 47 (2008) 9400–9409.
[294] R. Llusar, C. Vicent, Coord. Chem. Rev. 254 (2010) 1534–4548.
[295] A. L. Gushchin, Y. A. LAricheva, M. N. Sokolov, R. Llusar, Russ. Chem. Rev. 87 (2018) 670–706.
[296] R. -M. Olk, W. Dietzsch, J. Kahlmeier, P. Jörchel, R. Kirmse, J. Sieler, Inorg. Chim. Acta 254 (1997) 375–379.
[297] S. Sproules, A. A. Eagle, M. K. Taylor, R. W. Gable, J. M. White, C. G. Young, Inorg. Chem. 50 (2011) 4503–4514.
[298] K. Junold, C. Burschka, R. Bertermann, R. Tacke, Dalton Trans. 39 (2010) 9401–9413.
[299] M. Nomura, T. Cauchy, M. Formigué, Coord. Chem. Rev. 254 (2010) 1406–1418.
[300] M. Nomura, Dalton Trans. 40 (2011) 2112–2140.
[301] M. Formigué, Coord. Chem. Rev. 178/180 (1998) 823–864.
[302] M. Formigué, Acc. Chem. Res. 37 (2004) 179–186.
[303] M. Formigué, T. Cauchy, M. Nomura, CrystEngComm 11 (2009) 1491–1501.
[304] A. Sugimori, T. Akiyama, M. Kajitani, T. Sugiyama, C. Takayama, Sulfur Reports 22 (2000) 151–193.
[305] A. Sugimori, T. Akiyama, M. Kajitani, T. Sugiyama, Bull. Chem. Soc. Jpn. 72 (1999) 879–908.
[306] M. Nomura, T. Fujii, M. Kajitani, Organometallics 28 (2009) 3776–3784.
[307] M. Murata, S. Habe, S. Araki, K. Namiki, T. Yamada, N. Nakagawa, T. Nankawa, M. Nihei, J. Mizutani, M. Kurihara, H. Nishihara, Inorg. Chem. 45 (2006) 1108–1116.
[308] R. J. Walwyn, B. Chan, P. M. Usov, M. B. Solomon, S. G. Duyker, J. Y. Koo, M. Kawano, P. Turner, C. J. Kepert, D. M. D'Alessandro, J. Mater. Chem. C 6 (2018) 1092–1104.
[309] S. Zeltner, R. -M. Olk, M. Pink, S. Jelonek, P. Jörchel, T. Gelbrich, J. Sieler, R. Kirmse, Z. Anorg. Allg. Chem. 622 (1996) 1979–1986.
[310] M. Formigué, B. Domercq, I. V. Jourdain, P. Molinié, F. Guyon, J. Amaudrut, Chem. Eur. J. 4 (1998) 1714–1723.
[311] T. Bsaibess, M. Guerro, Y. Le Gal, D. Sarraf, N. Bellec, M. Formigué, F. Barrière, V. Dorcet, T. Guizouarn, T. Roisnel, D. Lorcy, Inorg. Chem. 52 (2013) 2162–2173.
[312] S. Habe, T. Yamada, T. Nankawa, J. Mizutani, M. Murata, H. Nishihara, Inorg. Chem. 42 (2003) 1952–1955.
[313] Y. Okano, M. Iso, Y. Kashimura, J. Yamaura, R. Kato, Synth. Met. 102 (1999) 1703–1704.
[314] K. P. C. Vollhardt, E. C. Walborsky, Polyhedron 7 (1988) 1023–1034.
[315] M. Nomura, T. Cauchy, M. Geoffroy, P. Adkine, M. Formigué, Inorg. Chem. 45 (2006) 8194–8204.
[316] J. Conradie, J. Molec. Struct. THEOCHEM 915 (2009) 51–57.
[317] J. W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.
[318] N. J. Wiebelhaus, M. A. Cranswick, E. L. Klein, L. T. Lockett, D. L. Lichtenberger, J. H. Enemark, Inorg. Chem. 50 (2011) 11021–11031.
[319] J. Conradie, S. Afr. J. Chem. 63 (2010) 65–71.

[320] A. Kuhm, A. Muller, J. Conradie, Polyhedron 28 (2009) 966–947.
[321] C. Guimon, G. Pfister-Guillouzo, P. Meunier, B. Gautheron, G. Tainturier, S. Pouly, J. Organomet. Chem. 284 (1985) 299–312.
[322] S. Vincendeau, V. Collière, C. Faulmann, Acta Cryst. E59 (2003) m268–m270.
[323] F. Guyon, C. Lenoir, M. Formigué, J. Larsen, J. Amaudrut, Bull. Soc. Chim. Fr. 131 (1994) 217.
[324] B. Joseph, S. Gomosta, R. Prakash, T. Roisnel, A. K. Phukan, S. Ghosh, Chem. Eur. J. 26 (2020) 16824–16832.
[325] T. Klapötke, Polyhedron, 6 (1987) 1593–1597.
[326] J. Yamada, Y. Amano, S. Takasaki, R. Nakanishi, K. Matsumoto, S. Satoki, H. Anzai, J. Am. Chem. Soc. 117 (1995) 1149–1150.
[327] A. Ueda, H. Kamo, H. Mori, Chem. Lett. 44 (2015) 1538–1540.
[328] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, Z. Naturforsch 57b (2002) 53–60.
[329] G. Heckmann, G. Wolmershäuser, Chem. Ber. 126 (1993) 1071–1076.
[330] A. J. Mayr, H. -S. Lien, K. H. Pannell, Organometallics (1985) 1580–1585.
[331] P. Mathur, M. Hossain, Organometallics 12 (1993) 2398–2400.
[332] P. Mathur, M. Hossain, K. Das, U. C. Sinha, J. Chem. Soc., Chem. Commun. (1993) 46–48.
[333] P. Mathur, M. Hossain, J. Organomet. Chem. 471 (1994) 185–191.
[334] P. Mathur, M. Hossain, V. G. Puranik, S. S. Tavale, Proc. Indian Acad. Sci. (Chem. Sci.) 107 (1995) 443–446.
[335] P. Mathur, A. K. Dash, M. Hossain, C. V. V. Satyanarayana, J. Organomet. Chem. 439 (1995) 257–260.
[336] P. Mathur, M. Hossain, S. Umbarkar, C. V. V. Satyanarayana, J. Organomet. Chem. 506 (1996) 313–319.
[337] P. Mathur, M. Hossain, A. L. Rheingold, J. Organomet. Chem. 507 (1996) 187–195.
[338] P. Mathur, A. K. Dash, M. Hossain, C. V. V. Satyanarayana, B. Verhese, J. Organomet. Chem. 506 (1996) 307–312.
[339] P. Mathur, A. K. Dash, M. Hossain, C. V. V. Satyanarayana, A. L. Rheingold, G. P. A. Yap, L. M. Liable-Sands, J. Organomet. Chem. 543 (1997) 135–143.
[340] P. Mathur, S. Ghosh, Organometallics 16 (1997) 4392–4398.
[341] P. Mathur, S. Ghosh, Organometallics 16 (1997) 6028–6031.
[342] P. Mathur, A. K. Dash, M. Hossain, C. V. V. Satyanarayana, A. L. Rheingold, L. M. Liable-Sands, G. P. A. Yap, J. Organomet. Chem. 532 (1997) 189–199.
[343] P. Mathur, S. Ghosh, A. Sarkar, A. L. Rheingold, I. A. Guzei, J. Organomet. Chem. 566 (1998) 159–164.
[344] P. Mathur, S. Ghosh, Organometallics 17 (1998) 3926–3930.
[345] P. Mathur, S. Ghosh, Organometallics 17 (1998) 770–772.
[346] P. Mathur, A. K. Dash, J. Cluster Sci. 9 (1998) 131–143.
[347] A. K. Dash, P. Mathur, T. -H. Lu, Y. -Y. Liu, S. -F. Tung, J. Organomet. Chem. 590 (1999) 46–51.
[348] R. Philip, G. R. Kumar, P. Mathur, S. Ghosh, Chem. Phys. Lett. 313 (1999) 719–724.
[349] P. Mathur, S. Ghosh, A. Sarkar, A. L. Rheingold, I. A. Guzei, Tetrahedron 56 (2000) 4995–5000.
[350] P. Mathur, R. S. Ji, M. Tauqeer, G. K. Lahiri, S. M. Mobin, J. Organomet. Chem. 721–722 (2012) 186–189.
[351] K. Ray, S. DeBeer George, E. I. Solomon, K. Wieghardt, F. Neese, Chem. Eur. J. 13 (2007) 2783–2797.
[352] R. Sarangi, S. DeBeer George, D. Jackson Rudd, R. K. Szilagyi, X. Ribas, C. Rovira, M. Almeida, K. O. Hodgson, B. Hedman, E. I. Solomon, J. Am. Chem. Soc. 129 (2007) 2316–2326.
[353] S. Sproules, K. Wieghardt, Coord, Chem. Rev. 255 (2011) 837–860.
[354] E. A. C. Bushnell, R. J. Boyd, J. Phys. Chem. A 119 (2015) 911–918.
[355] E. A. C. Bushnell, M. R. Adams, R. J. Boyd, Struct. Chem. 28 (2018) 1173–1180
[356] E. A. C. Bushnell, T. D. Burns, R. J. Boyd, Phys. Chem. Chem. Phys. 16 (2014) 10897–10902.
[357] R. -M. Olk, E. Hoyer, C. Faulmann, P. Cassoux, Synth. Met. 55–57 (1993) 2453–2458.
[358] V. V. Pavlishchuk, A. W. Addison, Inorg. Chim. Acta 298 (2000) 97–102.
[359] C. Faulmann, J. -P. Legros, P. Cassoux, Synth. Met. 55–57 (1993) 2063–2068.
[360] K. Wang from Dithiolene Chemistry: Synthesis, Properties, and Applications (Ed.: E. I. Stiefel), Wiley, Hoboken (2004) 267–314.
[361] T. Akiyama, Y. Watanabe, A. Miyasaka, T. Komai, H. Ushijima, M. Kajitani, K. Shimizu, A. Sugimori, Bull. Chem. Soc. Jpn. 65 (1992) 1047–1051.
[362] P. Deplano, L. Pilia, D. Espa, M. L. Mercuri, A. Serpe, Coord. Chem. Rev. 254 (2010) 1434–1447.
[363] B. Garreau de Bonneval, K. I. Moineau-Chane Ching, F. Alary, T. -T. Bui, L. Valade, Coord. Chem. Rev. 254 (2010) 1457–1467.
[364] A. Takenoshita, T. Yonezawa, K. Yamasaki, US 2014/0103271 A1 (2014).
[365] A. Pintus, L. Ambrosio, M. C. Aragoni, M. Binda, S. J. Coles, M. B. Hursthouse, F. Isaia, V. Lippolis, G. Meloni, D. Natali, J. B. Orton, E. Podda, M. Sampietro, M. Arca, Inorg. Chem. 59 (2020) 6410−6421.
[366] A. Mizuno, H. Benjamin, Y. Shimizu, Y. Shuku, M. M. Matsushita, N. Robertson, K. Awaga, Adv. Funct. Mater. 29 (2019) 1904181.
[367] C. Lauterbach, J. Fabian, Eur. J. Inorg. Chem. (1999) 1995–2004.

[368] B. S. Lim, D. V. Fomitchev, R. H. Holm, Inorg. Chem. 40 (2001) 4257–4262.
[369] F. Alary, J. -L. Huelly, A. Scemama, B. Garreau-de Bonneval, K. I. Chane-Ching, M. Caffarel, Theor. Chem. Acc. 126 (2010) 243–255.
[370] G. C. Papavassiliou, A. M. Cotsilios, C. S. Jacobsen, J. Mol. Struct. 115 (1984) 41–44.
[371] A. E. Underhill, M. M. Ahmad, J. Chem. Soc., Chem. Commun. (1981) 67–68.
[372] A. E. Underhill, P. I. Clemenson, M. B. Hursthouse, R. L. Short, G. J. Ashwell, I. M. Sandy, K. Carneiro, Synth. Met. 19 (1987) 953–958.
[373] P. Cassoux, L. Valade, in Inorganic Materials, (Eds.: D. W. Bruce, D. O'HAre) , 2nd ed. Wiley (1996) Chichester.
[374] P. Cassoux, J. S. Miller, in Chemistry of Advanced Materials, (Eds.: L. V. Interrante, M. J. Hampden-Smith, Wiley-VCH (1998) New York.
[375] P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, A. E. Underhill, Coord. Chem. Rev. 110 (1991) 115–160.
[376] J. Morgado, L. Alcàcer, M. Almeida, Solid State Commun. 89 (1994) 755–759.
[377] A. K. Whittaker, P. C. Stein, P. Bernier, W. B. Heuer, B. M. Hoffman, J. Phys. Chem. 93 (1989) 3038–3041.
[378] J. Khan, Y. Liu, T. Zhao, H. Geng, W. Xu, Z. Shuai, J. Comput. Chem. 39 (2018) 2582–2588.
[379] W. Shi, G. Wu, X. Yong, T. Deng, J. -S. Wang, J. -C. Zheng, J. Xu, M. B. Sullivan, S. -W. Yang, ACS Appl. Mater. Interf. 10 (2018) 35306–35315.
[380] C. H. Hendon, D. Tiana, T. P. Vaid, A. Walsh, J. Mater. Chem. C 1 (2013) 95–100.
[381] A. C. Scott, T. P. Vaid, E. J. Bylaska, D. A. Dixon, J. Phys. Chem. C 116 (2012) 8370–8378.
[382] M. T. Jones, S. Jansen, D. J. Sandman, B. M. Foxman, G. J. Ashwell, Mol. Cryst. Liq. Cryst. 125 (1985) 429–437.
[383] R. Kirmse, K. Köhler, R. -M. Olk, W. Dietzsch, E. Hoyer, G. Zwanenburg, Inorg. Chem. 29 (1990) 4073–4076.
[384] V. Gama, M. Almeida, Top. Organomet. Chem. 27 (2009) 97–140.
[385] M. T. Jones, S. Jansen, Physica 143B (1986) 515–517.
[386] J. Morgado, M. T. Duarte, L. Alcácer, I. C. Santos, R. T. Henriques, M. Almeida, Synth. Met. 86 (1997) 2187–2188.
[387] L. V. Interrante, J. W. Bray, H. R. Hart Jr., I. S. Jacobs, J. S. Kasper, P. A. Piacente, Lect. Notes Phys. 96 (1979) 55–68.
[388] M. T. Jones, J. H. Roble, M. Singh, T. Maruo, Synth. Met. 27 (1988) B469–B474.
[389] L. Binet, J. M. Fabre, C. Montginoul, K. B. Simonsen, J. Becher, J. Chem. Soc., Perkin Trans. 1 (1996) 783–788.
[390] J. Garín, J. Orduna, M. Savirón, M. R. Bryce, A. J. Moore, V. Morisson, Tetrahedron 52 (1996) 11063–11074.
[391] K. Ueda, T. Kominami, M. Iwamatsu, T. Sugimoto, Chem. Lett. (2000) 842–843.
[392] A. Chesney, M. R. Bryce, S. Yoshida, I. F. Perepichka, Chem. Eur. J. 6 (2000) 1153–1159.
[393] A. Chesney, M. R. Bryce, A. S. Batsanov, K. A. K. Howard, Chem. Commun. (1997) 2293–2294.
[394] G. C. Papavasssiliou, G. A. Mousdis, G. C. Anyfantis, N. Assimomytis, B. R. Steele, Z. Naturforsch. 58b (2003) 813–814.
[395] M. Wagner, D. Madsen, J. Markussen, S. Larsen, K. Schaumburg, K. -H. Lubert, J. Becher, R. -M. Olk, J. Chem. Soc., Perkin Trans. 1 (1996) 1995–1998.
[396] H. Fang, D. He, H. Luo, L. Wang, L. Wang, S. Wang, S. Wu, L. Zhang, Y. Zhang (2018) Pat. CN109134514A.
[397] Y. Misaki, Sci. Technol. Adv. Mater. 10 (2009) 024301.
[398] C. Mayer, J. Zambounis (1991) Pat. EP0408495B1.
[399] P. J. Nigrey, J. Org. Chem. 53 (1988) 201–203.
[400] J. Yamada, S. Satoki, H. Anzai, K. Hagiya, M. Tamura, Y. Nishio, K. Kajita, E. Watanabe, M. Konno, T. Sato, H. Nishikawa, K. Kikuchi, Chem. Commun. (1996) 1955–1956.
[401] J. Yamada, S. Takasaki, M. Kobayashi, H. Anzai, N. Tajima, M. Tamura, Y. Nishio, K. Kajita, Chem. Lett. (1995) 1069–1070.
[402] Y. Kimura, M. Misawa, A. Kawamoto, Phys. Rev. B 84 (2011) 045123-1–045123-5.
[403] T. Courcet, I. Malfant, K. Pokhodnia, P. Cassoux, New J. Chem. (1998) 585–589.
[404] T. Imakubo, H. Sawa, R. Kato, Synth. Met. 86 (1997) 1883–1884.
[405] T. Imakubo, T. Shirahata, Chem. Commun. (2003) 1940–1941.
[406] B. Zhang, D. Zhu, Z. Bin, Z. Daoben (2012) Pat. CN102757535.
[407] R. Sato, S. Sanada, M. Okanuma, T. Kimura, S. Ogawa, Tetrahedron Lett. 38 (1997) 5821–5824.
[408] T. Yamamoto, S. Ogawa, M. Sugawara, Y. Kawai, R. Sato, Bull. Chem. Soc. Jpn. 79 (2006) 460–467.
[409] S. Ogawa, M. Sugawara, Y. Kawai, S. Niizuma, T. Kimura, R. Sato, Tetrahedron Lett. 40 (1999) 9101–9106
[410] K. Sato, T. Kikuchi, A. Sasaki, S. Ogawa (1995) Pat. JPH07304766A.
[411] E. Cerrada, S. Elipe, M. Laguna, F. Lahoz, A. Moreno, Synth. Met. 102 (1999) 1759–1760.
[412] P. Meunier, B. Gautheron, A. Mazouz, J. Chem. Soc., Chem. Commun. (1986) 424–425.

[413]   A. Mazouz, P. Meunier, M. M. Kubicki, B. Hanquet, R. Amardeil, C. Bornet, A. Zahidi, J. Chem. Soc., Dalton Trans. (1997) 1043–1048.

[414]   P. Meunier, B. Gautheron, A. Mazouz, Phosphorus and Sulfur 33 (1987) 33–36.

[415]   Y. Le Gal, N. Bellec, F. Barriere, R. Clerac, M. Formigue, V. Dorcet, T. Roisnel, D. Lorcy, Dalton Trans. 42 (2013) 16672–16679.

[416]   M. Sakurada, J. Okubo, M. Kajitani, T. Akiyama, A. Sugimori, Chem. Lett. (1990) 1837–1840.

[417]   M. Sakurada, J. Okubo, M. Kajitani, T. Akiyama, A. Sugimori, Phosphorus, Sulfur, and Silicon 67 (1992) 145–150.

[418]   S. J. Nieter Burgmayer, Progr. Inorg. Chem. (2003) 491–537.

[419]   N. Ueyama, H. Oku, A. Nakamura, J. Am. Chem. Soc. 114 (1992) 7310–7311.

[420]   E. A. C. Bushnell, Comput. And Theor. Chem. 1139 (2018) 38–43.

[421]   A. J. Clough, J. W. Yoo, M. H. Mecklenburg, S. C. Marinescu, J. Am. Chem. Soc. 137 (2015) 118–121.

[422]   C. A. Downes, S. C. Marinescu, Dalton Trans. 45 (2016) 19311–19321.

[423]   C. A. Downes, S. C. Marinescu, J. Am. Chem. Soc. 137 (2015) 13740–13743.

[424]   K. Wang, E. I. Stiefel, Science 291 (2001) 106–109.

[425]   C. García-Símon, M. Garcia-Borràs, L. Gómez, I. Garcia-Bosch, S. Osuna, M. Swart, J. M. Luis, C. Rovira, M. Amieda, I. Imaz, D. Maspoch, M. Costas, X. Ribas, Chem. Eur. J. 19 (2013) 1445–1456.