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Review

Synthesis of ligands based on naphthalene *peri*-substituted by Group 15 and 16 elements and their coordination chemistry

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ABSTRACT

The synthetic aspects of chemistry of ligands based on naphthalene *peri*-substituted by heavier Group 15 elements (P, As, Sb, Bi) or Group 16 elements (S, Se, Te) are discussed in this review. An overview of coordination chemistry of these ligands is also given. In general, the area is dominated by bis(phosphines) $Nap(PR_2)_2$ and dithiolates $Nap(SR)_2$ (Nap = naphthalene-1,8-diyl), and most of the ligands act with chelating rigid C_3-backbones. Whilst all known bis(phosphine) complexes with Ni, Pd and Pt contain unmodified $Nap(PR_2)_2$ moieties, the reactions with a variety of metal carbonyls sometimes result in P–C bond cleavage within the ligand. A range of gold complexes with $Nap(PR_2)_2$ ligands have been investigated for material applications. $NapP_2$ ligands other than phosphines are also described, these include 1,2-diphosphaacenaphthenes, bis(phosphonites) and bis(phosphine oxides). Group 16 *peri*-dichalcogenolates used as ligands include $NapS_2$, $NapSe_2$ and NapSSe systems, but no tellurium congeners. Heterodentate ligands discussed in this review include those with NapPN, NapPO, NapPS, NapPF, NapPC and NapSN motifs. Ligands with heavier Group 15 donor atoms ($NapAs_2$, $NapSb_2$) are also reported. All possible oxides of the dithioles (monooxide to tetraoxide) as ligands are also discussed. Areas of interest for further work are outlined.

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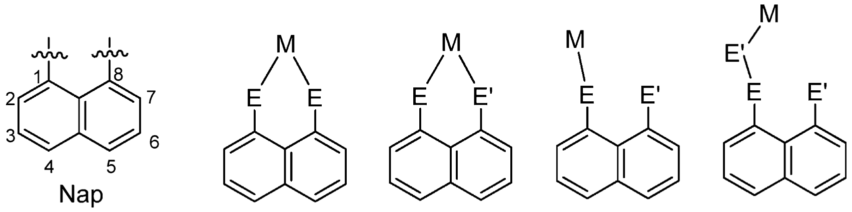


Fig. 1. Numbering scheme in naphthalene-1,8-diyl (abbreviated Nap throughout this paper) and general formula of ligands and complexes discussed in this review. E = heavier pnictogen (P, As, Sb, Bi) or chalcogen (S, Se, Te), E′ = any p-block element, M = transition metal.

1. Introduction

The development of synthetic methods to ligands with main group donor atoms is an important aspect of main group chemistry. In this review we describe the synthesis and coordination chemistry of ligands containing the 1,8-disubstituted (i.e. *peri*-substituted) naphthalene motif, with heavier Group 15 elements (P, As, Sb, Bi) or Group 16 elements (S, Se, Te) in at least one of the *peri*-positions. Species where at least one of these *peri*-atoms acts as a donor towards the metal are included; also included are some ligands with donor atoms being α- with respect to the *peri*-atoms (Fig. 1). The homodentate ligands dealt with here are mostly chelating, many heterodentate ligands are capable of forming hemilabile complexes. In some cases, monodenticity is also observed. For brevity, naphthalene-1,8-diyl is abbreviated as Nap throughout this paper.

Peri-substituted naphthalenes are rigid C_3-ligands. The rigidity stems from the aromatic nature of naphthalene. The molecule of naphthalene itself is planar, with all angles close to 120°, which results in the "ideal" *peri*-distance of ca 2.5 Å. Only in naphthalene itself are the two *peri*-atoms (in this case hydrogen atoms) placed comfortably. Because of the limited space available, the rigid geometry of naphthalene imposes strain on any other (i.e. non-hydrogen) *peri*-atoms, often forcing the two *peri*-atoms to form sub-van der Waals contacts. The *peri*-geometry is somewhat comparable to *ortho*- and bay-region geometries, the *peri*-distance being the intermediate between *ortho*- and bay-region distances (see Fig. 2).

The rigidity of the backbone and the close proximity of the *peri*-substituents have important implications for the chemistry of *peri*-substituted species. The reactivity of the *peri*-substituted species (like that of ortho-substituted ones) is often unconventional and specialised synthetic strategies are frequently required to achieve the desired functionalization pattern.

The special *peri*-naphthalene geometry has attracted a great deal of attention; a large number of studies focusing on bonding in main group systems have been reported. These aspects of *peri*-substituted naphthalenes and related systems were the subject of our recent review [1], whilst Group 13 [2] and "proton sponges" [3] were also reviewed recently. An early review reported on all types of *peri*-substituted species [4].

The coordination chemistry of *peri*-substituted naphthalenes has developed very rapidly mainly in the last 15 years. The majority of the work focused on bis(phosphines) and bis(thiolates); although mixed donor NapPN and NapSN systems received considerable attention too. The above mentioned proximity of the donor atoms in *peri*-substituted naphthalenes is rather unique; the related systems often studied in conjunction with naphthalene systems (in particular for applications in catalysis) are shown in Fig. 3. Very few of these confer the rigidity seen in *peri*-substituted naphthalenes.

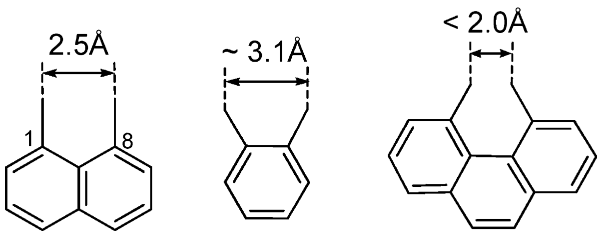


Fig. 2. Comparison of the geometry of *peri*-substitution in naphthalenes, *ortho*-substitution in benzenes, and bay-region disubstitution in phenanthrenes.

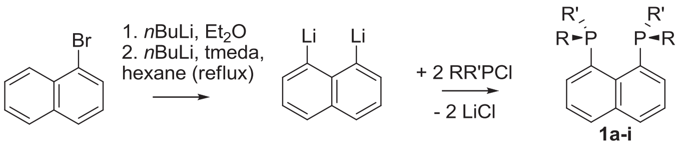
As will be demonstrated below, the large majority of transition metal complexes with *peri*-substituted naphthalene ligands features a rather limited number of ligands. For example, amongst Group 15 species, the bis(phosphine) $Nap(PPh_2)_2$ ligand is almost ubiquitous. We believe that the unconventional synthetic strategies required in the synthesis of some *peri*-substituted species, has resulted in a rather limited application of these more "exotic" ligands by chemists. In this review we attempt to enrich the coordination chemist's toolbox by listing all of the less common variations of substituent patterns of the well-established ligands, and we also demonstrate that a much wider variety of ligands with a range of donor atoms are synthetically accessible.

2. Ligands with Group 15 element(s) as *peri*-atoms

2.1. Naphthalene-1,8-bis(phosphines)

2.1.1. Synthesis of naphthalene-1,8-bis(phosphine) ligands

Bis(phosphines) have received the most attention amongst various structural variants of Group 15 *peri*-substituted naphthalenes, chiefly because of their usefulness as rigid C_3 bidentate ligands in transition metal complexes. In this regard, naphthalene-1,8-bis(phosphines) may be considered as a rigid version of bis(diorganylphosphino)propanes $R_2P(CH_2)_3PR_2$, and in many respects are comparable to *ortho*-substituted benzenes, i.e. *o*-$C_6H_4(PR_2)_2$. The calculated natural bite angle of the most widely used ligand dppn (**1f**) is ca 90° (for the free ligand) [5]. Ligand characteristics of dppn **1f** are discussed (amongst others) in the ligand knowledge base theoretical study [6]. In general terms, (in the vast majority of cases) chelation of dppn to the transition metal centre results in the lengthening of the P···P distance in the ligand by ca. 0.05–0.20 Å. This is a reversal of the process seen in proton sponges upon protonation [7].



	a[8,10,11]	**b**[10]	**c**[10]	**d**[10]	**e**[10]	**f**[9,10]	**g**[10]	**h**[13]	**i**[13]
R	Me	Et	*i*Pr	Cy	*t*Bu	Ph	*t*Bu	*t*Bu	Me
R'	Me	Et	*i*Pr	Cy	Ph	Ph	*t*Bu	C_6F_5	C_6F_5

Scheme 1. Synthesis of 1,8-bis(phosphino) naphthalenes **1a**–**i** [8–12]. Syntheses of **1g** [11] and **1h** [12] were attempted, but were not successful, see text. Tmeda = tetramethylethylenediamine.

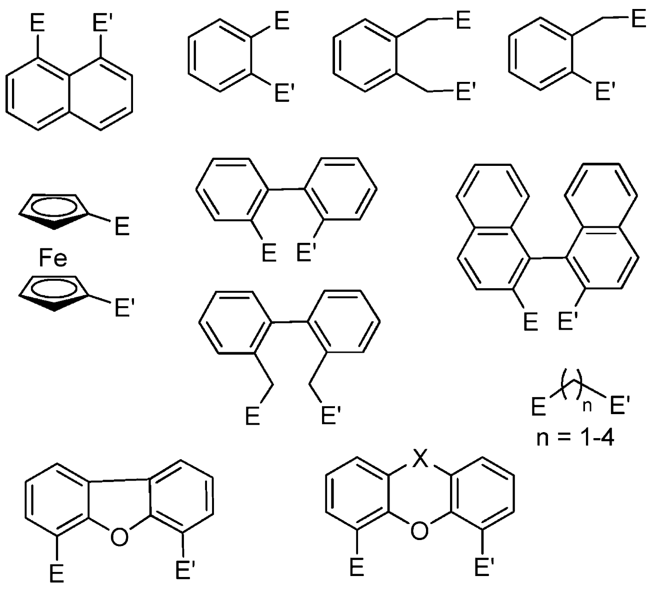


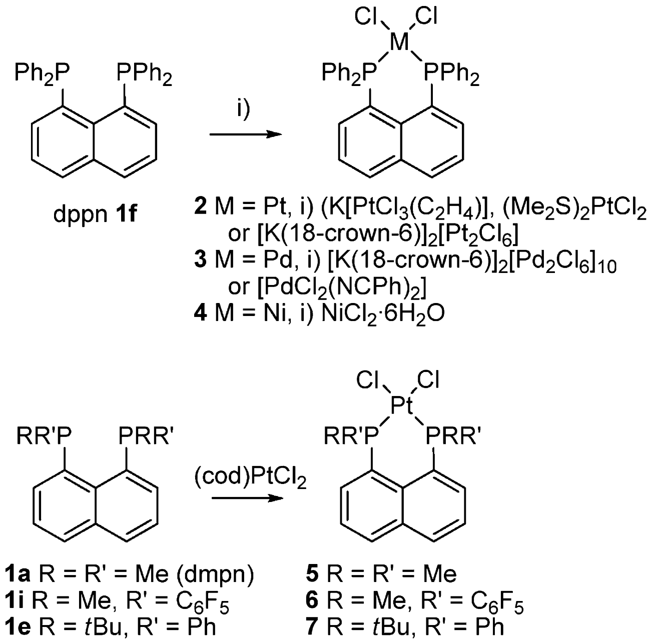
Fig. 3. Selection of C_1 to C_5 bidentate ligands often studied in conjunction with *peri*-substituted naphthalenes. E and E′ donor atoms may or may not be equal.

1,8-Bis(phosphino)naphthalenes are prepared in a "one pot" manner by the coupling of 1,8-dilithionaphthalene with two moles of the respective chlorophosphine (Scheme 1) [8–12]. In the initial studies, 1,8-dilithionaphthalene was made by double lithium-halogen exchange from 1,8-dibromonaphthalene [8,9]. An easier route to 1,8-dilithionaphthalene was reported by Brandsma et al. in 1994 [13], starting from commercially available 1-bromonaphthalene and avoiding the painstaking synthesis of 1,8-dibromonaphthalene (Scheme 1).

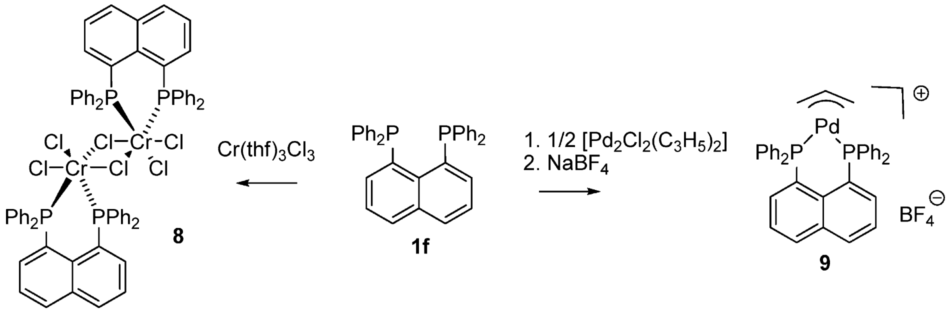
The reaction in Scheme 1 has its limitations with respect to the bulk of the substituents present on the phosphorus atoms. Thus no 1,8-bis(di-*t*-butylphosphino)naphthalene **1g** was obtained when 1,8-dilithionaphthalene was reacted with two equivalents of $t\mathrm{Bu}_2\mathrm{PCl}$. Instead, a small amount of di-*t*-butyl-1-naphthyl phosphine was isolated [11]. The same limitation was observed when the synthesis of pentafluorophenyl analogue **1h** was attempted later; steric hindrance prohibits the placement of the two bulky $(\mathrm{C_6F_5})t\mathrm{BuP}$-groups in 1,8-positions of the naphthalene ring [12]. In confirmation of the fact that steric, rather than electronic factors are responsible for this, an electronically related, but less bulky methyl(pentafluorophenyl) phosphine **1i** was obtained via the same synthetic route in a good yield [12].

When R and R′ are unequal (Scheme 1), two diastereomeric forms of the bis(phosphines) exist. Racemic Ph*t*BuPCl was used in the preparation of **1e**, and as expected, two diastereomers (*rac*-**1e** and *meso*-**1e**) were observed in the mixture after the reaction by ^{31}P NMR [10].

Initial reports stated that **1f** (abbreviated as dppn) and other bis(phosphines) are air stable, however this was disproved later, when all but **1e** were found to oxidise to



Scheme 2. Synthesis of Pt, Pd and Ni dichlorocomplexes **2**–**7** [9,12,15,16]. Cod = cycloocta-1,5-diene.



Scheme 3. Synthesis of chromium(III) halocomplex **8** [17] and palladium η^3-allyl complex **9** [18].

corresponding phosphine oxides (in air) even in the solid state [14].

Despite the relative ease of the synthesis of the bis(phosphines) **1a**–**1i**, only some of them were used as ligands. Recently, dppn **1f** became commercially available, which, coupled with its relative air stability, is likely to result in an even stronger preference of this ligand over others in the series.

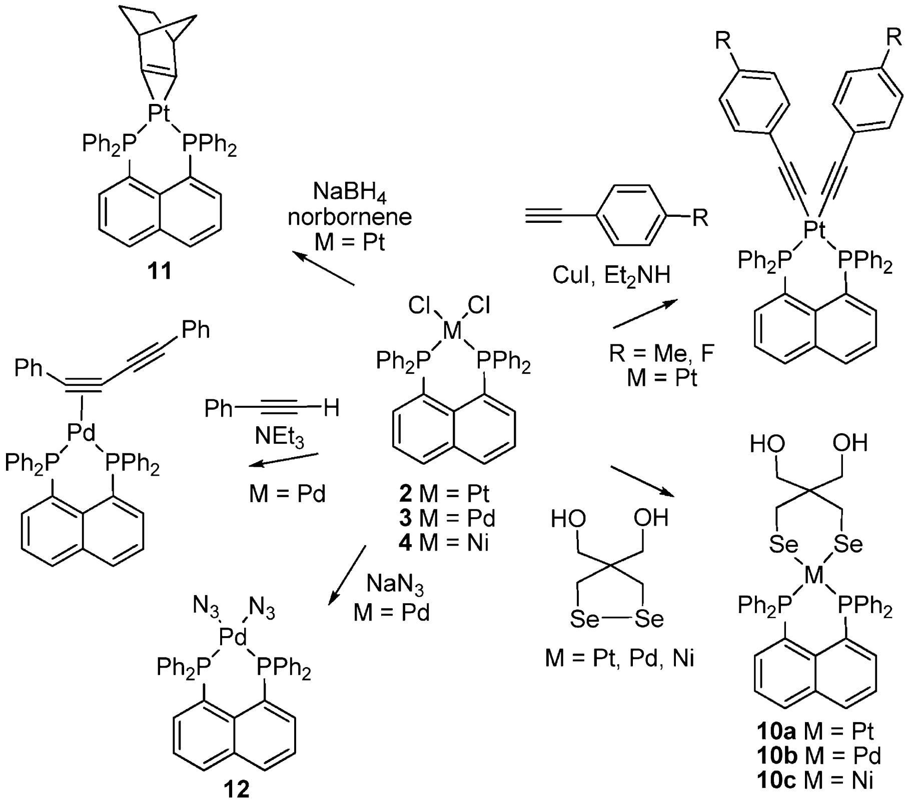
2.1.2. *Ni, Pd and Pt metal complexes with naphthalene-1,8-bis(phosphines)*

Several platinum complexes K[$PtCl_3(C_2H_4)$] [9], $(Me_2S)_2PtCl_2$ [15] and [K(18-crown-6)]$_2$[Pt_2Cl_6] [16] are used as precursors to make synthetically important dichlorocomplex **2** as shown in Scheme 2. The palladium congener **3** is accessible by the reaction of dppn **1f** with [K(18-crown-6)]$_2$[Pd_2Cl_6] [16] or [$PdCl_2(NCPh)_2$] [9]. Nickel species **4** is prepared by the reaction of dppn **1f** with $NiCl_2{\cdot}6H_2O$ [16]. The related platinum complexes **5**, **6** and **7** were prepared by the reaction of (cod)$PtCl_2$ with the free bis(phosphines) **1a** (dmpn), **1e** and **1i** (Scheme 2) [12].

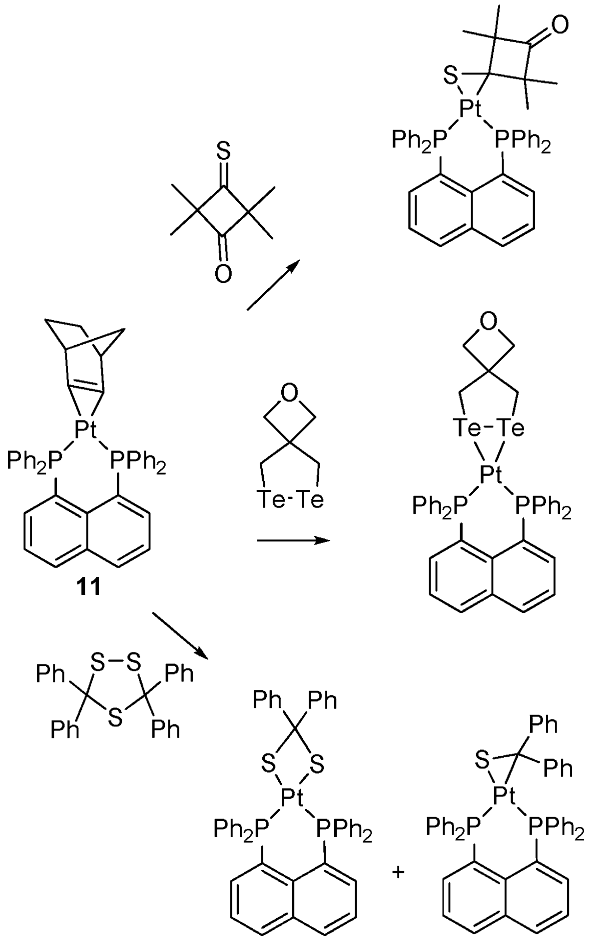
A binuclear chromium(III) halocomplex **8** is obtained by the reaction of $Cr(thf)_3Cl_3$ with dppn (**1f**) (Scheme 3) [17]. The cationic palladium η^3-allyl complex **9** is prepared by the reaction of [$Pd_2Cl_2(allyl)_2$] with dppn (**1f**) in the presence of $NaBF_4$ (Scheme 3) [18].

The platinum, palladium and nickel dichlorocomplexes **2**, **3** and **4** have been used as starting materials in transformations in which the chloro ligands were replaced with a range of other ligands (Scheme 4) [15,16,19,20]. The stability of complexes **10a**–**c** varies with the metal. Whilst the platinum species **10a** was isolated in the crystalline state, only solution NMR data are presented for the palladium complex **10b**, and no characterisation data are available for nickel complex **10c** due to fast decomposition of the complex at room temperature [16]. Notably, the norbornene complex **11** is suggested as an easily accessible and clean source of [dppnPt(0)], a 14 electron complex [20], and as such has been used in the insertion and other reactions shown in Scheme 5 [20–22].

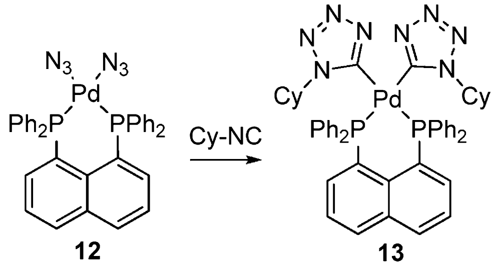
The Pd-bis(azido) complex **12** underwent [2+3] cycloaddition with isocyanide to give the bis(tetrazolate) **13**



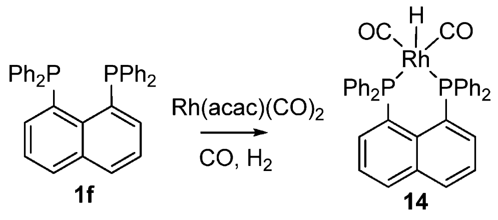
Scheme 4. Reactions of dichlorocomplexes **2**–**4** [15,16,19,20].



Scheme 5. Reactions of norbornene complex **11** [20–22].



Scheme 6. Synthesis of bis(tetrazolate) **13** [19].



Scheme 7. *In situ* synthesis of hydridocomplex **14** [5].

with square planar geometry at the Pd atom (Scheme 6) [19].

Dppn (**1f**) was tested as a ligand in several palladium catalysed reactions, namely in the reductive carbonylation of nitrobenzene [with $Pd(OAc)_2$ catalyst] [23] and in Heck coupling [with $Pd(dba)_2$ catalyst, dba = dibenzylideneacetone] [24]. In these instances the active species were generated *in situ* and were not characterised.

2.1.3. Reactions of metal carbonyl complexes with naphthalene-1,8-bis(phosphines)

Reactions of transition metal carbonyl clusters with naphthalene-1,8-bis(phosphines) have received a great deal of attention in the literature. The products of these reactions contain a wide range of structural motifs, and some general reactivity patterns have been observed. Ligand dppn (**1f**) has been used solely in these reactions, with the single exception of a ruthenium species, where dmpn (**1a**) was used as the ligand. In many cases several species were formed in the reactions, in all cases these were air/moisture stable enough to be purified by chromatography.

A rhodium hydridocomplex $HRh(CO)_2(dppn)$ **14** has been synthesised *in situ* from dppn (**1f**) and $Rh(acac)(CO)_2$ under a syngas atmosphere (Scheme 7), it was characterised by high pressure inverse 2D X, ^{103}Rh NMR experiments (X = ^{1}H, ^{31}P). Trigonal bipyramidal complexes with bidentate ligands, such as **14**, are attracting attention as catalysts in hydroformylation [5].

A mononuclear molybdenum complex has also been prepared from dppn (**1f**) and $[(nor)Mo(CO)_4]$, see Scheme 26 [25].

The tricobalt clusters $RCCo_3(CO)_9$ (R = Ph, H) display a range of reactivity towards dppn (Scheme 8) [26]. Clusters **15** result from a P–C bond cleavage reaction of dppn, followed by a simple substitution in which one of the CO ligands is replaced by the formed 1-(diphenylphosphino)naphthalene. Intact dppn is present in cluster **16**, where it acts as a chelating ligand. When the reaction is performed in the presence of Me_3NO, cluster **17** is formed by the oxidation of the dppn ligand and transfer of the phenyl group.

An interesting tetranuclear cluster **18** with a (μ_4-O) oxide motif was synthesised by the reaction of $Fe_3(CO)_{12}$ with dppn (**1f**) (Scheme 9) [27].

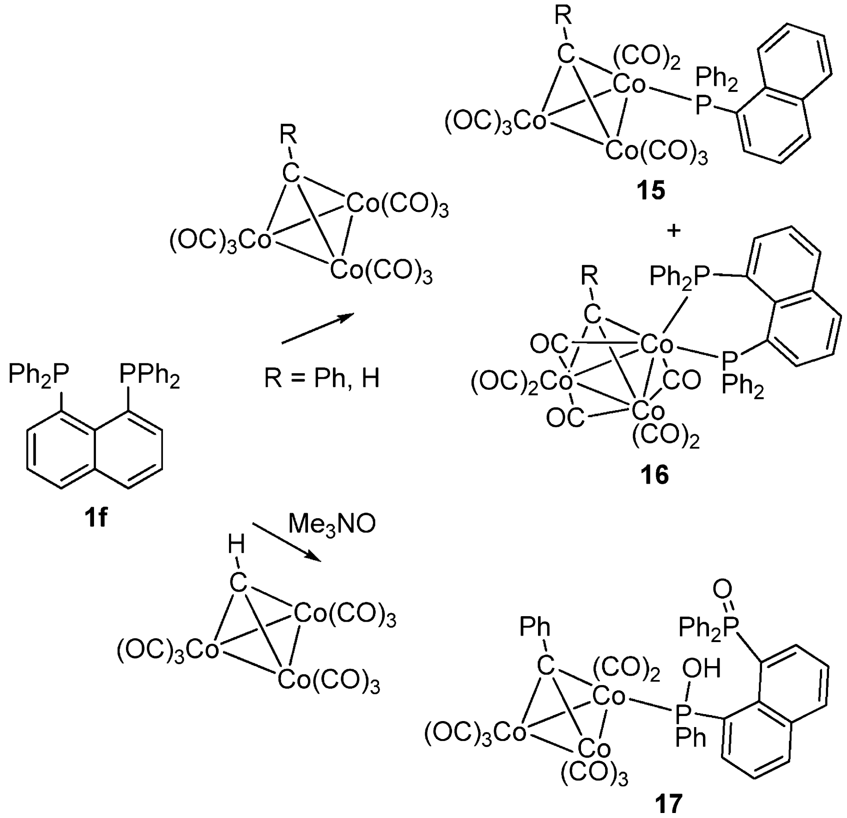
A trinuclear cluster **19** and two tetranuclear clusters **20** and **21** were obtained upon heating dppn (**1f**) with $Ru_3(CO)_{12}$ in thf under reflux (Scheme 10) [28]. Heating the same compounds in toluene under reflux gives another tetranuclear complex (**22**), with both Ph groups having been detached from one of the phosphorus atoms.

The reaction of $Ru_3(CO)_{12}$ with dmpn (**1a**) had a different outcome [29]. When the two components were reacted in thf at r.t. with Me_3NO added as an activator, three trinuclear clusters **23**, **24** and **25** were obtained, of which only **23** was formed by a simple chelation of the unmodified dmpn ligand (Scheme 11). In both **24** and **25** one of the two PMe_2 groups is detached during the reaction and the resulting $C_{10}H_7PMe_2$ is coordinated via its P atom [29].

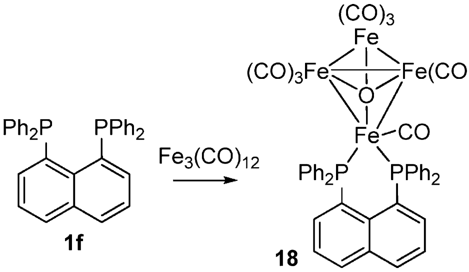
The reactions of both dppn (**1f**) and dmpn (**1a**) with the related Mo cluster **26** were also reported [28,29]. The reaction outcomes (Scheme 12) again indicate increased tendency of dmpn (**1a**) to lose the PMe_2 group. Notably, cluster **27** is closely related to cluster **23**, whilst **28** is closely related to **24**. Mild thermolysis of **24** as well as of **28** gives the (closely related) hydrido clusters **29** and **30** (Scheme 13) [29].

The hydrido cluster **31** reacts with dppn (**1f**) under thermal and Me_3NO activation to give a chelate product **32** via a CO substitution mechanism (Scheme 14) [30].

Reaction of $Os_3(CO)_{12}$ with dppn (**1f**) in boiling toluene gave three clusters **33**, **34** and **35** (Scheme 15) **[31]**. The hydrido clusters **33** and **34** are formed by an activation of the *ortho*-CH bond in the Ph ring of the dppn ligand, whilst formation of **35** involves a P–C bond cleavage reaction (loss of one PPh_2 group). Complex **34** is isostructural with the ruthenium cluster **19**. Addition of the activator Me_3NO to the reaction mixture of $Os_3(CO)_{12}$ and dppn (**1f**) resulted in the loss of one PPh_2 group from the ligand and formation of cluster **36** (Scheme 15). **36** is closely related to cluster **24** (see Scheme 11) obtained from the reaction of $Ru_3(CO)_{12}$ with dmpn **1a** under similar conditions [32].



Scheme 8. Reactivity of dppn towards tricobalt clusters $RCCo_3(CO)_9$ (R = Ph, H) [26].



Scheme 9. Reaction of dppn with $Fe_3(CO)_{12}$ [27].

Rhenium and manganese carbonyl clusters $[Re_2(CO)_8(MeCN)_2]$ and $[Mn_2(CO)_8(MeCN)_2]$ were reacted with dppn (**1f**). A range of reactivities was observed, including ligand chelation and C–H and C–P bond-cleavage (Scheme 16) [32]. It is possible that oxygen and chlorine atoms, found crystallographically in some of the products, were introduced at the crystallisation stage.

2.1.4. Gold complexes with naphthalene-1,8-bis(phosphines)

A significant amount of work has been undertaken by the group of Yam, investigating gold complexes of the dppn (**1f**) ligand and its dicyclohexyl analogue **1d**. Their investigations focused mainly on the potential use of these complexes as photo- and electroluminescent materials. In all of the reported gold complexes, the naphthalene-1,8-bis(phosphine) moiety remains intact.

To make the Au(I) halocomplexes **37a–c**, a freshly prepared solution of Au(I), prepared from Au(III) and 2,2′-thiodiethanol, is added to dppn (**1f**). **37a–c** were used in subsequent reactions with $[Ag(MeCN)_4]PF_6$ (and more **1f**) to give binuclear complexes **38**, which feature an unsupported Au(II)–Au(II) bond (Scheme 17) [33,34].

Spectrochemical and luminescence studies were undertaken on a series of gold(I) phosphine thiolates **39**, containing 1,8-bis(dicyclohexylphosphino)naphthalene ligand (Scheme 18) [35]. Substantial changes in UV–vis absorptions were observed on chelation of the benzo-15-crown-5 moiety to potassium ions. In addition, a binuclear gold complex with the two Au atoms bridged by both dppn (**1f**) and $S(CH_2)_3S$ linkages has been subject to a recent patent [36].

Two tetrahedral Au(I) bis(chelate) complexes **40** have been synthesised using the same reactants as in the reaction shown in Scheme 17, but in a different stoichiometric ratio (Scheme 19) [37].

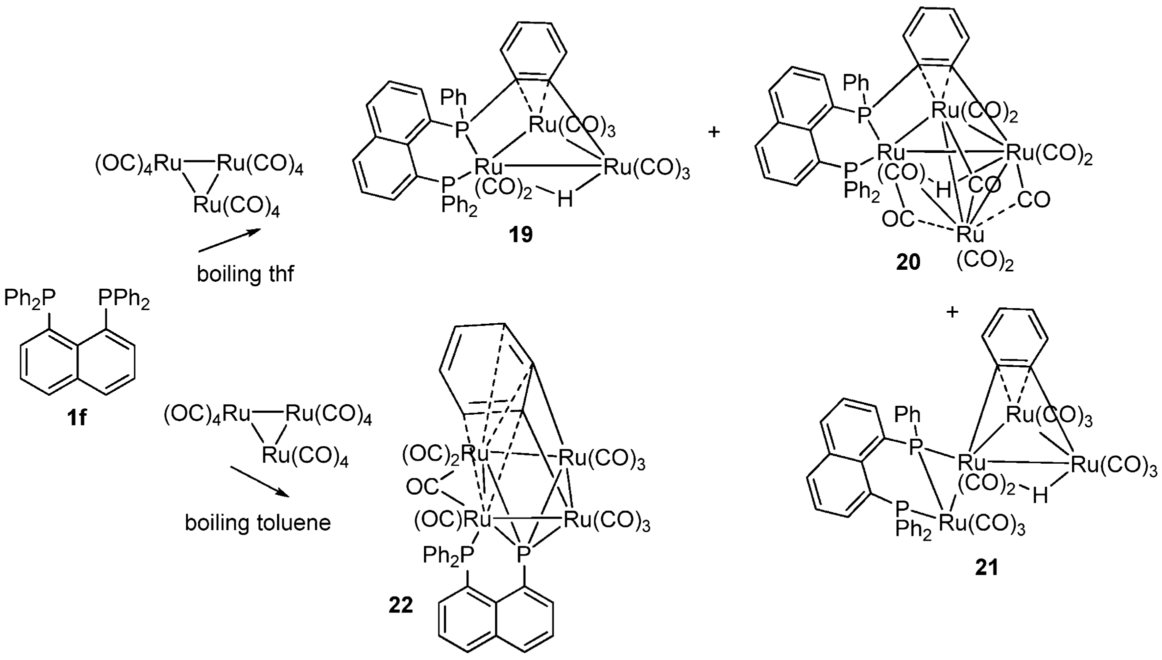
A series of binuclear gold complexes **41** with acetylide and bis(phosphine) ligands **1f** and **1d** were obtained from the reactions of the respective free phosphines with the Au(acetylide) polymers (Scheme 20) [38].

2.2. NapP$_2$ ligands other than bis(phosphines)

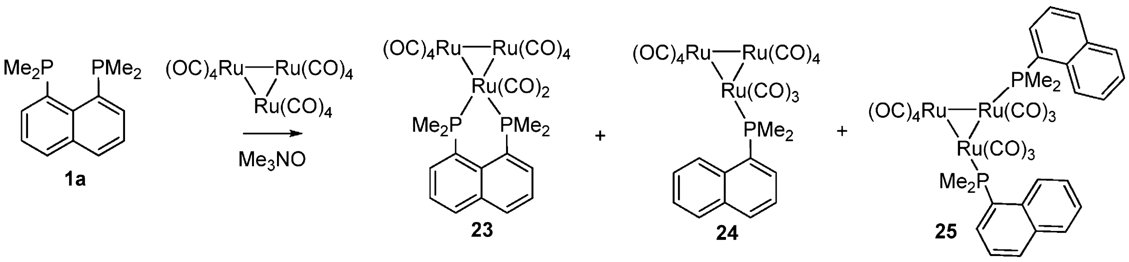
2.2.1. 1,2-Diphosphaacenaphthene ligands and complexes

The 1,2-diphosphaacenaphthene *trans*-**42** is synthesised by the reaction of 1,8-dilithionaphthalene with $PhPCl_2$ (Scheme 21). The *trans*-isomer is obtained solely after a chromatographic purification process [39,40].

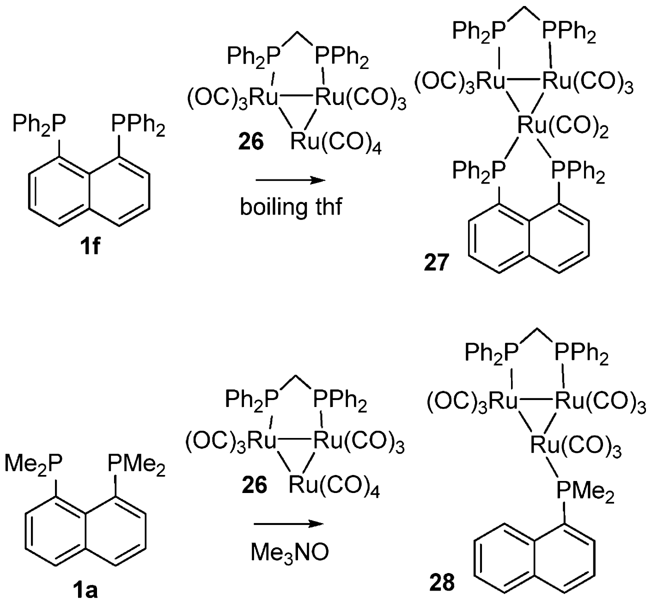
The reaction of *trans*-**42** with two equivalents of $M(CO)_5(thf)$ (M = W, Mo, Cr) afforded binuclear complexes *trans*-**43** (Scheme 22). The mononuclear complexes *trans*-**44** have been obtained by reacting *trans*-**42** with one equivalent of $M(CO)_5(thf)$. Heating of *trans*-**44** in boiling toluene gave mixtures of *cis*- and *trans*-**44**, which have then been reacted with a second equivalent of $M(CO)_5(thf)$. From the resulting mixture of *cis*-**43** and *trans*-**43**, the *cis*-isomer of the tungsten complex has been isolated and characterised [40].



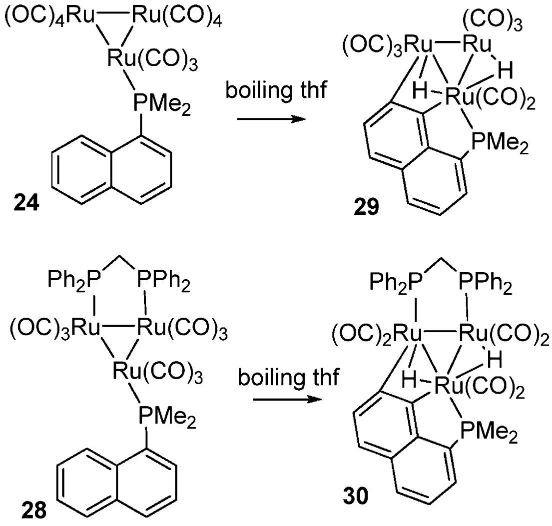
Scheme 10. Reactions of dppn with $Ru_3(CO)_{12}$ [28].



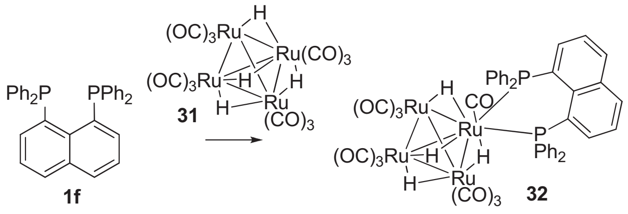
Scheme 11. Reaction of dmpn with $Ru_3(CO)_{12}$ [29].



Scheme 12. Reactions of dppn and dmpn with Mo cluster **26** [28,29].



Scheme 13. Mild thermolysis of **24** and **28** [29].



Scheme 14. Reaction of hydrido cluster **31** with dppn [30].

2.2.2. Bis(phosphonite) ligands and complexes

Phosphonites $RP(OR')_2$ are intermediary between phosphines R_3P and phosphites $P(OR')_3$. Bis(phosphonite) **46** is obtained in a two step synthesis via **45** (Scheme 23). **45** has been isolated and well characterised, however its coordination chemistry remains unknown. Bis(phosphonite) **46** acts as a standard chelating ligand towards Pd and Mo (Scheme 24) [41]. The palladium complex **47** was included in a theoretical study on screening catalyst libraries in silico [42].

2.2.3. Bis(phosphine oxide) ligands and complexes

A bis(phosphine oxide) complex was isolated from the reaction of $[Re_2(CO)_8(MeCN)_2]$ with dppn (**1f**) (Scheme 16) [32].

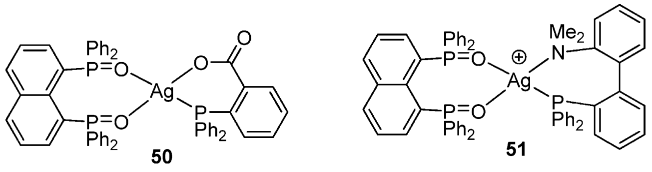


Fig. 4. Silver complexes with bis(phosphine oxide) chelating ligand [45].

The dppn bis(phosphine oxide) ligand was incorporated in complex **49** to obtain desirable thermal and electroluminescent properties of the europium species (Scheme 25) [43]. The dioxide **48** was prepared by the reaction with hydrogen peroxide. Acetylacetonate complex **49** and related compounds are the subject of a patent for their photoelectric properties [44]. Two silver complexes **50** and **51** containing the bis(phosphine oxide) ligand **48** were listed amongst a range of new luminescent materials in another patent [45] (Fig. 4).

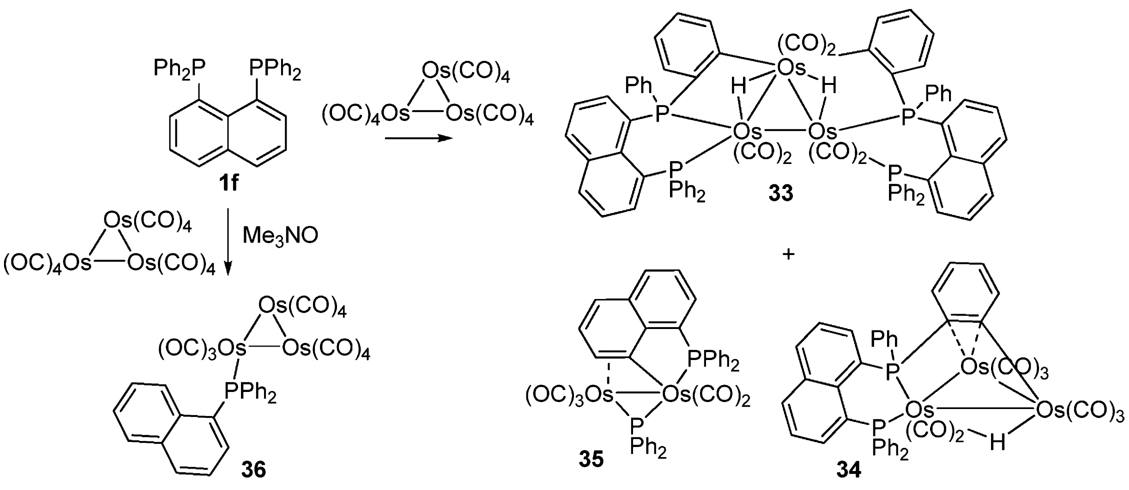
2.2.4. Heterodentate phosphine—phosphine chalcogenide ligands and complexes

Surprisingly little is known on the coordination chemistry of monooxidised naphthalene-1,8-diyl phosphines, which have the potential to behave as hemi-labile ligands. Only the sulfide **52** and the selenide **54** were used as ligands in the two Pt and Mo complexes **53** and **55** [25]. Whilst the dichloroplatinum sulfide complex **53** was stable, its selenium congener decomposed with formation of **2** and elemental selenium. Similar behaviour was observed with the molybdenum complexes, although the monoselenide ligand containing complex **55** was fully characterised, it decomposed spontaneously to **56** and elemental selenium. The mechanism was confirmed by the independent synthesis of **56** from dppn (**1f**) and $[(nor)Mo(CO)_4]$ (Scheme 26) [25].

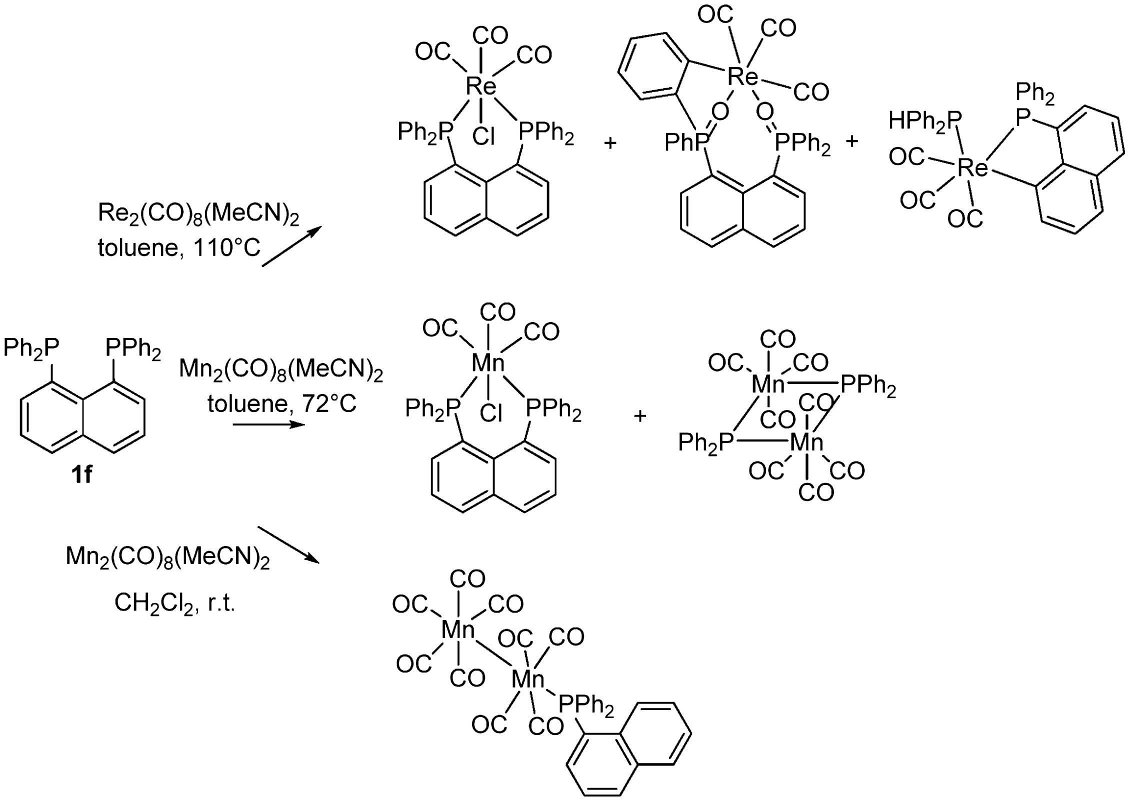
2.3. NapPN ligands and complexes

1-Dimethylamino-8-diphenylphosphinonaphthalene **57** is an archetypal P,N *peri*-substituted naphthalene ligand. The synthesis of **57** starts from commercially available 1-dimethylaminonaphthalene, which is firstly *peri*-lithiated as reported by van Koten [46]. The lithiated species is then coupled with chlorophosphine to give ligand **57** [47].

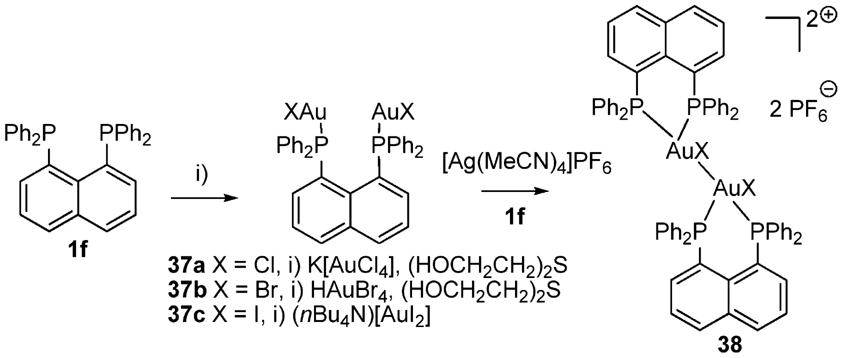
In an extensive synthetic and kinetic study by the group of Vrieze, a range of Pt and Pd complexes with ligand **57** were obtained (Scheme 27) [47]. Only phosphine groups are coordinated to the palladium atom in the (square planar) complex **59**, whilst in com-



Scheme 15. Reaction of $Os_3(CO)_{12}$ with dppn [31].



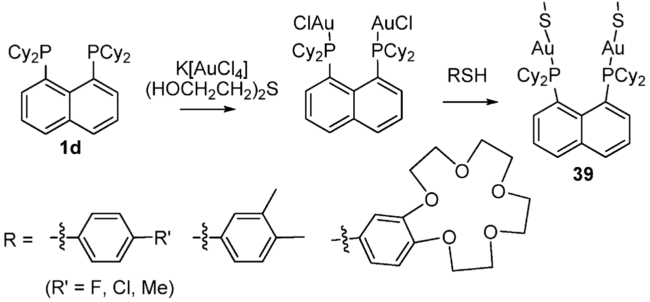
Scheme 16. Reactions of dppn with rhenium and manganese carbonyl clusters [32].



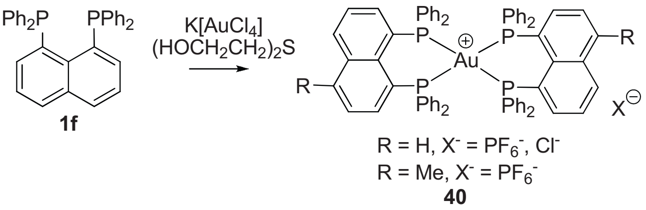
Scheme 17. Synthesis of Au(I) halocomplexes **37a–c** and binuclear complexes **38** [33,34].

plexes **58** the P,N ligand is chelating (bidentate). Cationic complexes **61** and **62** (with OTf$^-$ and BF$_4$$^-$ as counteranions) were synthesised via chloride **60**, which itself was made by the reaction of the free ligand **57** with (cod)M(CH$_3$)Cl (M = Pt, Pd). The main focus of the study was the carbonylation of the metal–carbon bond, which leads to acyl complexes **63** (Scheme 28). Species **63** were observed in high pressure NMR and low temperature IR experiments [47].

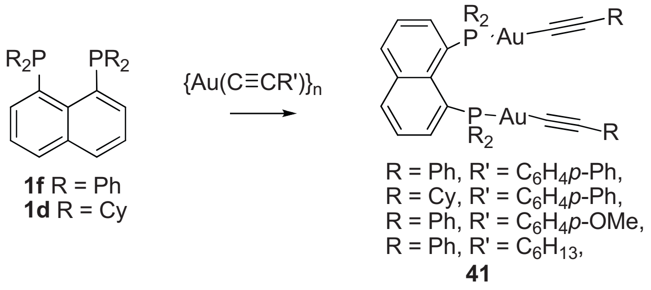
The above work was expanded by synthesising palladium complexes **64** and **65** (Scheme 29) [48,49]. The 1-dimethylamino-8-(dicyclohexylphosphino)naphthalene ligand was synthesised by the coupling of 8-dimethylamino-1-naphthyllithium with ClPCy$_2$.



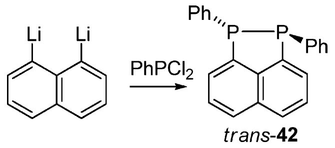
Scheme 18. Synthesis of gold(I) phosphine thiolates **39** [35].



Scheme 19. Synthesis of Au(I) bis(chelate) complexes **40** [37].



Scheme 20. Synthesis of binuclear gold complexes **41** [38].



Scheme 21. Synthesis of 1,2-diphosphaacenaphthene *trans*-**42** [39,40].

The complexes **60**, **64** and **65** were reacted with CO and the resulting species were trapped by norbornene. A detailed mechanistic study on relative rates of reactions shown in Scheme 30 and related processes was provided [48,49].

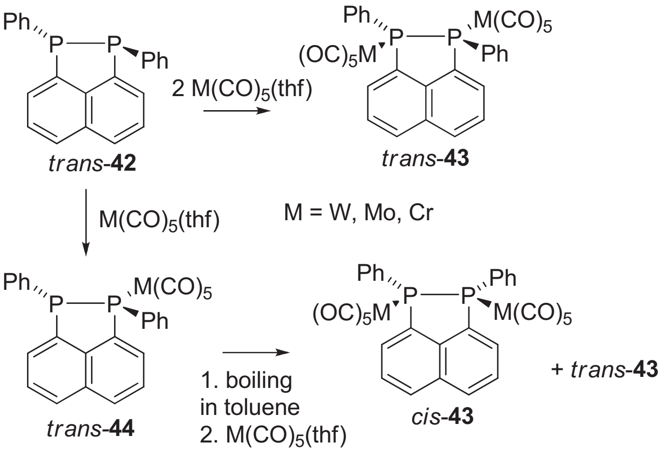
A range of iridium complexes **66** with sulfoximine and phosphine donors is synthesised as shown in Scheme 31 [50]. The synthesis starts with 1,8-diiodonaphthalene, synthesis of which is rather troublesome [51], however the following steps proceed with good yields. The resulting complexes **66** are air/moisture stable and were purified by column chromatography. They were used as catalysts in a range of asymmetric hydrogenations [50,52,53].

An elegant synthetic pathway to a potentially highly valuable synthon **67** was reported recently by Zheng (Scheme 32) [54]. It starts with commercially available 1-aminonaphthalene, which is protected with a trimethylsilyl group, *peri*-lithiated (with partial regioselectivity only), coupled with chlorophosphine $ClPPh_2$ and deprotected by acidic aqueous workup. **67** was coupled with an *S*-enantiomer of a binap derivative **68** to give an air stable phosphine-phosphoramidite ligand **69**. The ligand was successfully used together with $[Rh(cod)_2]BF_4$ in a range of catalytic asymmetric hydrogenations, however no attempts were made to isolate the active Rh species [54].

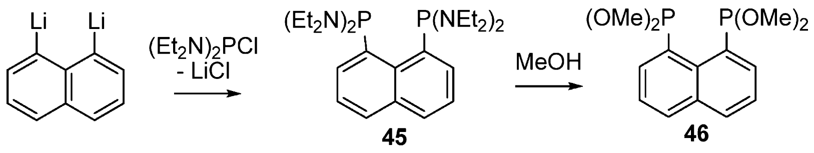
2.4. NapPO ligands and complexes

Only a few ligands containing phosphorus and oxygen atoms in the *peri*-positions of naphthalene have been reported. They invariably act as monodentate ligands, only the phosphorus atom is coordinated to the metal in their complexes.

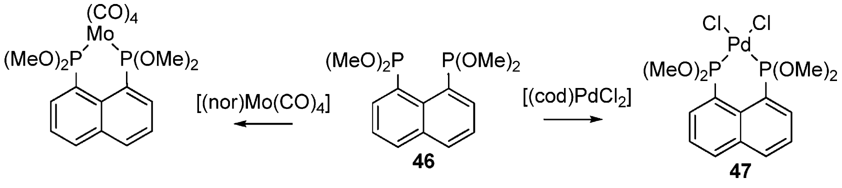
Peri-lithiation of 1-methoxynaphthalene proceeds efficiently with *t*BuLi in an inert solvent (cyclohexane). The subsequent coupling reaction with $ClP(OEt)_2$ affords **70**, which without isolation



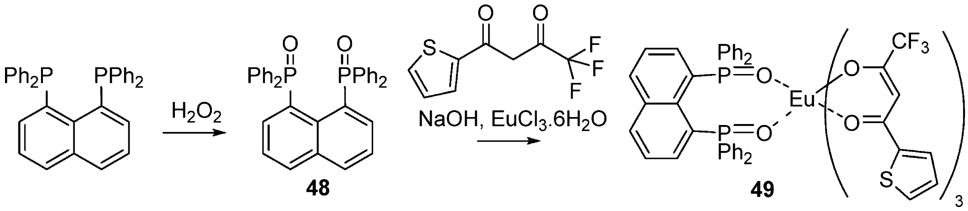
Scheme 22. Synthesis of *cis*- and *trans*-binuclear complexes 43 [40].



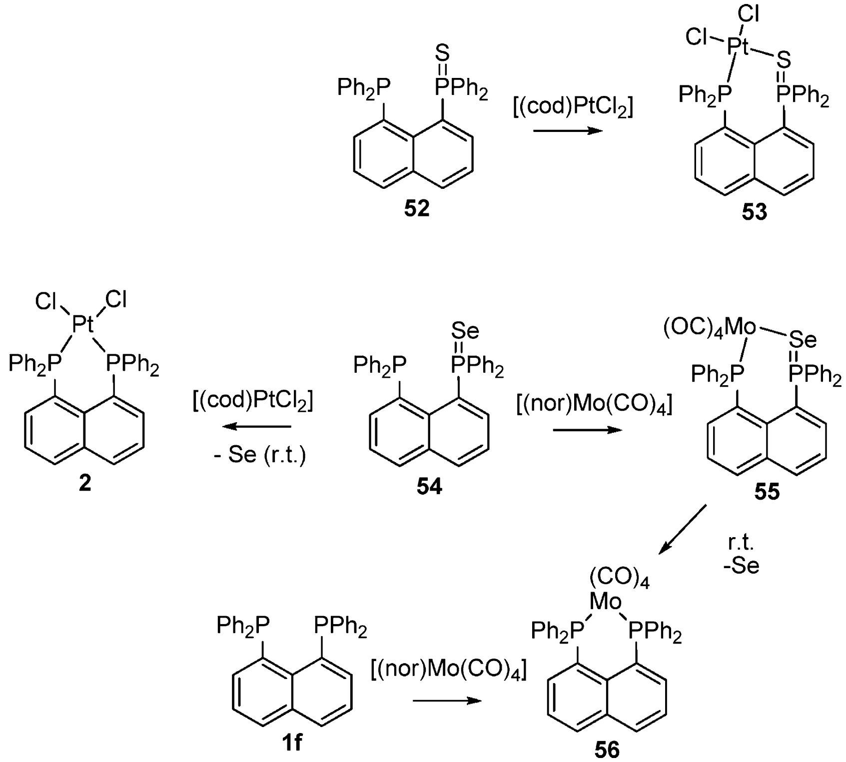
Scheme 23. Synthesis of bis(phosphonite) ligand **46** [41].



Scheme 24. Coordination chemistry of bis(phosphonite) ligand **46** [41]. Cod = cycloocta-1,5-diene, nor = norbornadiene.



Scheme 25. Synthesis of bis(phosphine oxide) europium complex **49** [43,44].



Scheme 26. Syntheses of complexes with heterodentate phosphine/chalcogen ligands [25].

was transformed into ruthenium complex **71** [55]. Although the preparation of the related ligand **72** is mentioned, no coordination chemistry of it has been reported (Scheme 33).

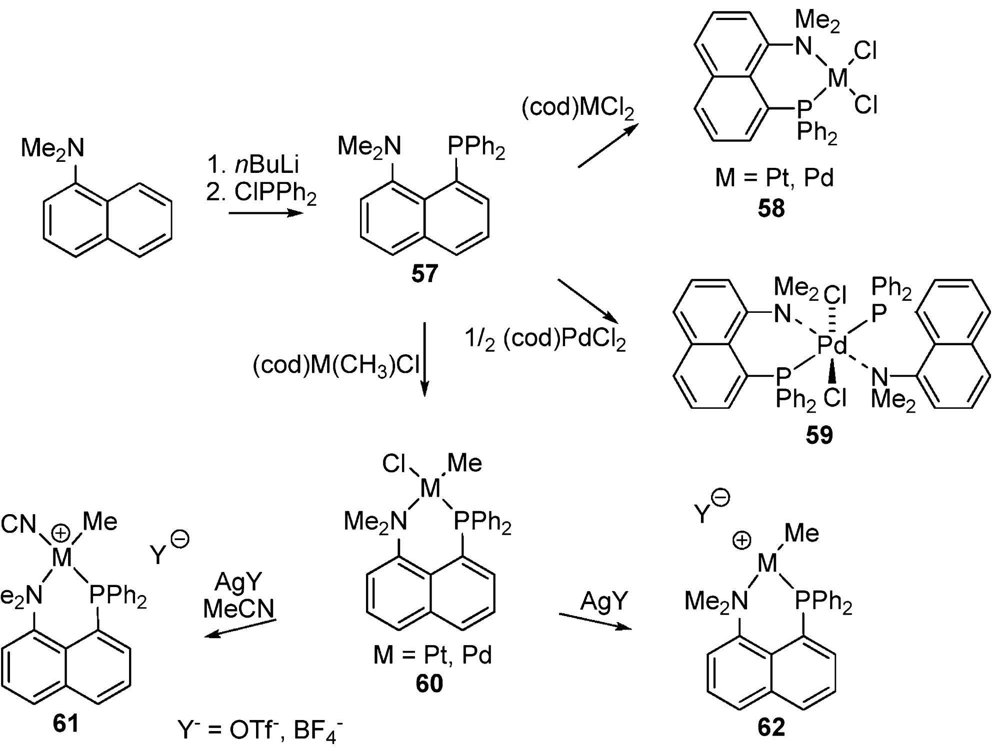
Peri-substitution found an interesting application in the construction of hypervalent phosphoranide "R_4P^-" ligand **74** (Scheme 34) [56]. The ligand is generated by deprotonation from phosphorane **73**, and displays helical chirality. A range of its metal complexes and other derivatives have been synthesised (Scheme 35). The palladium(II) and platinum(II) complexes **75** have a *cis* arrangement of the bulky phosphoranido substituents [56,57]. Both *rac*- and *meso*-diastereomers of **75** were observed, however not separated. The iridium complex **76** has piano-stool geometry and is formed as a mixture of the two diastereomers. Its thermolysis gives **77** and **78** with a newly formed Ir-C bond [58]. A rhodium(III) tetraphenylporphyrin complex **79** has the rhodium atom only slightly out of the basal plane of the porphyrin ring, and rather surprisingly the P-Rh bond is not elongated in comparison to that in the related less sterically congested compounds [59]. Platinum complexes **80** are obtained when ligand **74** is reacted with *cis*-$PtCl_2(PR_3)_2$ where R = OPh, OMe and Me. When two equivalents of the ligand are used a *trans*-bis(phosphoranido) complex **81** is obtained [60].

2.5. NapPS ligands and complexes

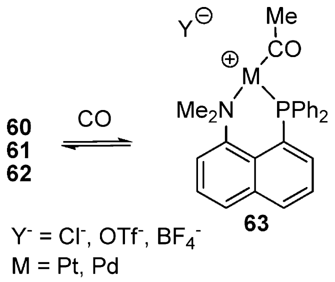
Only a single phosphorus-sulfur mixed donor ligand based on *peri*-substituted naphthalene has been used to form transition metal complexes. Ligand **82** is synthesised using a sequential lithiation of 1,8-dibromonaphthalene (Scheme 36) [61]. The phenylthio-group is introduced first, as it is tolerant to *n*BuLi used in the second lithium-halogen exchange reaction, prior to P–C bond formation with chlorophosphine.

Ligand **82** was reacted with copper halides CuX (X = Cl, Br, I) to give binuclear complexes **83** (Scheme 37) [61]. The rigid nature of the naphthalene backbone dictates the geometry of the complexes and has a greater influence compared with the stereochemical preference of copper to attain a perfect tetrahedral configuration. Surprisingly, and counter intuitively, with the increasing size of the halide, the two copper atoms are forced closer together, and Cu···Cu distances approach the sum of van der Waals radii of two copper atoms (2.80 Å) in the case of the diiodide.

In an additional study, the range of metal complexes with ligand **82** was expanded by square planar platinum(II) complexes **84**, obtained from the reactions with PtX_2(cod) (X = Cl, Br, I) (Scheme 37) [62]. The ruthenium(II) complex **85** was



Scheme 27. Syntheses of Pt and Pd complexes of 1-dimethylamino-8-diphenylphosphinonaphthalene **57** [47].



Scheme 28. Carbonylation of the metal–carbon bond in complexes **60–62** [47].

obtained by the reaction of **82** with $[\text{Ru}(\eta^6\text{-MeC}_6\text{H}_4{}i\text{Pr})\text{Cl}_2]_2$ dimer [62].

2.6. NapPF ligands and complexes

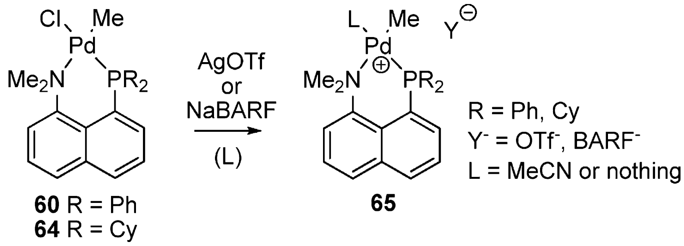
Only recently naphthalene *peri*-geometry was used to study possible fluorine-metal interactions in late transition-metal complexes. A series of 5,6,7,8-tetrafluoronaphthalene-1-yl phosphine ligands **86** was synthesised as shown in Scheme 38. Their coordination chemistry was studied in detail by nmr and structural techniques [63]. Cationic species **88** is made from **87** by halide abstraction using $AgSbF_6$. It has J(PF) 80 Hz, which is comparable to the value found in P-CF_3 group. Compound **88** is representative of these species; whilst the nature of the interaction remains unclear, rather large J(PF) (range 40–100 Hz) were observed in all the complexes shown in Scheme 38 [63].

2.7. NapPC ligands and complexes

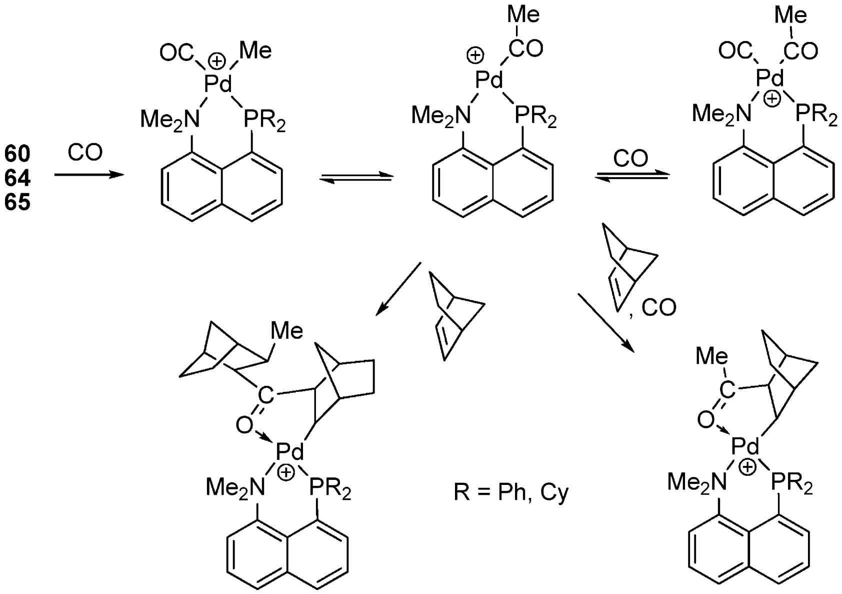
Ligands possessing phosphorus and carbon atoms in the *peri*-positions of the naphthalene ring generally act as monodentate via phosphorus [64,65]. An exception to this is an organometallic species **90**, which is obtained by the elimination of methane on coordination of $[\text{CoMe}(\text{PMe}_3)_4]$ to **89** (Scheme 39) [66].

2.8. NapAs$_2$ and NapSb$_2$ ligands and complexes

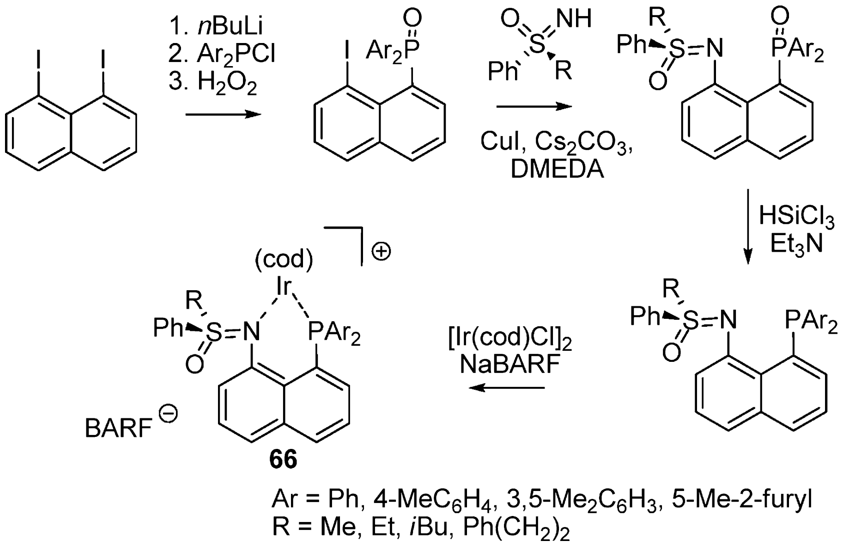
Very few heavier congeners of naphthalene-1,8-diyl bis(phosphines) have been reported in the literature, and reports on the coordination chemistry of those that have are similarly scarce. Those reported were complexes of 1,8-bis(dimethylarsino)



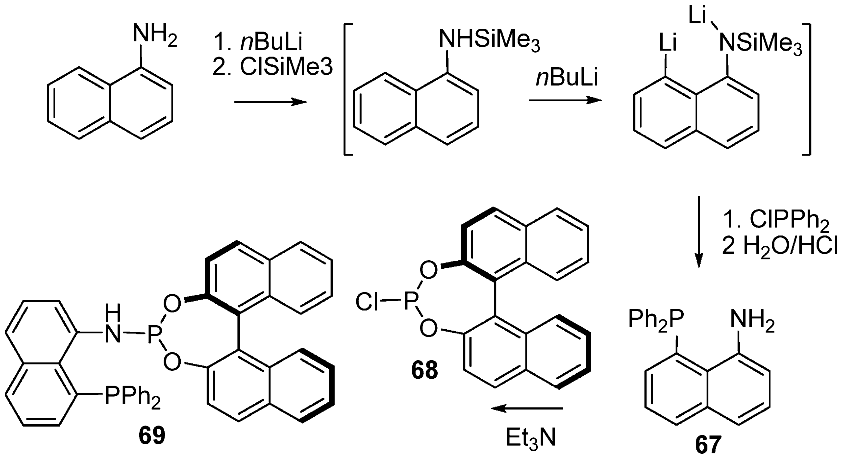
Scheme 29. Synthesis of palladium complexes **65** [48,49]. $\text{BARF}^- = [\text{B}[3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3]_4]^-$.



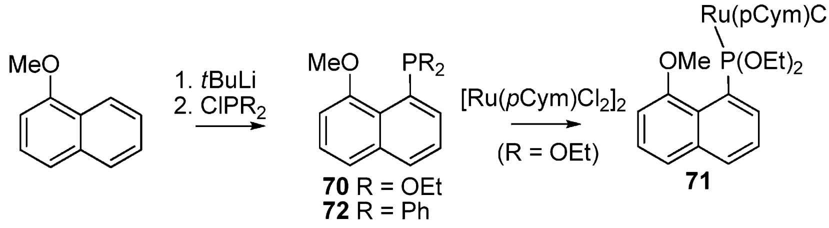
Scheme 30. Reactions of complexes **60**, **64** and **65** with CO and consequent trapping reactions with norbornene [48,49].



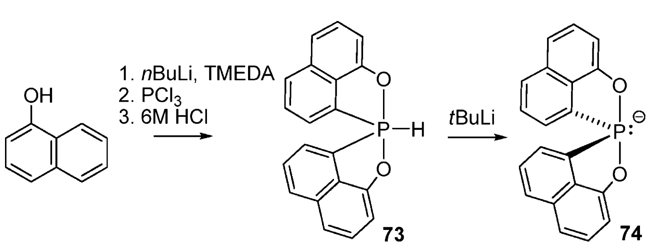
Scheme 31. Synthesis of iridium complexes **66** used in asymmetric hydrogenations [50,52,53]. DMEDA = N,N′-dimethylethylenediamine.



Scheme 32. Synthesis of 1-amino-8-diphenylphosphinonaphthalene **67** and phosphine-phosphoramidite ligand **69** [54].



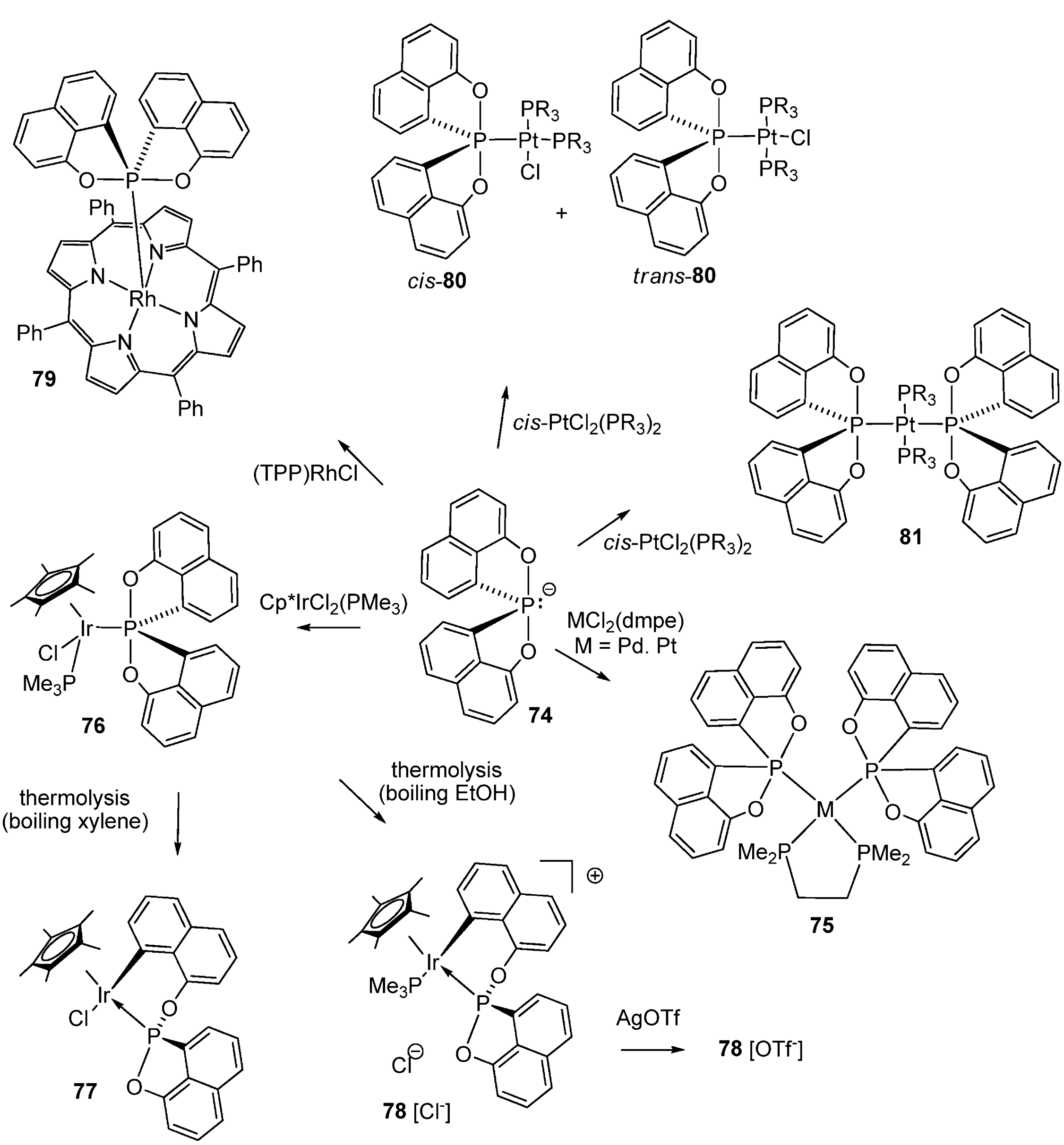
Scheme 33. Synthesis of NapPO ligands **70** and **72** and the ruthenium complex **71** [55]. *p*Cym = η^6-*p*-cymene.



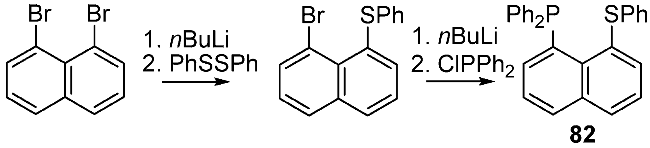
Scheme 34. Generation of phosphoranide ligand **74** [56].

naphthalene **91**, 1,8-bis(dimethylstibino)naphthalene **93a** and 1,8-bis(diphenylstibino)naphthalene **93b**.

1,8-Bis(dimethylarsino)naphthalene **91** is accessible by the reaction of 1,8-dichloronaphthalene with Me_2AsLi (Scheme 40) [67]. **91** has been used as a bidentate chelating ligand towards a wide range of metals, including Ni(II) [68,69], Cr(0), Mo(0), W(0) [70], Pd(II), Pt(II) [69,71], Ti(IV), Nb(IV) [72] and Co(II) [73]. The variety of structural motifs claimed to be adopted by these complexes is shown in Scheme 40. In addition, an electrochemical study of heteroleptic nickel complexes **92** showed relative stability of a



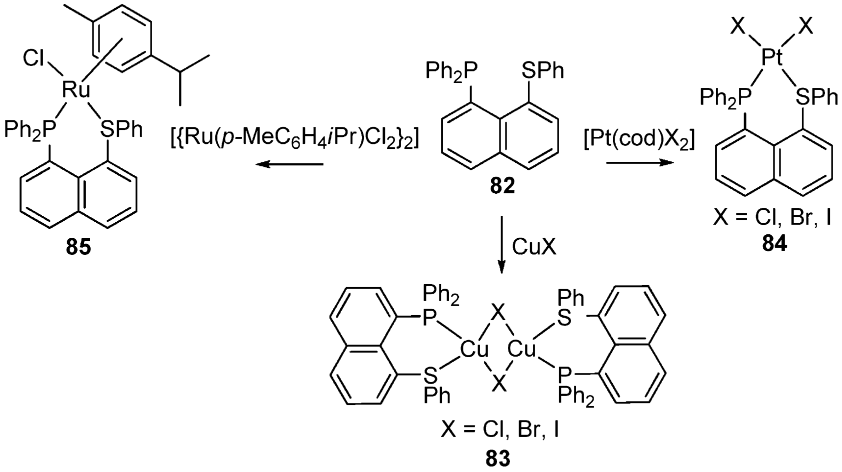
Scheme 35. Coordination chemistry of phosphoranide ligand **74** [56–60].



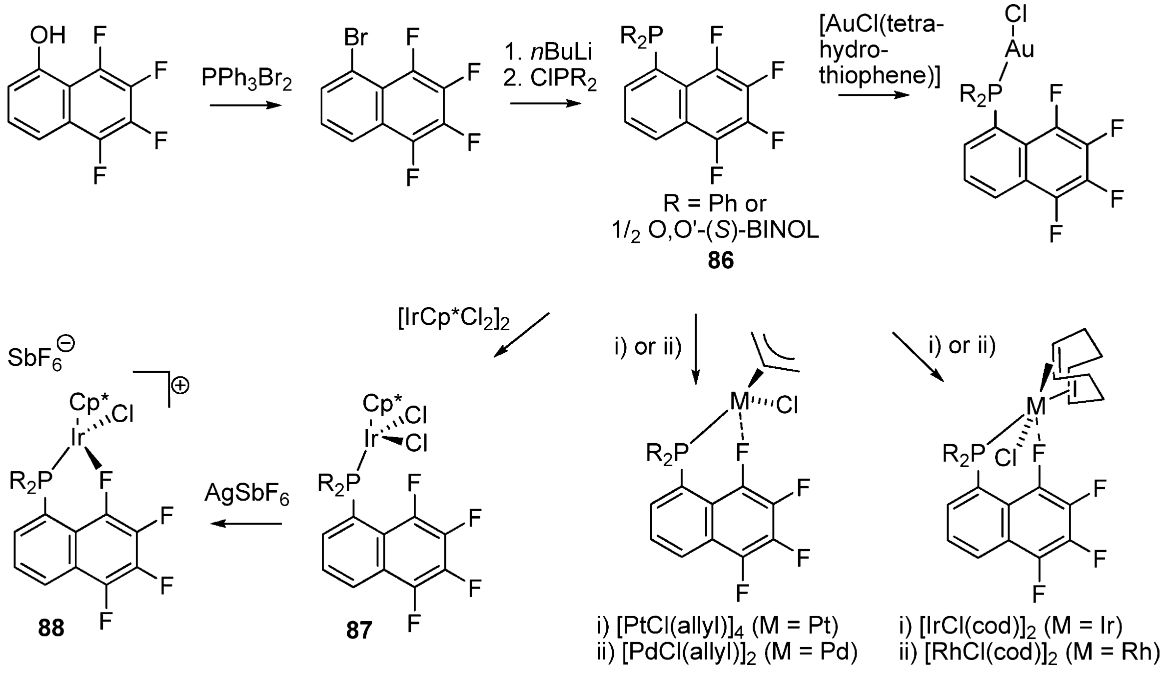
Scheme 36. Synthesis of NapPS ligand **82** [61].

variety of central atom oxidation states [74]. More recently, silver complexes of **91** were studied by electrospray mass spectrometry [75].

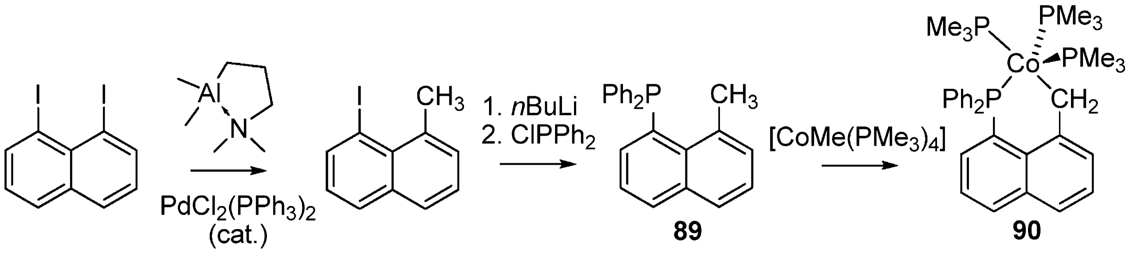
Naphthalene bis(stibines) **93a**,**b** were synthesised recently via a route normally used in phosphine chemistry, with good yields (Scheme 41) [76]. **93a**,**b** behave as chelating ligands towards Pt(II), Mo(0) and Rh(I) metal centres.



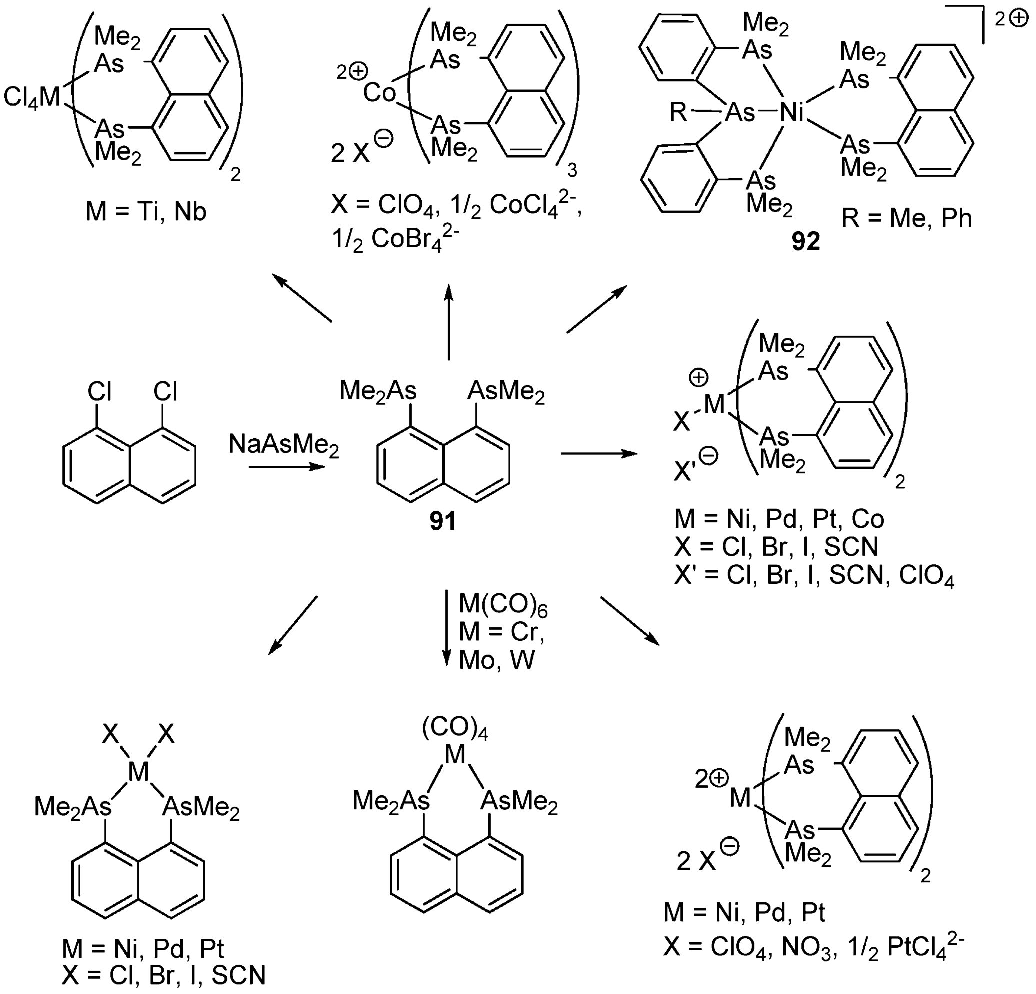
Scheme 37. Coordination chemistry of NapPS ligand **82** [61,62].



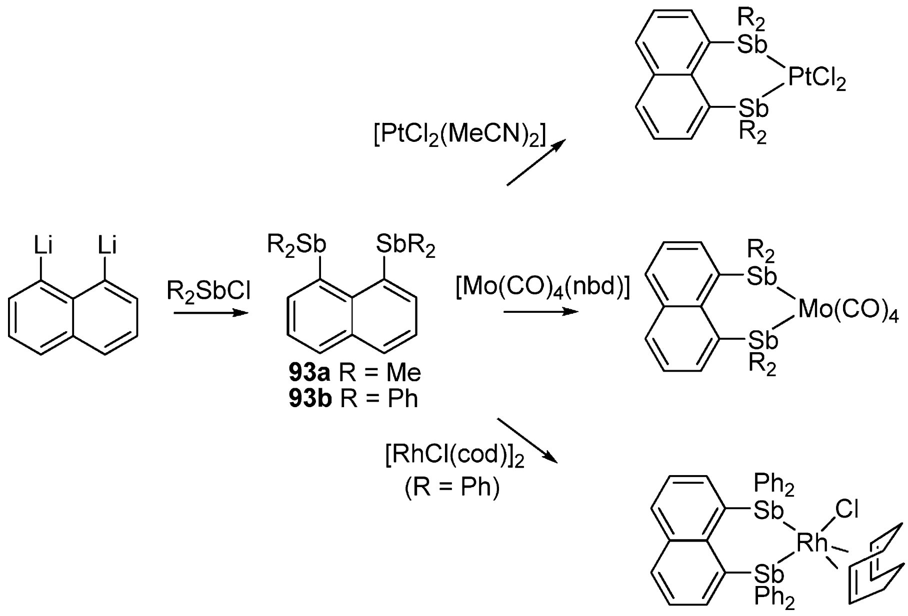
Scheme 38. Synthesis of NapPF ligand **86** and its coordination chemistry [63].



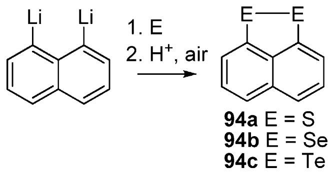
Scheme 39. Synthesis of the cobalt complex **90** [66].



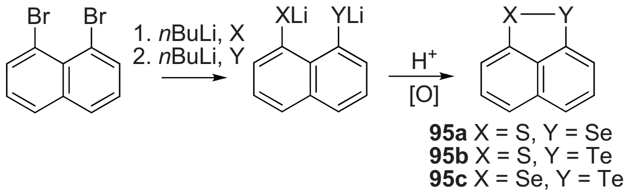
Scheme 40. Synthesis [67] and coordination chemistry [68–74] of 1,8-bis(dimethylarsino)naphthalene **91**.



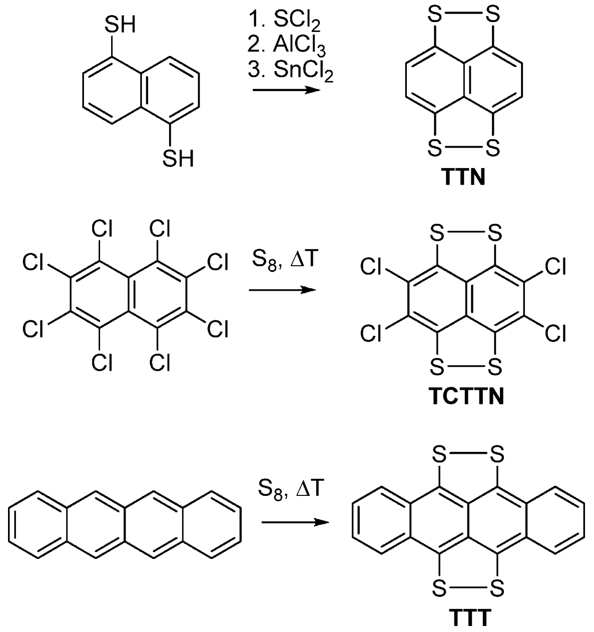
Scheme 41. Synthesis and coordination chemistry of bis(stibines) **93a,b** [76].



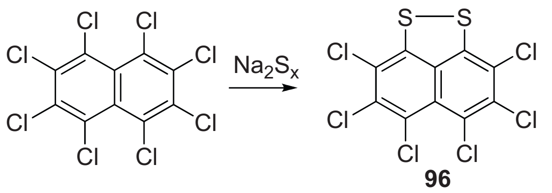
Scheme 42. Synthesis of dichalcogenoles **94a**–**c** from 1,8-dilithionaphthalene [78,79,83].



Scheme 43. The synthesis of the unsymmetrical dichalcogenoles **95a**–**c** [84].



Scheme 44. Synthesis of TTN and its analogues [85,86].

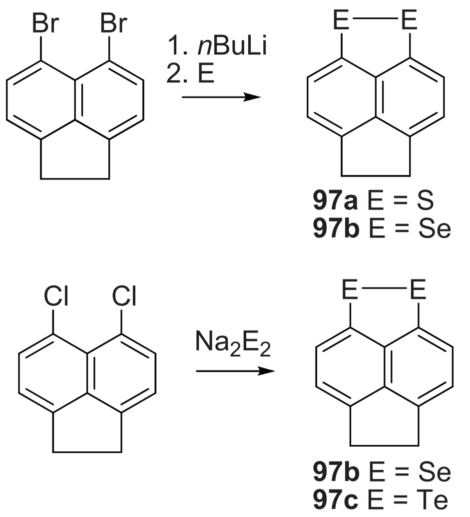


Scheme 45. Synthesis of hexachlorinated dithiole **96** [89].

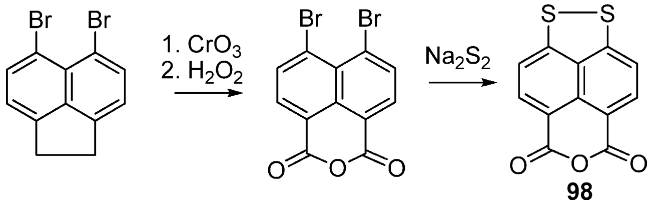
3. Ligands with Group 16 element(s) as *peri*-atoms

3.1. Naphthalene-1,8-diyl dichalcogenoles (NapE$_2$ and NapEE′ systems, E, E′ = S, Se, Te)

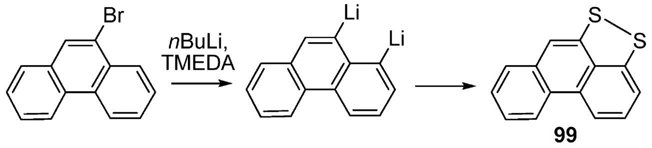
3.1.1. Synthesis of the dichalcogenole ligands



Scheme 46. Syntheses of acenaphthene derived dichalcogenoles **97a**–**c** [91].



Scheme 47. Synthesis of naphthoic anhydride **98** [94].



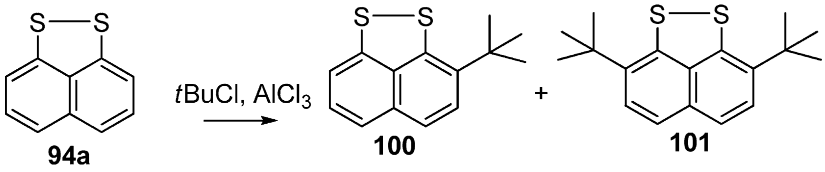
Scheme 48. Synthesis of phenanthrene-derived dithiole **99** [79].

A number of dichalcogenoles [77] are derived from *peri*-substituted naphthalene. An efficient one-step synthesis of the parent compound naphtho[1,8-cd]-1,2-dithiole **94a** by the reaction of 1,8-dilithionaphthalene with sublimed sulfur was reported in 1977 by Meinwald et al. [78] (Scheme 42). A simplified procedure, starting with un-substituted naphthalene was published later by Ashe et al. [79]. Perhaps the most convenient route to 1,8-dilithionaphthalene was reported by Brandsma et al. in 1994, starting from commercially available 1-bromonaphthalene [13]. These have replaced the less convenient historical syntheses of **94a** [80–82]. Comparable reactions with elemental selenium and tellurium give the heavier congeners **94b** and **94c** (Scheme 42) [78,83].

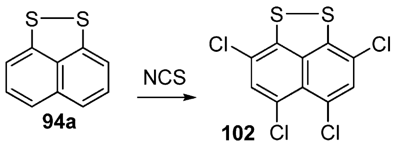
Modification of the method using 1,8-dilithionaphthalene affords mixed chalcogen bridged naphthalenes (Scheme 43). Consecutive lithiation and chalcogen addition, followed by acidification and oxidation gives all possible chalcogen permutations **95a**–**c** [84].

Tetrathionaphthalene (TTN), tetrachlorotetrathionaphthalene (TCTTN) and tetrathiotetracene (TTT) were historically the first dithioles to be used as ligands in complex forming reactions. Their syntheses are in general low yielding, although easily accessible low cost starting materials are used (Scheme 44) [85,86]. An improved synthesis of TTT starting from 5,6,11,12-tetrachlorotetracene has been subject to a more recent patent [87]. The intermediary 5,6,11,12-tetrachlorotetracene can be synthesised in several steps from 1,4-dihydroxynaphthalene and phthaloyl chloride [88].

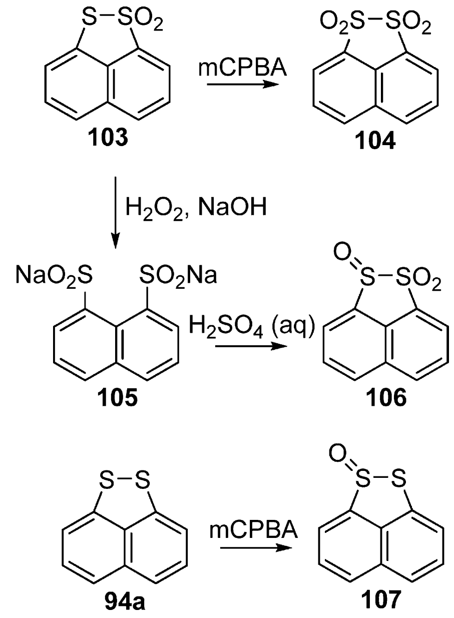
The related hexachlorinated ligand **96** is made from octachloronaphthalene as shown in Scheme 45 [89].



Scheme 49. Friedel–Crafts alkylation of dithiole **94a** [94,95].



Scheme 50. Chlorination of dithiole **94a** [96].



Scheme 52. Synthesis of mono-, tri- and tetraoxides of dithiole **94a** [98–100].

The synthesis of a range of anthracene based dichalcogenoles (E = S, Se, Te) was reported by Ogura [90].

The acenaphthene-derived dithiole **97a** and its Se and Te congeners **97b,c** are obtained either via dilithiated species (E = S, Se), or by the reaction of 5,6-dichloroacenaphthene with Na$_2$E$_2$ (E = Se, Te) (Scheme 46) [91]. Related acenaphthylene [92] and fluoranthene [93] derivatives were also obtained from 5,6-dibromoacenaphthene and 5,6-dichloroacenaphthene.

A related naphthoic anhydride **98** is synthesised via the dibromide as shown in Scheme 47 [94].

The phenanthrene-derived dithiole **99** was obtained by double lithiation of 9-bromophenanthrene, followed by quenching with sulfur (Scheme 48) [79].

One or two bulky *tert*-butyl groups can be regiospecifically attached to positions 2- (and 7-) of the dithiole **94a** under standard Friedel Crafts conditions, to give sterically constrained dithioles **100** and **101** (Scheme 49) [94,95].

Chlorination of **94a** with N-chlorosuccinimide (NCS) afforded **102** in good yield (Scheme 50) [96].

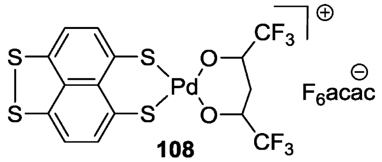
Meinwald's synthesis (Scheme 42) made the less convenient synthesis of dithiole **94a** shown in Scheme 51 obsolete, however the route remained important since it afforded an oxidised derivative naphtho[1,8-*cd*]-[1,2]dithiole 1,1-dioxide **103** [82]. The yield of the 1,1-dioxide (**103**) was later greatly improved by a modification of the original procedure [97].

The remaining three oxidised derivatives of dithiole **94a** are prepared as shown in Scheme 52. The reaction of 1,1-dioxide **103** with *m*-chloroperoxybenzoic acid (mCPBA) in chloroform affords 1,1,2,2-tetroxide **104** [98], whilst reaction of **103** with hydrogen peroxide in alkaline conditions affords disulfinate **105** [99]. Acidification of disulfinate **105** with sulfuric acid is found to give 1,1,2-trioxide **106** [99]. Allenmark et al. have presented the synthesis of 1-oxide **107** by the reaction of **94a** with mCPBA [100].

3.1.2. Dichalcogenolate complexes

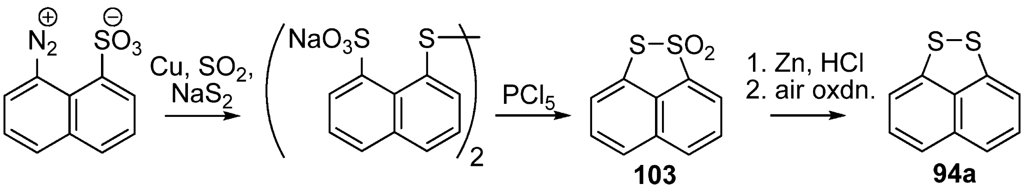
The coordination chemistry of the naphthalene dichalcogenoles and related derivatives was initially investigated by the group of Teo in connection with the extensive redox chemistry of these "non-innocent" ligands and their potential use as organic solid-state conductors [101]. Oxidative addition reactions of TTN, TCTTN and TTT to low-valent platinum and iridium complexes gave a series of singly and doubly bridged transition metal complexes (Scheme 53). Five classes of compounds were prepared containing one to four metal centres, in which the ligand acts as a (formally) two-, four-, six-, eight- and 12-electron donor. Other metals that were coordinated to TTN type ligands include Fe, Co, Ni [102,103].

(TTN)Pd(F$_6$acac)$_2$ **108** is prepared by the formal oxidative addition of TTN to Pd(F$_6$acac)$_2$ (F$_6$acac = hexafluoroacetylacetonate) [104].

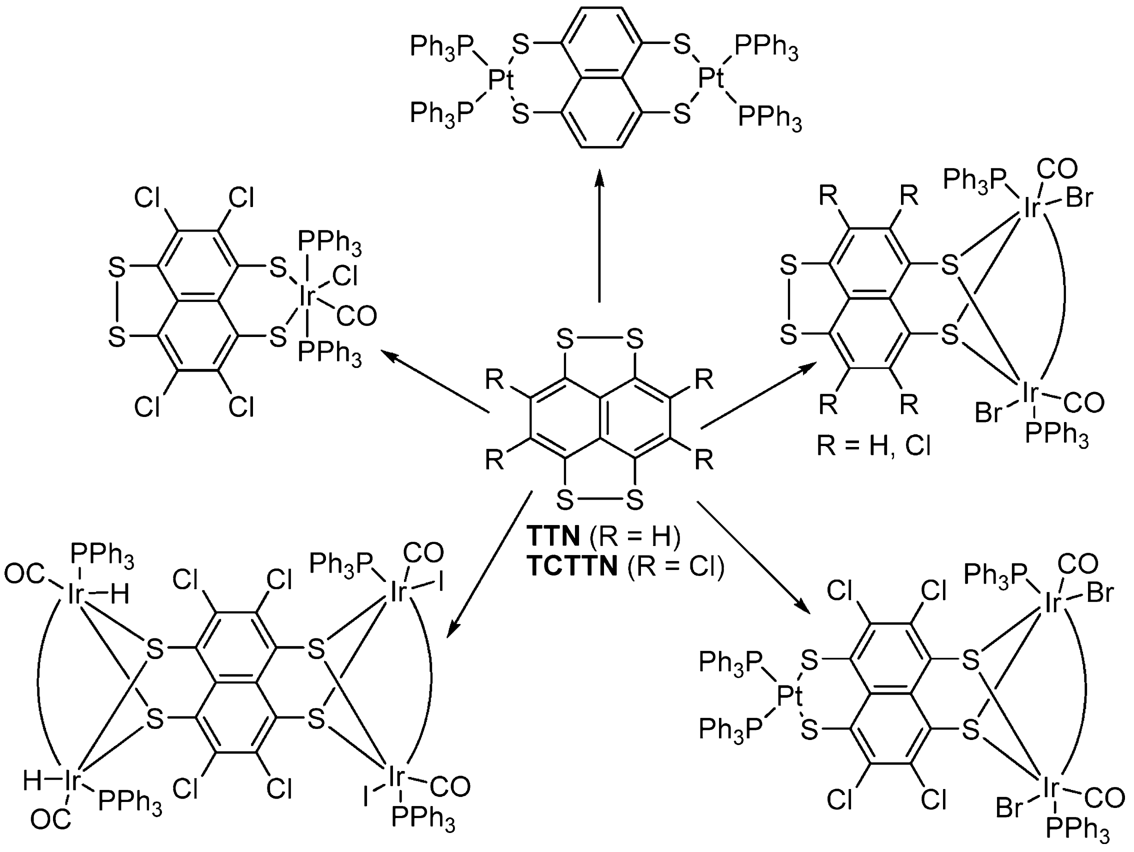


108

Treatment of the hexachloronaphthalene-1,8-dithiole **96**, with [Pd(PPh$_3$)$_3$] or [Pt(PPh$_3$)$_4$] affords mononuclear square-planar complexes **109** (M = Pd, Pt, Scheme 54) [89,105]. Oxidative addition also occurs upon treatment of **96** with RhCl(PPh$_3$)$_3$; Rh



Scheme 51. Alternative synthesis of **94a**, proceeding via its 1,1-dioxide 103 [82,97].



Scheme 53. Illustrative examples of the five classes of dichalcogenolate metal complexes prepared by Teo, containing one to four metal centres [101–103].

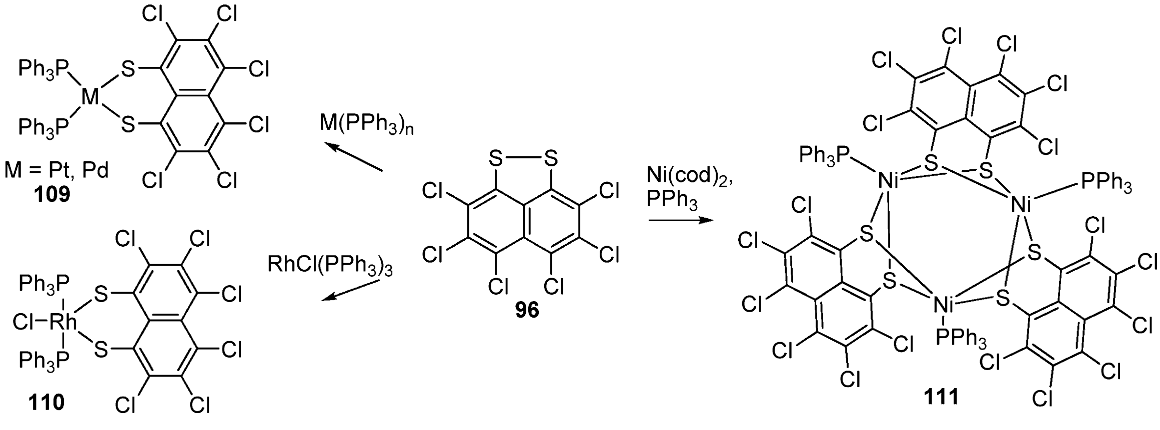
inserts into the S–S bond to form complex **110** containing Rh(III) and a S,S-coordinated chelating ligand [105]. In contrast, treatment of **96** with [Ni(cod)$_2$] and triphenylphosphine results in the formation of an unusual trinuclear nickel(II) complex **111** [89]. After reduction to its respective dithiol (using NaBH$_4$), **96** forms mononuclear complexes [R$_4$N]$_2$[M(**96**)$_2$] with M = Ni, Pd, Pt and Zn [89,106].

A comprehensive series of mononuclear platinum(II) complexes with a range of naphthalene dithioles, their oxides and also thiaselenole **95a** and diselenole **94b** has been reported by us [107]. Oxidative addition reactions are carried out by treating the dichalcogenoles with zero-valent platinum species [Pt(PPh$_3$)$_4$] and [Pt(C$_2$H$_4$)(PMe$_3$)$_2$] (Scheme 55).

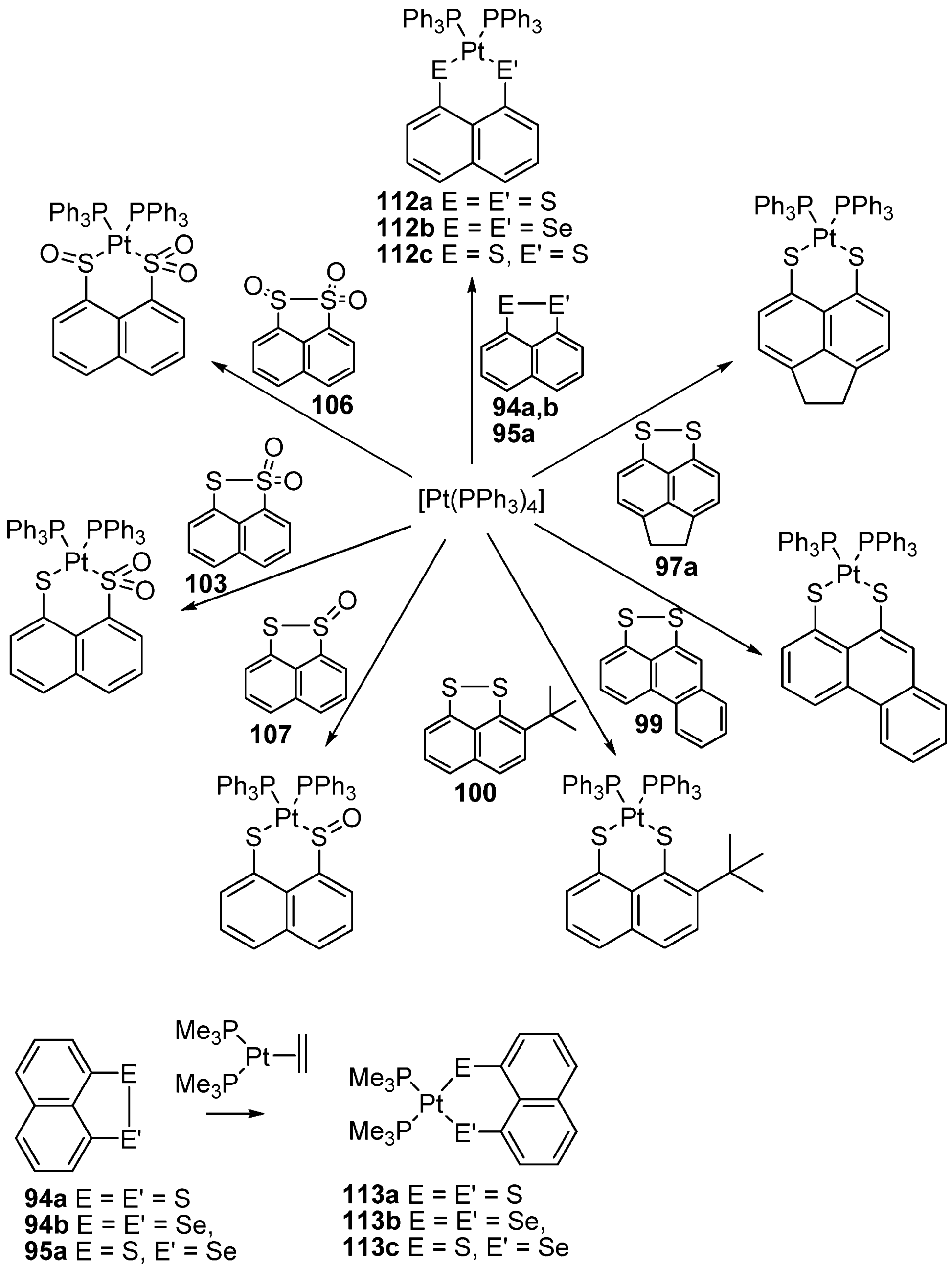
Both triphenylphosphine derivatives **112a–c** and trimethylphosphine complexes **113a–c** were also obtained by metathesis reactions from the dichalcogenates prepared *in situ* by reduction of the E–E bond with lithium triethylborohydride LiBEt$_3$H (Scheme 56) [107].

Similar metathetical reactions were carried out in the preparation of tetraoxide complexes **114**, which were formed from [PtCl$_2$(PR$_3$)] (PR$_3$ = PPh$_3$ or PMe$_2$Ph) and the disodium salt of naphthalene 1,8-disulfinic acid **105** (Scheme 57) [107].

In a closely related study, coordination chemistry of a group of diselenolate ligands containing a variety of backbones was investigated [83]. Complexes **115** were obtained by the reaction of *in situ* generated diselenolates with [PtCl$_2$(P(OPh)$_3$)$_2$] (Scheme 58).



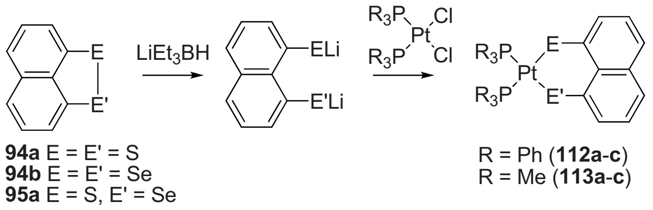
Scheme 54. Oxidative additions with hexachloronaphthalene-1,8-dithiole **96** [89,105].



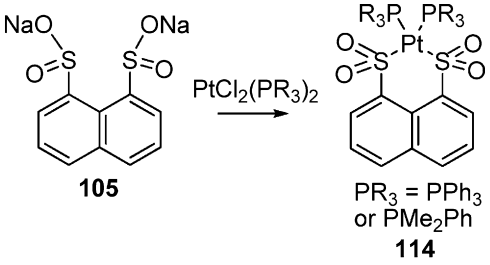
Scheme 55. Synthesis of platinum(II) complexes using variety of naphthalene dichalcogenole species [107].

A series of binuclear iridium(II) complexes was synthesised by the oxidative addition reactions of a range of dithiole ligands with $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ (Scheme 59) [95].

Bimetallic complexes are of particular interest due to their potential catalytic activity. The presence of a second metal in close proximity to the first can be used to modify the reactivity and electronic properties of the overall metallic system thus tailoring it for specific catalytic applications. A series of bimetallic complexes was obtained by reacting the readily prepared platinum complex **112a** with a range of Pt, Pd, Rh, Ir and Mo complexes



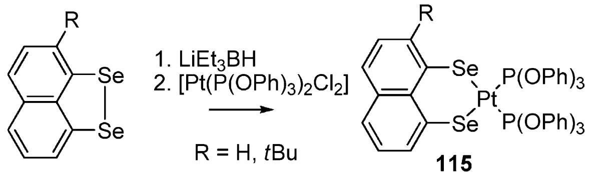
Scheme 56. Synthesis of platinum complexes **112a–c and 113a–c** via dichalcogenates [107].



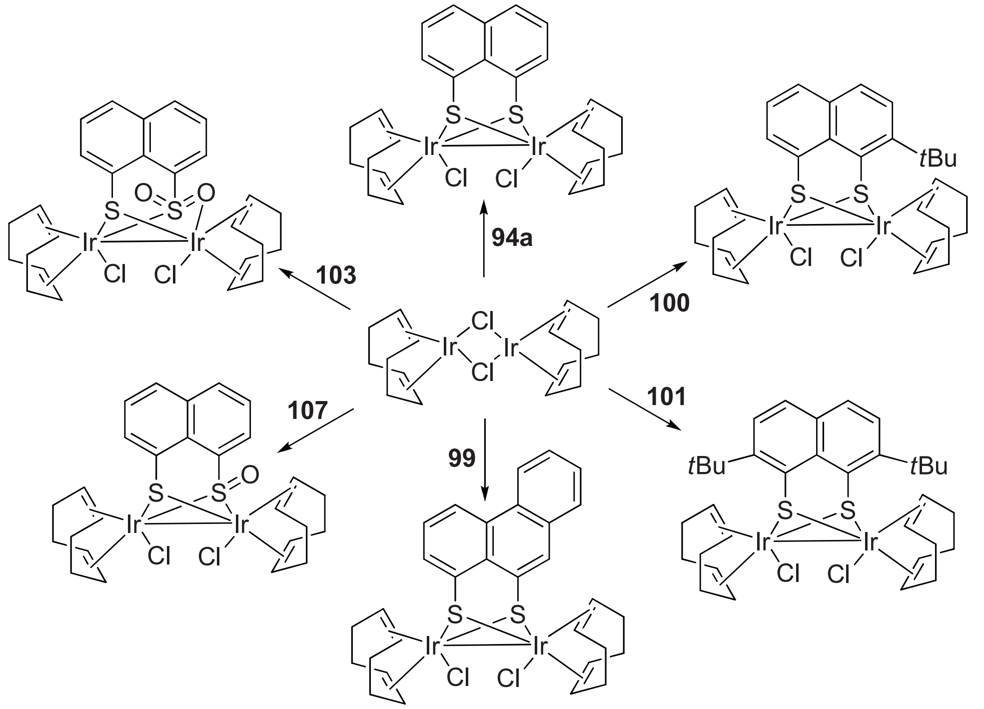
Scheme 57. Synthesis of dithiolate tetraoxide complexes **114** [107].

(Scheme 60). The two metal centres are bridged by the two sulfur atoms of the naphthalene, giving rise to an M_2S_2 core [108].

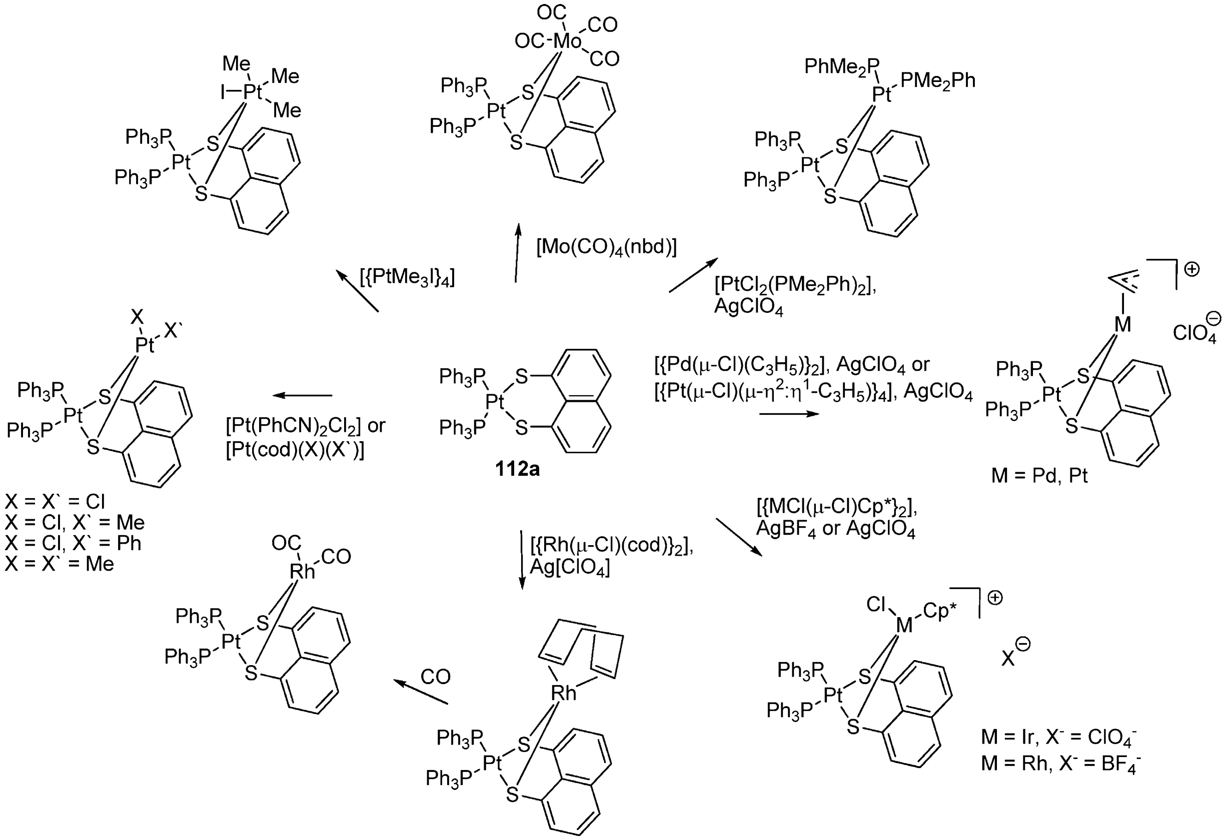
Bimetallic systems containing a group 11 metal (Au, Ag) in addition to platinum are prepared by the reactions of the platinum complex **112a** with $[Ph_3PAu]ClO_4$ or $AgClO_4$ (Scheme 61). Depend-



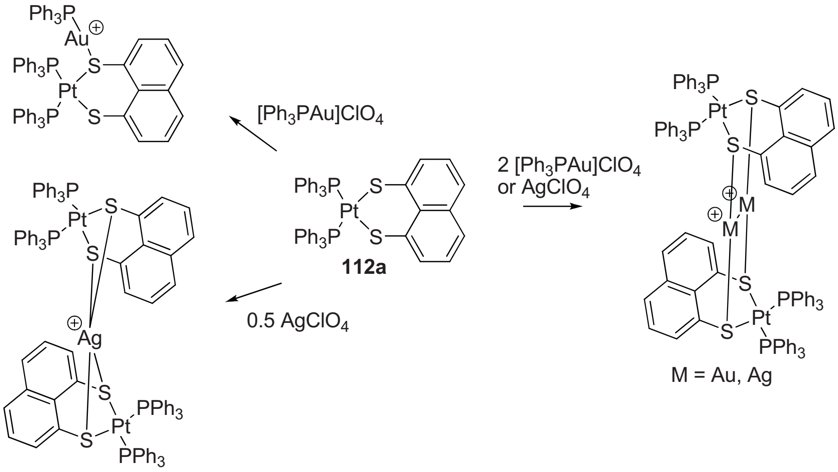
Scheme 58. Synthesis of platinum complexes with diselenolate ligands [83].



Scheme 59. Synthesis of binuclear iridium(II) complexes with variety of naphthalene dithiolate motifs [95].



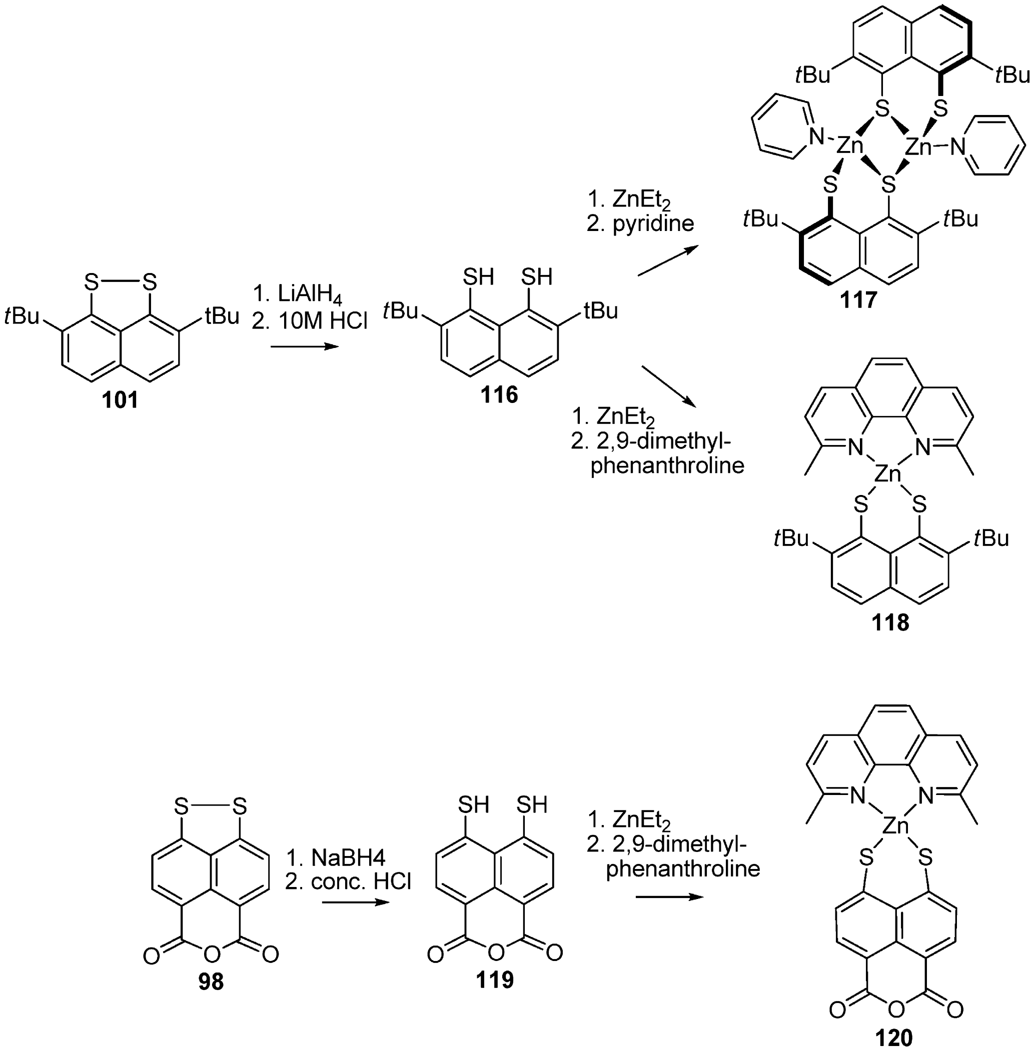
Scheme 60. Synthesis of naphthalene dithiolate bimetallic complexes from platinum complex **112a** [108].



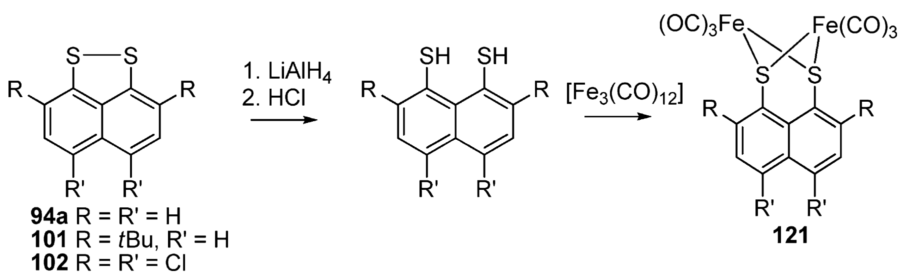
Scheme 61. Synthesis of naphthalene dithiolate bimetallic systems containing platinum and silver or gold [109].

ing on the stoichiometry, binuclear and tetranuclear gold clusters are obtained; the binuclear complex is fluxional in its bonding to the ligand in solution. Tri- or tetranuclear clusters are obtained with silver [109].

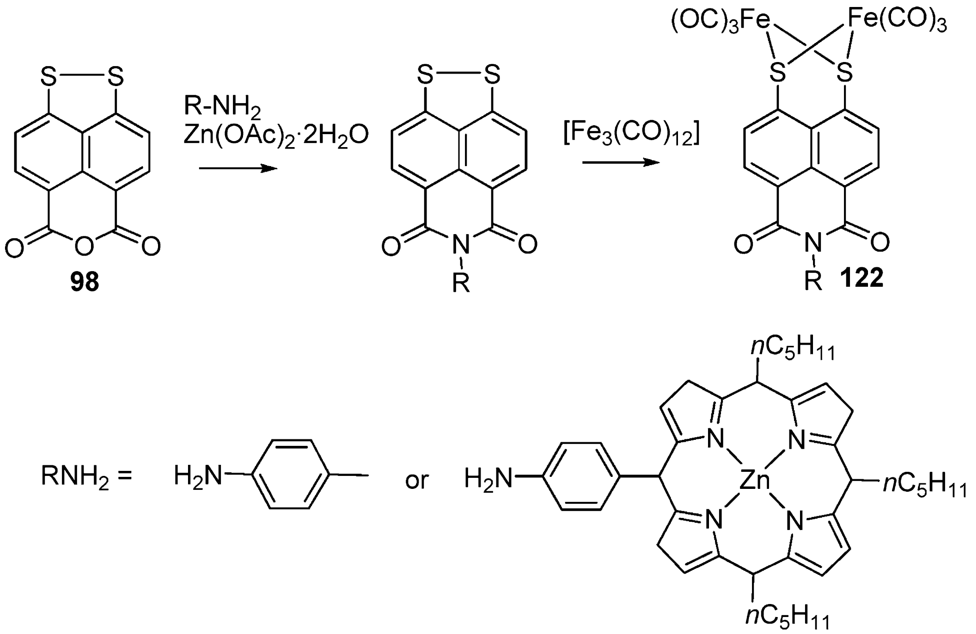
Further examples of multimetallic dithiolate complexes have been reported recently in the literature. Tetranuclear and pentanuclear copper(I) dithiolate complexes have been synthesised from the reactions of 1,8-naphthalene dithiolate (obtained by the reduc-



Scheme 62. Zinc complexes with sterically crowded dithiole **116** and electron poor dithiole **119** [94].



Scheme 63. Synthesis of complexes **121** containing a butterfly Fe_2S_2 core [96].

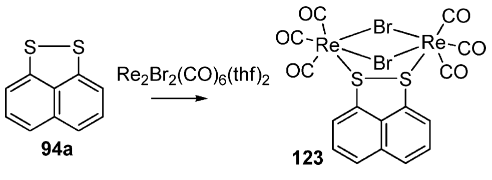


Scheme 64. Synthesis of system **122** combining diiron naphthalene-1-8-dithiolate motif with the zinc porphyrin motif [111].

tion of dithiole **94a** by $NaBH_4$) and $[Cu_2(\mu^2\text{-dppm})_2(MeCN)_2](PF_6)_2$ [110] (dppm = 1,1-bis(diphenylphosphino)methane). The tetranuclear complex has a square Cu_4 core capped by a 5-coordinate sulfur atom, whilst the pentanuclear complex has a Cu centred square planar Cu_5 core.

Vahrenkamp reported a series of oligomeric, dimeric and monomeric zinc complexes of sterically crowded 2,7-di-*tert*-butylnaptho[1,8-c,d][1,2]dithiole **101** and electron poor naphthoic anhydride dithiole **98** (Scheme 62) [94]. The dithiols **116** and **119** were isolated, before being reacted with diethylzinc. The resulting presumably polymeric material was reacted with mono- and bidentate N-donors. Thus reaction with pyridine gave the dimer **117**, whilst reactions with 2,9-dimethylphenanthroline gave the mononuclear complexes **118** and **120**.

A series of diiron complexes **121** containing a butterfly Fe_2S_2 core was synthesised and their redox properties were studied. The synthesis proceeded via the dithiols, which were isolated and subsequently reacted with $[Fe_3(CO)_{12}]$ (Scheme 63). The study focused on the proton reduction capabilities of these hydrogenase mimics [96].



Scheme 65. Synthesis of binuclear Re(I) dithiolate complex **123** [113].

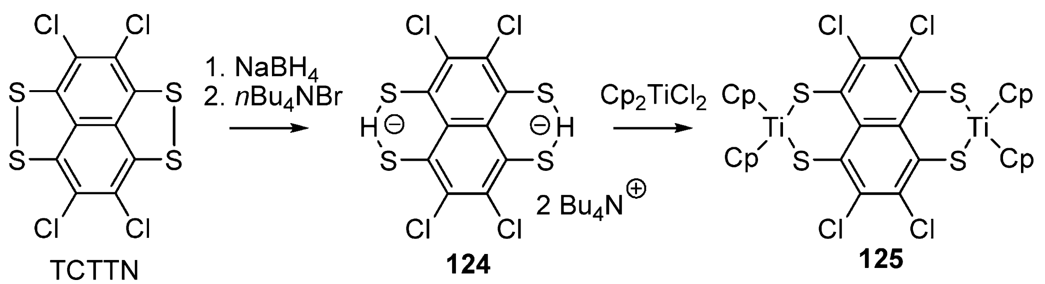
The butterfly diiron naphthalene-1-8-dithiolate motif has been combined with the zinc porphyrin motif in a molecular system, with the aim of developing a system capable of the photogeneration of H_2. Two complexes **122** were synthesised as shown in Scheme 64 [111].

Two group 6 mononuclear pentacarbonyl complexes were obtained by reacting dithiole **94a** with $[W(CO)_5(thf)]$ and selenothiole **95a** with $[Cr(CO)_5X]$ (X = halogen) [112]. Elemental analysis suggests the composition of the complexes is $[M(CO)_5(NapEE')]$, however little extra data apart from variable temperature NMR are reported.

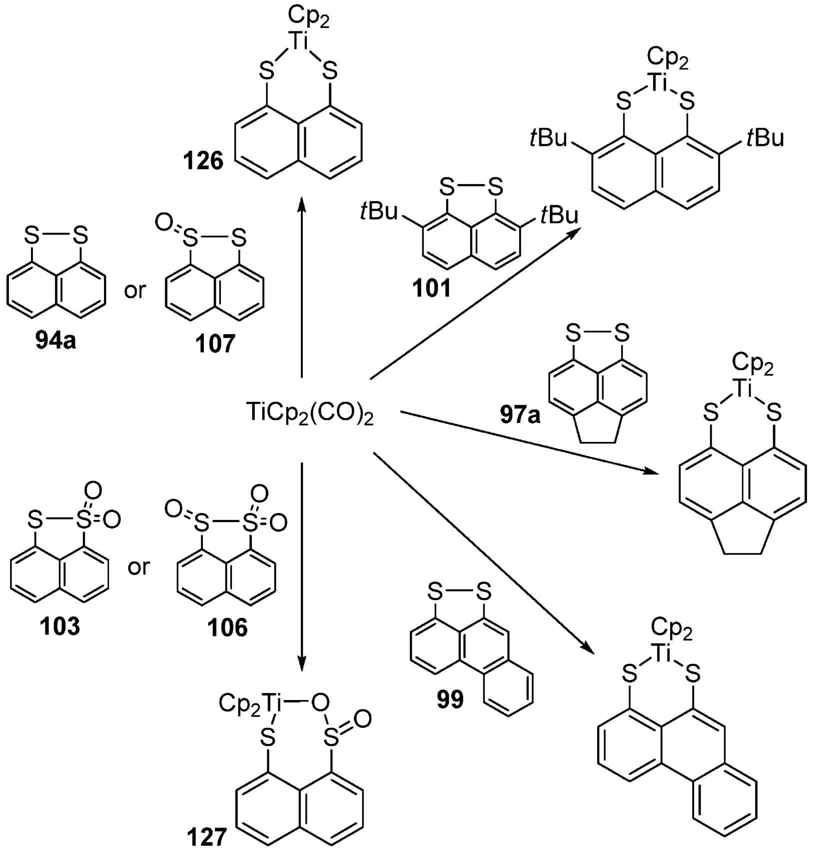
A binuclear Re(I) system **123** with bridging bromide ligands has been prepared by the reaction of dithiole **94a** with $Re_2Br_2(CO)_6(thf)_2$ (Scheme 65) [113].

Complexes formed between sulfur ligands and titanocene are used as sulfur ligand transfer reagents because of the stability of the titanocene unit towards nucleophiles [114].

In the synthesis of the binuclear complex **125**, the bis(dithiolate) salt **124** is formed in the first step. This is done by reduction of tetrachlorotetrathionaphthalene (TCTTN) with sodium borohydride to the respective thiol, and subsequent transformation to its bis(tetra-*n*-butylammonium) salt (**124**) by addition of nBu_4NBr. The reaction of **124** with Cp_2TiCl_2 affords a bimetallic complex **125** (Scheme 66) [114].

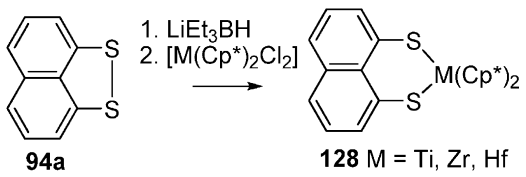


Scheme 66. Synthesis of a bimetallic titanocene complex **125** via the reduction of TCTTN [114].



Scheme 67. Synthesis of titanocene complexes with variety of naphthalene dithiolate ligands [115].

The series of titanocene complexes was extended by us recently [115]. Dithiolato complexes with a variety of modified naphthalene-1,8-diyl backbones were synthesised by oxidative addition of the respective dithioles to $TiCp_2(CO)_2$ (Scheme 67). Reactions with oxidised dithiole ligands were also studied. Interestingly, oxygen elimination reaction is observed for the $S{=}O$ fragments, but not for the $S(=O)_2$ groups, thus the same product (**126**) is obtained from dithiole **94a** or dithiole monoxide **107**. In the same manner, dithiole dioxide **103** or dithiole trioxide **106** both afford the dioxide motif containing product **127** [115].



Scheme 68. Homologous series of Group IV metallocene complexes **128** containing naphthalene dithiolate ligand [116].

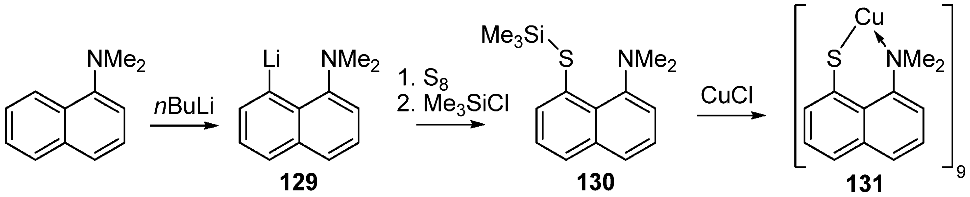
In a subsequent paper we reported a homologous series of three group IV metallocene complexes. In this case the dithiolate, formed *in situ* from dithiole **94a**, was reacted with $[MCp^*{}_2Cl_2]$ (M = Ti, Zr, Hf) to give the titanocene complexes **128** (Scheme 68) [116].

A silver(I) coordination polymer has been prepared from the reaction of sterically encumbered octakis(cyclohexylsulfanyl)naphthalene with silver trifluoroacetate [117]. The naphthalene ring in the complex has end-to-end twist 35° as a consequence of large steric strain.

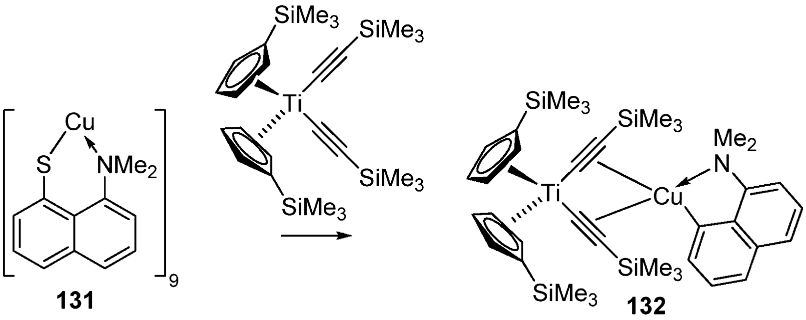
3.2. NapSN ligands and complexes

Several thiolato complexes bearing an amino group in the *peri*-position were reported by van Koten and coworkers.

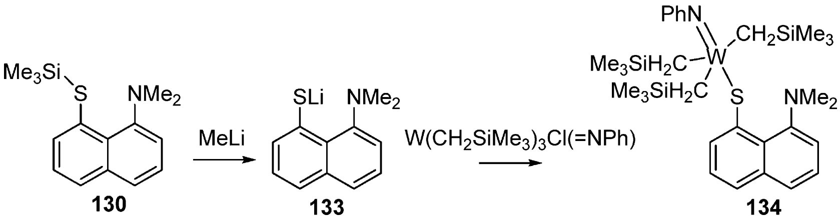
A nonameric copper(I) cluster **131** with the N,S-chelating *peri*-naphthalene ligand is prepared as shown in Scheme 69 [118]. The



Scheme 69. Synthesis of nonameric copper(I) cluster **131** containing the N,S-chelating *peri*-naphthalene ligand [46].



Scheme 70. Synthesis of copper-titanium complex **132** [122].



Scheme 71. Synthesis of tungsten complex **134** [123].

lithiation of 1-dimethylaminonaphthalene gives the *peri*-lithiated species **129** regiospecifically [46]. **129** is then reacted with sulfur, and the resulting sulfide is transformed to its trimethylsilyl derivative **130**, which is reacted with CuCl to give **131**. The intramolecularly coordinating amine group in **131** is believed to contribute to the well-defined structure of the cluster. The complex has been used as a catalyst in a number of transformations [119–121].

A related bimetallic copper-titanium complex **132** was prepared by the reaction of the nonameric **131** with bis(alkyne) titanocene complex as shown in Scheme 70 [122].

In an attempt to synthesise tungsten alkylidene complex, the lithium thiolate **133** was reacted with $W(CH_2SiMe_3)_3Cl(=NPh)$ as shown in Scheme 71 to give the alkylidene precursor **134** [123].

4. Conclusion

A large amount of coordination chemistry of ligands based on *peri*-substituted naphthalene has been done with a rather limited number of ligands. Despite this, the diversity of the research in the area is tremendous, as indicated by recent highlights, which include applications of the resulting complexes in the manufacture of electroluminescent materials [45], photogeneration of H_2 [111], as well as asymmetric hydrogenation [52].

As heavier elements receive renewed interest in many areas of main group chemistry (for example in the area of stabilisation of multiply bonded or low-valent species), it is likely that *peri*-substituted ligands with heavier donor atoms will become increasingly studied in the near future. With regards to Group 15 chemistry, rather promisingly the synthesis of the $NapSb_2$ ligands was recently demonstrated to be comparable in yields to well established $NapP_2$ species [76]. This indicates that the synthesis of bismuth species may be possible, and opens up the possibilities of synthesising mixed donor ligands with different Group 15 elements as *peri*-atoms. On a similar note, it is likely that the interest in heavier Group 16 element ligands will increase. Notably, although the ditellurole **94c** was synthesised in the 70 s [78], no coordination chemistry of ditelluroles has been reported so far.

Exciting future work may be envisaged in many areas of *peri*-substituted coordination chemistry. Hemilabile heterodentate ligands, such as NapPS and NapPN are likely to be of increasing interest in catalysis. Organometallic species, such as NapPC (for an example see complex **90**), are interesting from a bonding point of view, and many permutations of metals and donor atoms can be foreseen. Bimetallic complexes with dichalcogenolato ligands are also of high interest for their bonding and potential applications in catalysis.

Another noteworthy aspect of *peri*-substituted naphthalene ligand chemistry is the large scope for improving the syntheses of some well-established ligands. For example, a variety of procedures for the synthesis of the parent naphtho[1,8-cd]-1,2-dithiole **94a** have appeared in the literature over the last century (the first report appearing in 1911 [80] and the latest one so far in 1994 [79]). Despite all this effort, the overall efficiency of the synthesis of **94a** remains rather low and is resisting the attempts for scaling-up. The reasons for this are variable yields obtained using even the best available procedure, coupled with the requirement for a lengthy purification process by column chromatography.

It is the opinion of the authors of this paper, that many recently synthesised main group *peri*-substituted naphthalene species will be capable of acting as ligands, and we eagerly await significant development of their coordination chemistry in the near future.

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