Coordination Chemistry Reviews 255 (2011) 574–590

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Sulfur-functionalized *N*-heterocyclic carbenes and their transition metal complexes

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Contents

ARTICLE INFO

Article history:
Received 25 August 2010
Accepted 28 October 2010
Available online 5 November 2010

Keywords:
N-Heterocyclic carbenes
Sulfur
Transition metal complexes
Catalysis
Ionic liquids

ABSTRACT

Donor group functionalized *N*-heterocyclic carbenes (NHC) are an important class of ligands used in transition metal complex chemistry. Herein, the growing field of sulfur-functionalized NHC compounds and their respective transition metal complexes are described comprehensively. The sulfur-functionalized NHC compounds are categorized by functional groups such as thiolate, thioether, sulfoxide, thiophene, sulfonate and sulfonamide. Chiral compounds and the hemilabile behaviour of sulfur-functionalized NHC compounds are reported.

1. Introduction

The discovery of *N*-heterocyclic carbenes (NHCs) by Wanzlick and Öfele in the 1960s [1–4] and the isolation of the first isolable NHC by Arduengo in 1991 [5] has attracted enormous attention for NHCs and their corresponding metal complexes in the past two decades [6–17]. The chemistry of NHC ligands has become ubiquitous in organometallic chemistry rivaling that of phosphine ligands [18], which is also reflected by the current commercial availability of a wide range of NHCs and their precursors. The usefulness of NHCs is due to the relative ease of synthetic preparations, nearly independent manipulations of the

Abbreviations: Ac, acetyl; bipy, 2,2′-bipyridine; ^{n}Bu, *n*-butyl; ^{t}Bu, *tert.*-butyl; Bz, benzyl; COD, 1,5-cyclooctadiene; Cy, cyclohexyl; dba, 1,3-dibenzylacetone; DCC, 1,3-dicyclohexylcarbodiimide; DIPP, 2,6-diisopropylphenyl; dme, 1,2-dimethoxyethane; DMF, *N*,*N*-dimethylformamide; DMSO, dimethylsulfoxide; ee, enantiomeric excess; Et, ethyl; HOBT, 1-hydroxybenzotriazole; MAO, methyl aluminum oxide; Me, methyl; Mes, mesityl; NHC, *N*-heterocyclic carbene; NMR, nuclear magnetic resonance; OTf, triflate; phen, 1,10-phenanthroline; ^{i}Pr, isopropyl; pyr, pyridine; RT, room temperature; S–NHC, sulfur-functionalized NHC; THF, tetrahydrofuran; thp, thiophene; TON, turnover number.

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doi:10.1016/j.ccr.2010.10.040

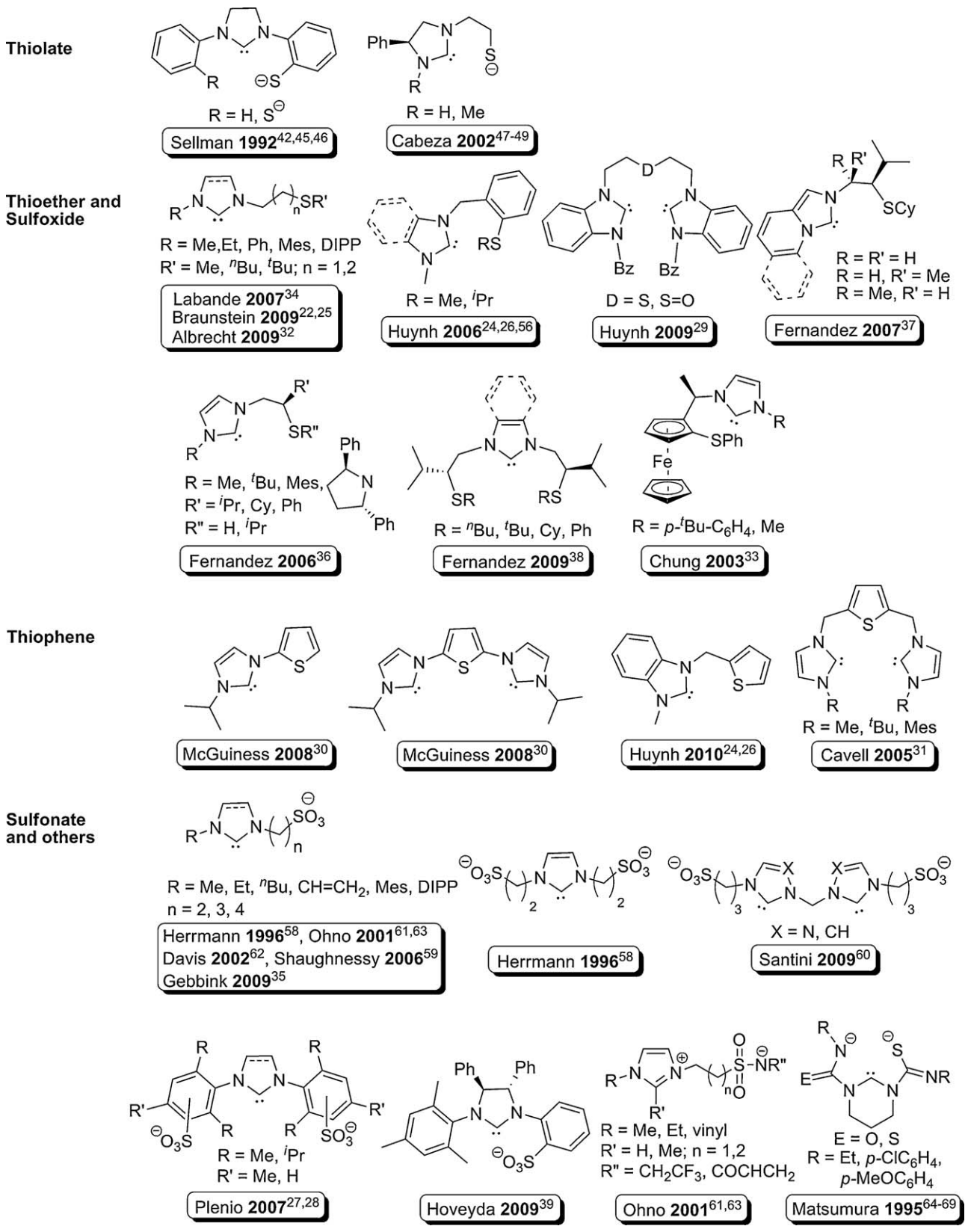


Fig. 1. Comprehensive overview of representative structures of sulfur-functionalized NHCs discussed in this review.

electronic and steric properties, and the strong σ-donating character resulting in stronger metal–NHC bonds compared to related metal–phosphine bonds [10]. In addition, a wide range of synthetic methodologies have been reported to generate metal–NHC complexes such as direct complexation of isolated NHCs to metals, deprotonation or α-elimination of imidazolium and imidazolinium salts and the transmetalation reaction with silver–NHC complexes [6,8]. Furthermore, NHCs containing additional donor functionali-

ties provide enhanced metal centre stability through chelation of these polydentate ligands [9,19]. Among these complexes, ligand architectures range from simple chelating bidentate structures, tridentate pincer ligands [20] and tripodal structures [21], to intricate oligodentate and macrocyclic systems [6,7] which are widely used, with the pivotal concept of hemilability being observed throughout [9,22]. Hybrid ligands, i.e. ligands containing two or more different donor functionalities, can exhibit hemilability when complexed to a metal. Hemilability can be defined as "the ability to provide open coordination sites at the metal during reaction that are 'masked' in ground state structure, and to stabilize reactive intermediates" [22]. Such hemilability property is predominantly observed when the donor-functions in a hybrid ligand vary greatly such as hard and soft donor functions as described by Pearson's Hard–Soft Acid–Base theory [23]. The structural architectures of donor-functionalized NHCs are wide ranging and incorporate many neutral and anionic two-electron donor functionalities from groups 15 and 16, reported by Cavell [9] and Lee [19]. These review articles provide a good overview of donor-functionalized NHCs and their complexes with emphasis on the majority of donor-functionalized NHC containing various N, O and P donor functions. Surprisingly, relatively little has been reported about sulfur-functionalized NHCs (S–NHCs) and their corresponding transition metal complexes, which have seen a remarkable growth of publications in the past few years (Fig. 1). Compared to other donor-functionalized NHCs, the usage of S–NHC complexes is in its infancy. Their versatility has however been demonstrated in catalytic transformations such as Suzuki–Miyaura [24–29], Mizoroki–Heck [30], Sonogashira [29], ethylene polymerization [31], aryl amination [32], hydrogenation [33,34], hydrosilylation [35,36], allylic substitution [37,38], asymmetric 1,3-cylcoaddition of imino glycinates [39], asymmetric 1,4 addition of γ-keto esters [40] as well as the palladium-catalyzed 1,2-addition of aldehydes with boronic acids [41] and trifluoroborates [42]. The intent of this review is to provide a comprehensive review on sulfur-functionalized NHCs and their transition metal complexes by categorization according to sulfur functionalities.

2. Sulfur-functionalized NHC compounds

2.1. Thiolate-tethered NHCs

In 1992, Sellmann et al. [43] reported the first sulfur functionalized NHC compound (**1**) discovered in the unexpected formation of the dimeric nickel complex, $[Ni(S–C–S)_2]_2$, by the reaction of 1,2-ethanediamine-*N*,*N*′-*bis*(2-benzenethiolate) (**2**) with nickel(II) chloride in DMF. The intended target was the N_2S_2-chelation complex with a Ni centre as a biomimetic model for the active sites of nickel containing CO dehydrogenases. The dimeric nickel complex **1** demonstrates remarkable thermal and chemical stability and can be obtained by a more efficient template synthesis using ethyl orthoformate, nickel(II) chloride and **2** as outlined in Scheme 1 [43]. **2** was synthesized by a sodium borohydride reduction of the 1,2-*bis*-(2-mercaptoanilino)ethane zinc complex that was formed by the template synthesis reaction of *ortho*-aminothiophenol, glycol and zinc acetate [44,45]. Alternatively, **1** can also be synthesized in high yields using nickel(II) chloride and the dimerized S–NHC compound **9b** that generates the monomeric S–NHC (**9a**) *in situ* by thermal cleavage of the $N_2C{=}CN_2$ bond (Scheme 2) [46]. The dimeric nickel complex **1** is extremely stable even against concentrated sulfuric and hydrochloric acids and typically precipitates out of organic solutions. However, the mononuclear nickel complexes (**3a**–**c**) were obtained by cleavage of the nickel dimer **1** by addition of excess coordinating neutral monodentate ligands, trimethylphosphine and triphenylphosphine, and anionic cyanide. The formation of **3a**–**c** is reversible and dimeric structure

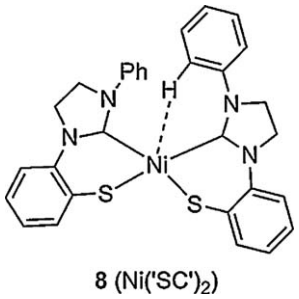


Fig. 2. S–NHC nickel complex **8** with proposed agnostic Ni–H interaction [43].

1 precipitates readily upon dissolving in organic solvents in the absence of the auxiliary ligand [43]. The Ni–methyl complex (**3d**) is generated by reaction of **1** with excess of methyl lithium and presence of crown ether, 12-crown-4. **3d** is remarkably thermally stable at ambient temperature but sensitive to air and decomposes to unidentified products. Ni–methyl complex (**3d**) reacts with hydrogen gas and methyl iodide to liberate methane and ethane, respectively. **3d** also forms a very labile Ni–acetyl complex (**3e**) under CO atmosphere. While **1** does not react with $NaBH_4$, treatment with $LiBEt_3H$ in THF suspension produces the desulfurized mononuclear, homoleptic nickel complex $Ni(S\text{-}C)_2$ (**8**). **8** contains an unsymmetrical S–NHC ligand and exhibits a relatively short Ni–*ortho*-phenyl-CH distance of 262 pm in the crystal structure, an indication of agnostic interaction (Fig. 2). The mechanism for this desulfuration reaction is unknown.

The chemistry of the S–C–S ligand was expanded to include other group 10 elements, Pd (**4**, **5**) and Pt (**6**, **7**) as shown in Fig. 3, through ligand displacement reactions using $MCl_2[COD]$ (M = Pd, Pt) as the metal precursors in a template synthesis reaction with $N_2S_2H_4$ (**2**) and ethyl orthoformate [46,47]. Cleavage of the dimeric palladium and platinum complexes (**4**, **6**) to form the respective mononuclear complexes **5** and **7** was observed with neutral phosphine and *t*-butylisonitrile ligands, anionic sulfur reagents such as hydrogensulfide (HS^-), ethylthiolate, phenolthiolate and *ortho*-aminophenolthiolate. Neutral sulfur reagents, such as S_8 and protonated thiols did not cleave the dimers [47]. The mononuclear nickel complex (**3**·L) with 1,3-diphenylimidazoline-2-ylidene as the auxiliary ligand L is highly insoluble in any organic solvent and proved useless for further investigation. Isolation of the free S–NHC compound (**9a**) was unsuccessful and resulted in the formation of the S–NHC dimer **9b** which oxidizes in air and elevated temperature to the *bis*-disulfide macrocycle (**10**) containing two urethane functionalities (Scheme 2) [46]. Cat-

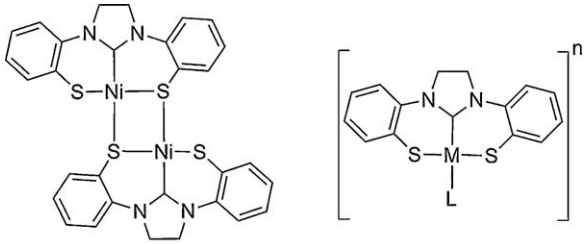
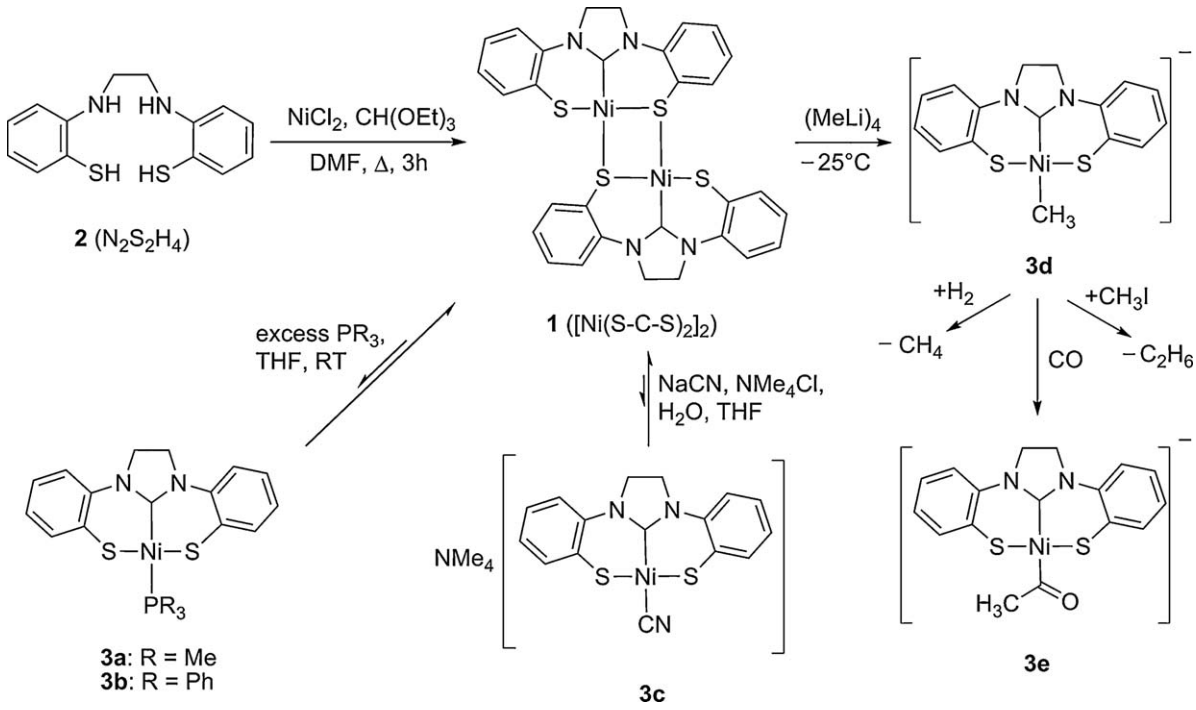


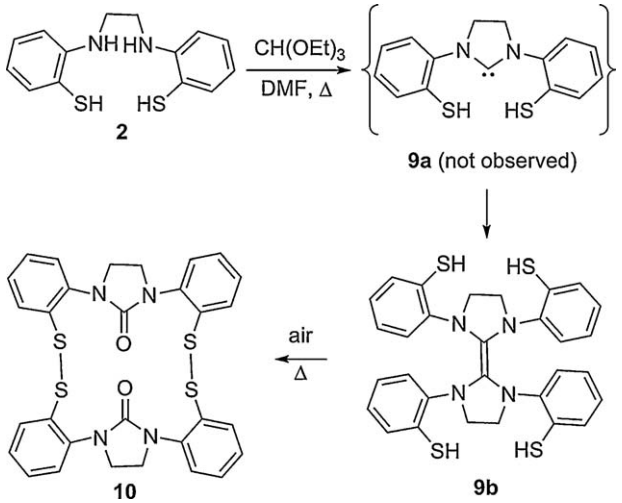
Fig. 3. Dimeric and mononuclear S–C–S complexes with neutral ligands ($n = 0$) and anionic ligands ($n = -1$) [43,46,47].



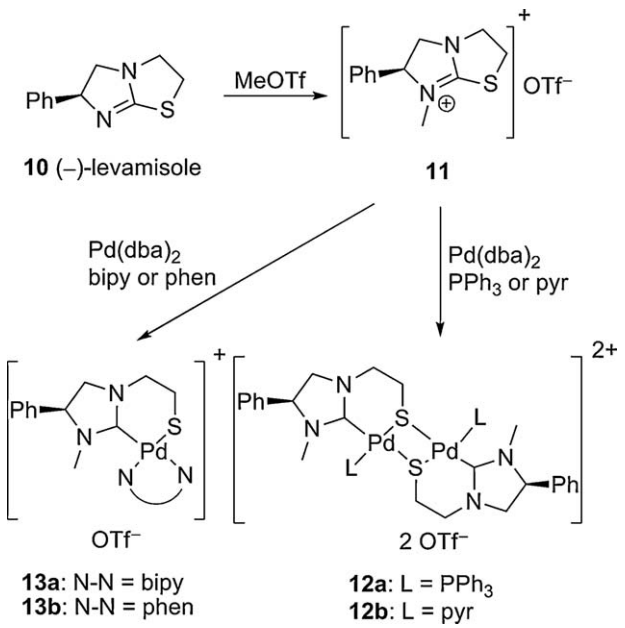
Scheme 1. Synthesis and chemical properties of the first reported sulfur-functionalized NHC nickel complex (**1**) [43,46].

alytic applications of group 10 complexes (**1**, **3**–**7**) have not been reported.

A very elegant synthesis forming S–NHC complexes with thiolate donors was developed by Cabeza et al. [48–50] using the inexpensive, commercially available and enantiopure natural product (−)-levamisole (**10**). *N*-Methylated levamisole (**11**), a masked NHC-thiolate ligand generated by reaction of methyl triflate and (−)-levamisole (**10**) [51,52], can be complexed to palladium forming a dimeric (**12**) or monomeric complex (**13**) as outlined in Scheme 3. The resulting S–NHC compound is obtained by the oxidative addition of a $Pd(dba)_2$ solution prepared *in situ*, yielding dimeric binuclear Pd complexes in the presence of triphenylphosphine (**12a**) and pyridine (**12b**), featuring a slightly bent Pd_2S_2 ring system [49]. Mononuclear Pd complexes were obtained with the chelating ligands 2,2′-bipyridine (**13a**) and 1,10-phenanthroline (**13b**). Typically, neutral (−)-levamisole (**10**) does not undergo C–S bond activation, and binds through the sp^2nitrogen as a two electron donor to metals such as Co, Ni, Cu, Zn, Pd and Pt [53–56]. C–S activation was only observed in Pd, Ru, and Os complexes involving the cationic ligand **10**·HCl or the *N*-methylated derivative (**11**) [48–50]. Trinuclear carbonyl metal clusters with Ru [50] and Os [48,50] have been reported with **10**·HCl and **11** in which the metal, Ru (**14a**, **b**) or Os (**14c**, **d**) added oxidatively across the C–S bond (Fig. 4); the *N*-methylated (−)-levamisole (**11**) forms the chloride bridging complexes, and the protonated (−)-levamisole (**10**·HCl) forms the hydride bridging complexes as a mixture of two diastere-



Scheme 2. Synthesis of **9** and **10** [46].



Scheme 3. Palladium NHC–thiolate complexes (**12**, **13**) derived from (−)-levamisole (**10**) [48,49].

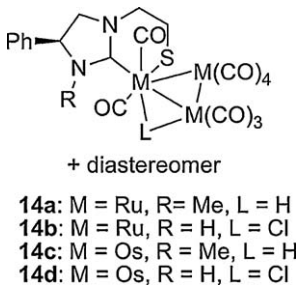


Fig. 4. Trinuclear metal complexes with C–S activated (−)-levamisole ligand [50].

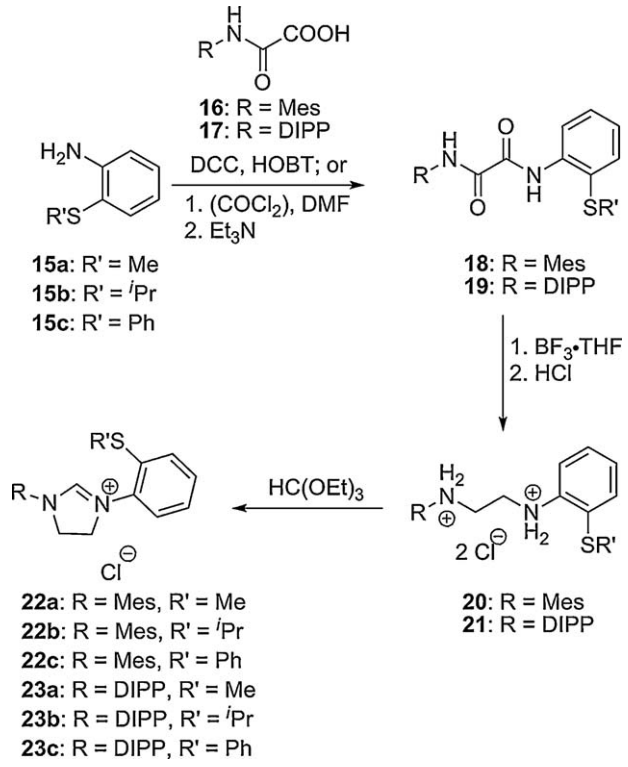
omers in an approximately 1 to 1 ratio. Catalytic activities of **12**–**14** were not reported.

2.2. Thioether-tethered NHCs

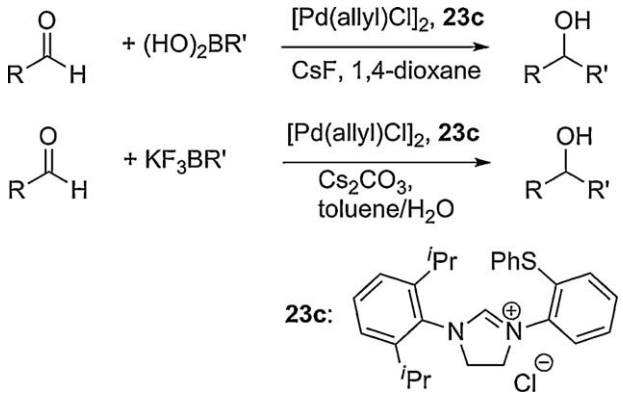
The most common sulfur functional group in S–NHCs is the thioether group which can be dialkyl, diaryl and aryl alkyl mixed thioether functionalities.

2.2.1. Aryl-tethered thioethers

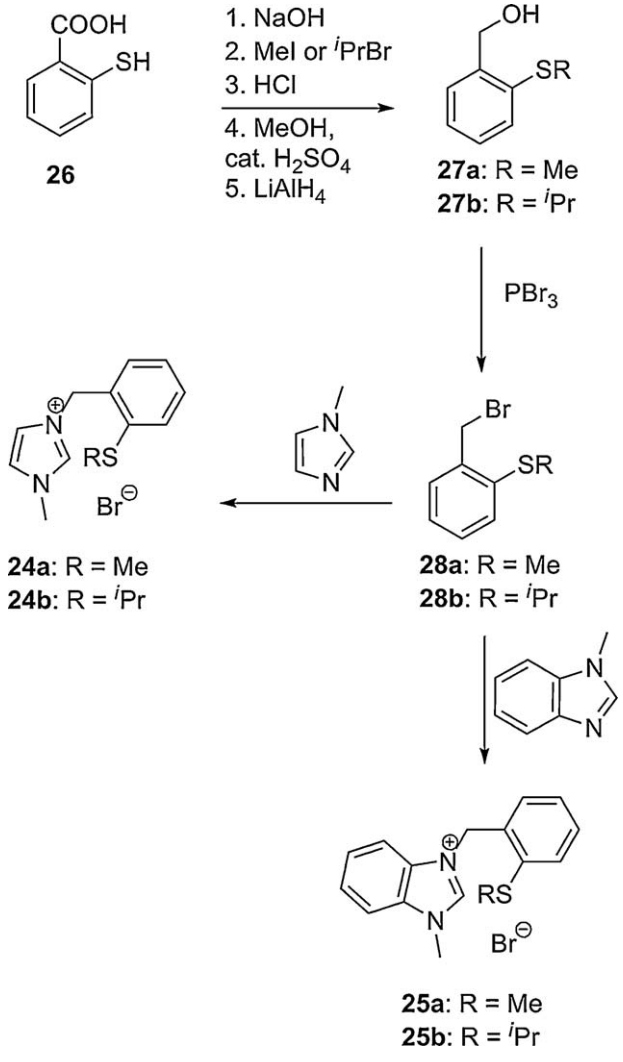
Kuriyama et al. [24] reported the first aryl thioether-tethered imidazolinium salt synthesis (**22** and **23**) from *S*-alkylated *ortho*-aminothiophenols (**15a**–**c**), and mesityl and 2,6-diisopropyl anilinyloxamic acids (**16** and **17**) as outlined in Scheme 4. The three-step pathway involves the formation of the *N*,*N*′-disubstituted oxalamides (**18** and **19**) by the reaction of oxamic acids with 1,3-dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBT), or alternatively with oxalic chloride and catalytic amounts of DMF followed by treatment with triethyl amine. The oxalamide intermediates (**18** and **19**) were reduced with BF_3• THF at room temperature, and the *N*,*N*′-disubstituted ethylene diamines as hydrochloride salts (**20** and **21**) were afforded in moderate to high yields upon treatment with hydrochloric acid. The imidazolinium compounds (**22** and **23**) were then obtained by the cyclization reaction with ethyl orthoformate. These aryl-tethered imidazolinium ligands were evaluated for palladium-catalyzed transformations by *in situ* generation of the palladium catalyst involving the combining of $[Pd(allyl)Cl_2]_2$, **22** or **23** in presence of cesium carbonate. Analysis and characterization of these pal-



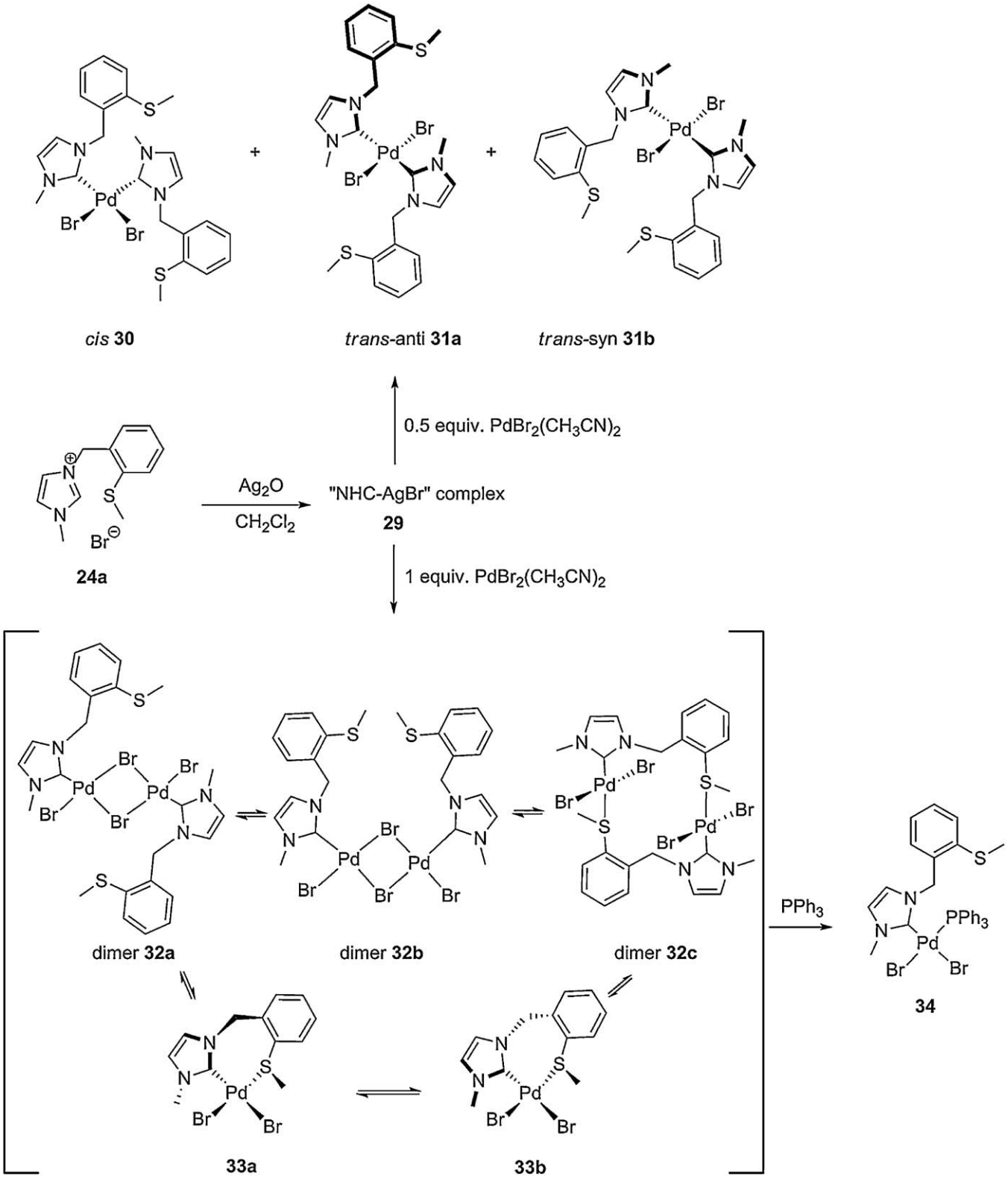
Scheme 4. Aryl thioether-tethered imidazolinium compounds [24].



Scheme 5. Palladium catalyzed 1,2-additions of aldehydes with boronic acids and trifluoroborates [41,42].



Scheme 6. Synthesis of aryl-tethered imidazolium and benzimidazolium S–NHC [25,57].



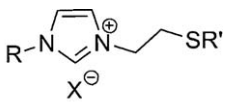
Scheme 7. Reactivity and hemilability of S–NHC (**24a**) with palladium [25].

ladium complexes was not reported. S–NHC palladium complexes with ligand precursors **22a** and **22b** showed the highest activity towards Suzuki–Miyaura coupling reactions of substituted bromobenzenes and substituted phenyl boronic acids with excellent isolated yields of the desired biaryl products [24]. These reaction conditions also provided excellent yields for the C–C coupling of bromo-*N*-heterocyclic compounds with substituted phenyl boronic acids [24]. The new S–NHC ligands were further evaluated in other catalytic transformations as outlined in Scheme 5 [41,42]. S–NHC precursors **22** and **23** showed catalytic reactivity of palladium allyl chloride catalyzed 1,2 addition of aldehydes with aryl and alkenyl boronic acids to secondary alcohols [41]. This transformation is

generally applicable to a wide range of aryl and alkyl aldehydes, and also boronic acids of aryl, alkenyl and heterocyclic aromatic compounds, producing the secondary alcohols in high yields. In addition, the S–NHC ligands are also suitable for the 1,2-addition of aldehydes with trifluoroborates [42] rather than boronic acids [41]. Again, **23c** showed the highest reactivity and the secondary alcohols were obtained as racemic mixtures in excellent yields within short reaction times (30 min to 2 h) [42]. This transformation is also applicable to a wide range of aryl and alky aldehydes and the potassium salts of trifluoroborate substituted aromatic, olefinic and aromatic heterocyclic compounds.

Huynh et al. reported the first experimental evidence of hemilability in an aryl tethered thioether S–NHC complexed to a palladium centre [25,57]. The imidazolium salts **24a** [57] and **24b** [25] and the benzimidazolium salts **25a**, **b** [25] were synthesized in a five step synthesis from commercially available thiosalicylic acid (**26**) as outlined in Scheme 6. The thiophenol group is alkylated using methyl iodide or isopropylbromide, and the hydroxymethyl group (**27**) is obtained by conversion of the carboxylic acid group to the methyl ester followed by reduction with lithium aluminum hydride. Bromination to **28** is accomplished by reaction with phosphorus tribromide. The imidazolium salts (**24**) and benzimidazolium salts (**25**) are obtained by the *N*-alkylation reaction of 1-methylimidazole and 1-methylbenzimidazole, respectively, in overall isolated yields from **26** of 57–64%. The resulting palladium complexes were obtained by treatment of **24** [57] and **25** [25] with silver oxide in dichloromethane to generate the corresponding NHC–Ag complex (**29**), which was reacted without isolation with *cis*-palladium diacetonitriledibromide (0.5–1 equiv.) (Scheme 7). When a ligand to palladium ratio of 2 to 1 is employed a set of three *bis*-NHC complexes **30** and **31**were observed with a *cis* and a *trans* configuration, respectively, which can be easily separated by washing with acetone. The insoluble *trans*-isomer **31** is obtained as a mixture of *trans*-anti (**31a**) and *trans*-syn (**31b**) rotamers which cannot be further separated. If ligand and palladium are present in an equimolar ratio, a complex mixture of palladium–NHC complexes is present forming three postulated dimeric complexes (**32a**–**c**) that can be cleaved at the bridging μ-bromide ligands (**32a**, **b**) or at the S–Pd bonds in **32c** to form the mononuclear palladium–NHC complexes **33a** and **33b**. ^{1}H NMR spectroscopic evidence of diastereotopic benzylic CH_2 in **33a**, **b** at −30 °C supports the formulation of an *S*-complexed tether as proof of hemilability. The interconversion of **33a** and **33b** at room temperature produces a broadened ^{1}H NMR resonance of the benzylic protons. In addition, the ^{1}H NMR resonance of the *N*-CH_3 and *S*-CH_3 protons are observed as two sets of signals. Complex **33a** was obtained as single crystals and X-ray crystallographic analysis confirmed an *anti* configuration of the *N*-CH_3 and *S*-CH_3 groups. Upon addition of triphenylphosphine, the mononuclear palladium–NHC complex **34** was obtained in quantitative yield shifting the equilibrium between dimeric $(Pd–NHC)_2$ (**32a**–**c**) and mononuclear Pd–NHC (**33a**, **b**) completely to **34**. Similar reactivity and hemilability properties, as outlined in Scheme 7 with the benzimidazolium (**25a**, **b**) derived Pd–NHC complexes, have also been observed [25].

Complexes **31** and the related benzimidazolium–Pd complex (**25a**) show high catalytic activities in the Suzuki–Miyaura C–C cross-coupling reaction of substituted *para*-bromobenzenes with phenyl boronic acid to the biaryl products in aqueous solution at room temperature in high yields after 8 h [25]. The monosubstituted (S–NHC)–Pd complexes catalytic reactivity are also similar to the *bis*-(S–NHC)–Pd complex. Unfortunately, the activity cannot be identified for a particular catalyst as dimeric $(Pd–NHC)_2$ (**32a**–**c**) and mononuclear Pd–NHC (**33a**, **b**) complexes are present in equilibrium. The activity for the coupling of aryl chlorides is poor with these complexes. The phosphine adduct mononuclear triphenylphosphine palladium–NHC complex (**34**) showed the highest catalytic activity in the Suzuki–Miyaura reaction [25].



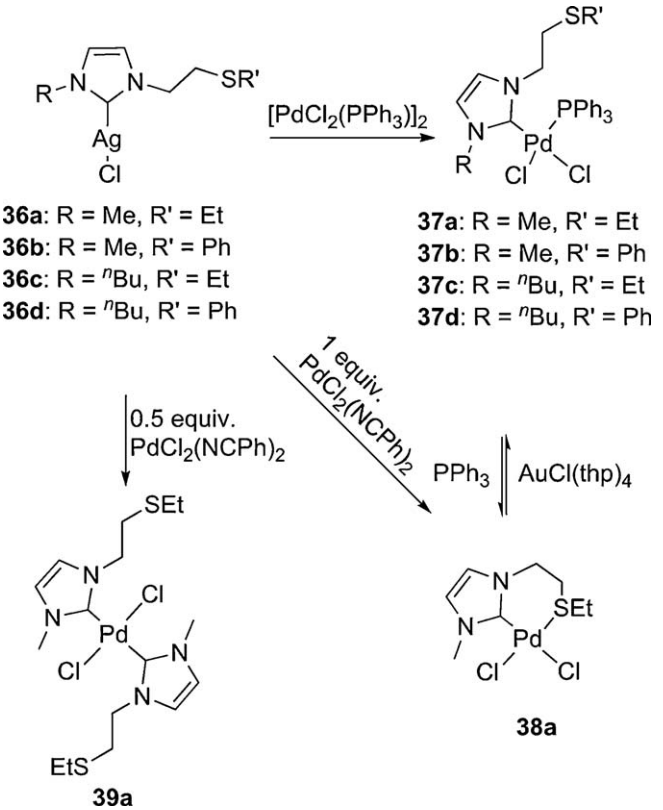
X = Br, PF_6, BF_4

35a: R = Me, R' = Et
35b: R = Me, R' = Ph
35c: R = ^{n}Bu, R' = Et
35d: R = ^{n}Bu, R' = Ph

Fig. 5. Alkyl thioether-tethered imidazolium salts [26].

2.2.2. Alkyl-tethered thioethers

Hemilability was also observed in the dialkyl thioether-functionalized S–NHC palladium complexes derived from the imidazolium salts (**35**) presented in Fig. 5 [26]. Compounds **35a**–**d** were synthesized by alkylation of 1-methylimidazole and 1-(*n*-butyl)imidazole with 2-chloroethyl ethyl sulfide and 2-chloroethyl phenyl sulfide. Different salts of **35** were obtained by a metathesis reaction using potassium hexafluorophosphate and sodium tetrafluoroborate. The Ag–(S–NHC) complexes (**36a**–**d**) were generated using silver oxide with the corresponding imidazolium salt (**35a**–**d**). The chemistry of the Ag–(S–NHC) complexes (**36a**–**d**) is outlined in Scheme 8 [26]. Reaction of **36a**–**d** with one half equivalent of $[Pd(\mu\text{-}Cl)Cl(PPh_3)]_2$ generates in high yields the mono-palladium NHC complexes **37a**–**d** in a square planar geometry with *cis* configuration. The thioether functionality does not show complexation to the Pd centre in **37a**–**d**. However, removal of the triphenylphosphine ligand of **37a** by the scavenging reac-



Scheme 8. Hemilability of S–NHC compounds and their Pd complexes [26].

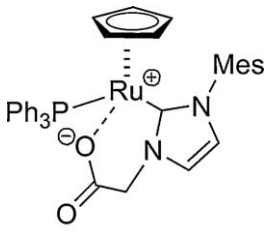


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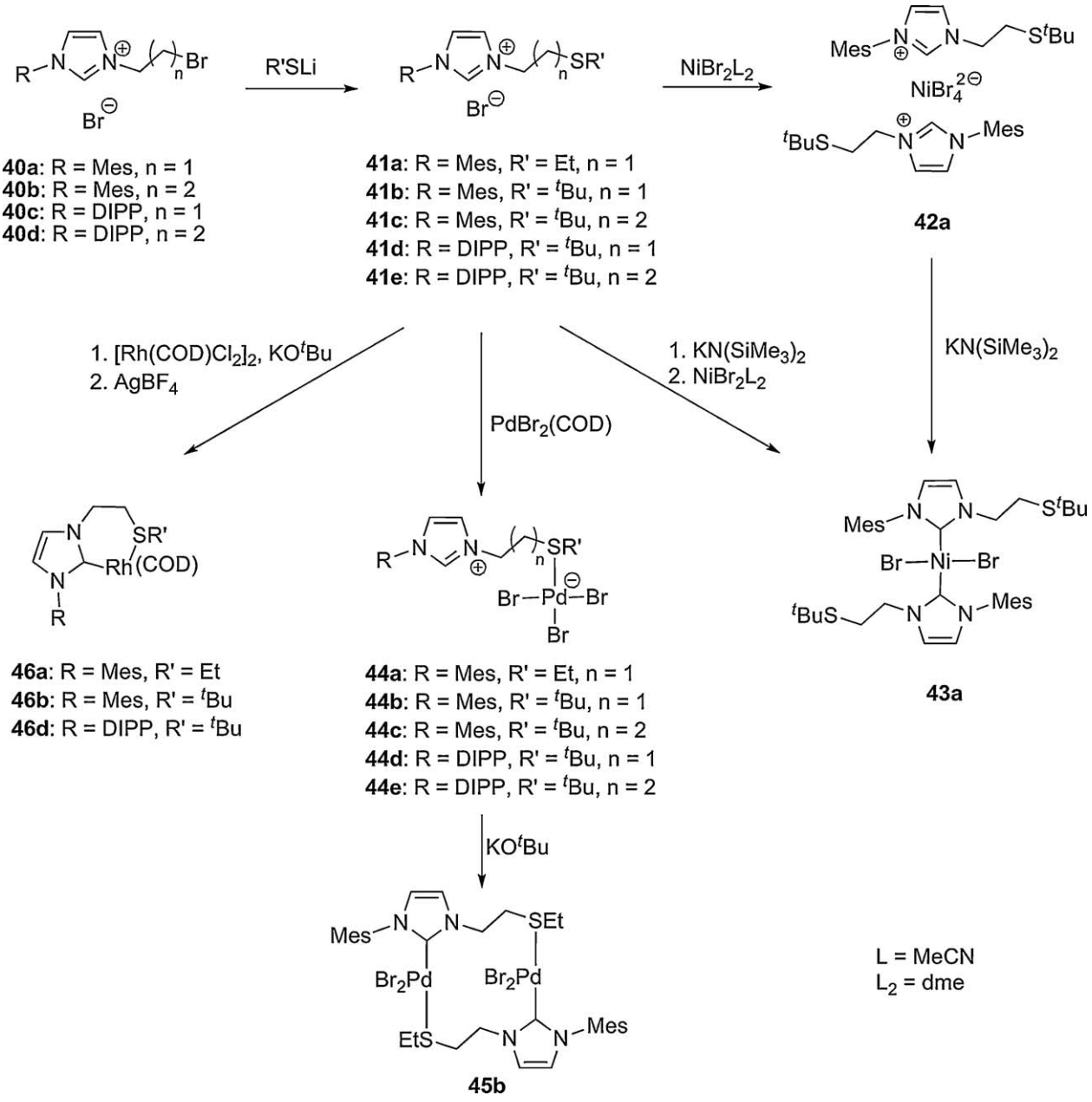
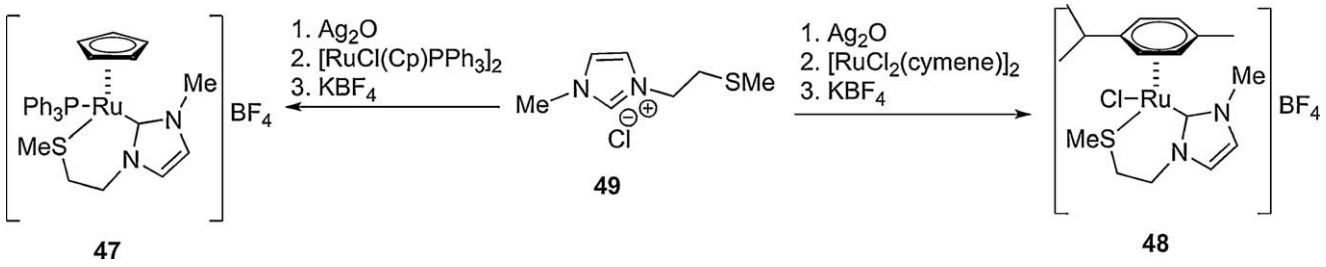
Fig. 6. Hemilability in ruthenium carboxylate complex (**50**) analogous to **47** [33].

tion with gold (I) chlorotetrathiophene complex produces the chelated S–NHC palladium complex **38a**, confirmed by X-ray structure analysis. This step is evidence for hemilability as the reaction, monitored by ^{31}P NMR spectroscopy, is fully reversible and **37a** is regenerated by addition of triphenylphosphine. Alternatively, **38a** can be synthesized directly from the silver complex **36a** by reaction with one equivalent dibenzisonitriledichloro palladium. Addition of one half equivalent of dibenzisonitriledichloro palladium produces the *bis*-(S–NHC) Pd complex **39a** in *trans*-configuration. Thioether coordination was not observed in **39a** as confirmed by X-ray crystallography. Complexes **37a** and **38a** exhibit C–C cross-coupling activity in the Suzuki–Miyaura reaction of *para*-bromotoluene with phenyl boronic acid in 78% and 80% conversion using the reaction conditions reported by Nolan and co-workers [58]. The reactivity of the complexes is enhanced in DMSO solvent due to a better solubility of the complexes.

Labande and co-workers [35] reported the formation of alkyl tethered thioether NHC compounds containing nickel, palladium and rhodium centres. The thioether imidazolium salts (**41a**–**e**) were obtained by nucleophilic substitution of alkyl bromide tethered (2-bromoethyl) and (3-bromo-*n*-propyl) mesityl and 2,6-diisopropylphenyl imidazolium salts (**40a**–**d**) with ethylthiolate and *t*-butylthiolate as outlined in Scheme 9. Reaction of **41a** with nickel(II) bromide did not yield the *bis*-(S–NHC) nickel complex



Scheme 9. Synthesis and reactions of alkyl-tethered thioether S–NHCs [35].



Scheme 10. Ruthenium complexes containing bidentate S–NHC [33].

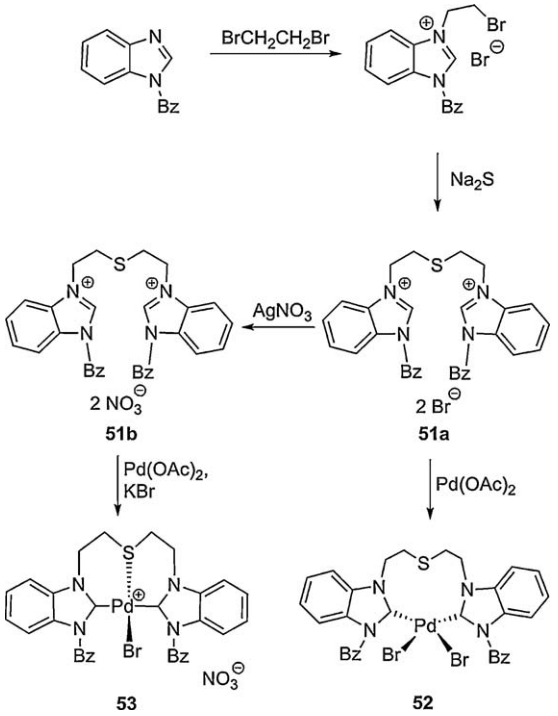
but rather the tetrabromonickelate salt with two imidazolium ions (**40a**) as the counter cations. In order to increase the basicity of the reaction solution for the deprotonation of the α-hydrogen of **40a**, addition of base, such as potassium *t*-butoxide or potassium *bis*(trimethylsilyl)amide, deprotonated the imidazolium salt and formed the *trans* dibromonickel complex **43a**, which can also be synthesized directly from **41a**. S–Ni coordination was not observed in **43a** presumably due to the steric bulk of the *t*-butyl group. In addition, no sulfur coordination was observed with the smaller ethyl *S*-substituent indicating that the thioether group has a low donor ability towards nickel. In contrast to nickel, palladium does complex to the thioether function but, in absence of base, no NHC–Pd bond is formed. Instead the zwitterionic compounds **44a**–**e** with the imidazolium moiety as the cation are generated. Deprotonation of the α-hydrogen of the imidazolium moiety with potassium *t*-butoxide leads to the formation of a bridging *bis*(S–NHC) ligand to form the dinuclear palladium complex **45a**. In contrast to nickel and palladium, the rhodium(I) chloro COD complex is basic enough and forms bidentate S–NHC ligand mononuclear rhodium chloro complexes **46a**, **b** and **d** independent on the substituents on sulfur and nitrogen (Scheme 9). The rhodium complexes **46a**, **b** and **d** show high activity in the catalytic hydrosilylation reaction of substituted acetophenones to the corresponding secondary alcohols with quantitative yields after a few hours at room temperature [35].

Albrecht and co-workers [33] reported two ruthenium S–NHC bidentate complexes **47** and **48** that were prepared from the imidazolium salt (**49**) as shown in Scheme 10. The analogous ruthenium carboxylate complex (**50**) demonstrated hemilability between R–COO^- and the Ru centre (Fig. 6). The silver complex of **49** is generated by addition of silver oxide and is further reacted with the ruthenium cyclopentadienide triphenylphosphine complex or ruthenium dichloro *para*-cymene dimer. The tetrafluoroborate salts of **47** and **48** were obtained by metathesis reaction using potassium tetrafluoroborate. The ruthenium complexes were characterized spectroscopically and by X-ray crystallography (**47**). The catalytic activity of **47** and **48** was tested with the hydrogenation reaction of styrene to ethyl benzene; both complexes show little activity.

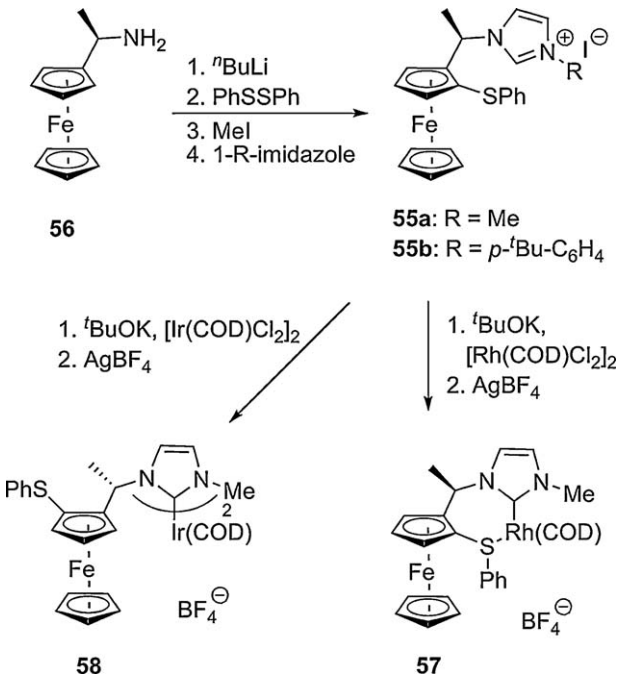
Huynh et al. prepared a tridentate benzimidazolium derived NHC–S–NHC ligand (**51a**, **b**) and reported a counterion dependent palladium complex formation process (**52**, **53**) (Scheme 11) [30]. **51a** is synthesized from 1-benzylbenzimidazole by alkylation with 1,2-dibromoethane followed by a nucleophilic substitution reaction of sodium sulfide. Particularly interesting is the dependency on the nature of the counterion such as coordinating bromide (**51a**) and non-coordinating nitrate (**51b**). The pincer type tridentate palladium complex **53** was generated using palladium acetate in DMSO at 80 °C. **53** has square planar geometry with a *trans* arrangement of the two benzimidazol-2-ylidiene ligands and a Pd-S bond with the thioether bridge. The bromide ligand is opposite of the sulfur ligand and the overall cationic palladium complex has a non-coordinating nitrate anion. However, under the same conditions for the formation of **53**, the neutral *bis*-NHC palladium complex (**52**) with *cis* configuration is formed in the presence of the additional bromide counterion. **52** does not possess any S coordination to the palladium centre as the dialkyl thioether bridge is bent away from the Pd centre [30]. Complexes **52** and **53** demonstrated high catalytic activities in the Mizoroki–Heck reaction in a broad range of aryl bromide substrates with *t*-butyl acrylate. Notably, pincer complex **53** had the highest activity with a TON as high as 180,000 for the reaction of *para*-bromobenzaldehyde and *t*-butyl acrylate [30]. The complexes **52** and **53** are also moderately active towards chloroarene substrates. The formation and the chemistry of the sulfoxide ligand derivative (**54**) by oxidation of the thioether functionality on **51a** by hydrogen peroxide is discussed in the sulfoxide-functionalized NHC (Section 2.3).

2.2.3. Ferrocenyl-tethered thioethers

Chung and co-workers [34] reported the synthesis and chemistry of ferrocenyl tethered thioether imidazolium compounds (**55a**, **b**). **55a**, **b** are synthesized in a two-step synthesis from chiral ferrocenylamine (**56**) by *ortho*-lithiation of the ferrocene with *n*-butyl lithium followed by addition of diphenyl sulfide. This intermediate is transformed to **55a**, **b** by methylation of the amine group with methyl iodide and *N*-substitution of 1-methylimidazole and 1-(*para*-*t*-butylphenyl)imidazole, respectively (Scheme 12). Reac-



Scheme 11. Palladium complexes of benzimidazolium C–S–C pincer ligands **51** [30].



Scheme 12. Rh and Ir complexes containing chiral ferrocenyl thioether NHC ligands [34].

tion with rhodium(I) affords the S–NHC bidentate ligand complex **57** isolated as tetrafluoroborate salt, while the iridium(I) complex **58** does not form the S–NHC bidentate chelating ligand complex, but rather two imidazol-2-ylidiene bound complexes without coordination of the thioether functionality. The structures of both complexes were confirmed by X-ray crystallography. Both complexes, **57** and **58**, were tested in the catalytic hydrogenation of dimethyl itaconate. Iridium complex **58** showed no catalytic reactivity and the rhodium complex **57** demonstrated only minor activity [34].

2.2.4. Chiral ligands with thioether functionality

Chiral compounds (−)-levamisole derived NHC–thiolate complexes **12**–**14** [48–50] and the planar chirality containing ferrocenyl thioether complexes **57** and **58** [34] were described above. Hoveyda's [40] asymmetric aryl sulfonate ligand and silver complex (**84** and **85**) is described under sulfonate functionalized NHCs (Section 2.5).

A suite of chiral thioether functionalized imidazolium and benzimidazolium salts (**59–63**) for asymmetric reactions have been reported by Fernandez (Fig. 7) [37–39]. Generally, the compounds are synthesized from commercially available (2*S*,5*S*)-1-amino-2,5-diphenylpyrrolidine by reaction with formylaminoacetaldehyde and phosphoroxy chloride, forming the imidazole intermediate, followed by a reaction with halo thioether reagents to form optically active S–NHC precursors (**59**–**63**). The corresponding palladium–NHC complexes are obtained by the complexation reaction of palladium allyl centre with the respective silver–NHC complex, and a subsequent transmetallation reaction with palladium allyl chloride. A representative synthesis for allyl palladium complexes (**65d**–**f**) is outlined in Scheme 13 [37]. In all cases, the S–NHC compound binds in a chelating mode to the palladium centre and forms a Pd–S bond, which can exhibit hemilability. The complexes **65d**–**f** show catalytic activity towards the enantioselective allylic substitution of 1,3-diphenylpropenyl acetate and dimethyl malonate with high yields [37]. The enantiomeric ratios ranged between 6% ee to 82% ee with the *S* isomer product in excess [37]. The most active catalyst (**65e**) contained the S–NHC derived from **59e**, a thioether with an ethyl tether providing the most flexibility and least S-donor ability, and thus, the greatest hemilability of the thioether group. Complex **65f**, derived from **59f** with R = cyclohexyl and R′ = isopropyl, imparted the highest ee which was explained by the highly stereogenic palladium centre which is additionally shielded by the cyclohexyl group. In an analogous fashion, ligands **59a**–**c**, **60a**–**c** and **61** were successfully complexed to palladiumallyl centres (**66–68**) and rhodium–COD (**69**) via the Ag–NHC route described above (Fig. 8) [37,38]. Complexes **66** and **67** showed high activities in the enantioselective allylic substitution of 1,3-diphenylpropenyl acetate and dimethyl malonate with ee ranging from 10% to 91% [38]. Complexes **70**–**72** belong to a new class of C_2 symmetric S–NHC–S pincer ligands, derived from imidazolium salts **62** and benzimidazolium salt **63**, of which the silver complexes and one palladium complex (**61**) have been reported (Fig. 9) [39]. The square planar palladium complex **61** contains two thioether pendants which coordinate to the Pd centre and stabilize it while providing hemilability. In addition, the silver complexes **70** and **72** have shown good reactivity in the asymmetric catalytic 1,3-cylcoaddition of *t*-butyl acrylate and iminoesters albeit with poor to moderate ee [39]. The square planar Pd complex with a *cis* arrangement of dichlorides was obtained in quantitative yield by reacting **67a** with $PdCl_2(MeCN)_2$.

2.3. Sulfoxide-tethered NHCs

The most common derivatization of thioether groups is the oxidation to the corresponding sulfoxide. The only reference of an NHC ligand with sulfoxide tether is by Huynh et al. [30] describing the C–S–C pincer-type ligand (**54**) which is obtained by oxidation of the thioether bridged benzimidazolium salt (**51a**) as outlined in Scheme 14. The corresponding palladium complex (**73**) is obtained similarly to the related palladium complex **52** by reaction of **54** with palladium acetate (Scheme 11). **73** does not possess a Pd–S nor Pd–O coordination of the sulfoxide group as the S=O functionality points away from the Pd centre, demonstrated by X-ray crystallography [30]. Similar to **52**, complex **73** showed high catalytic activity in the Mizoroki–Heck reaction of activated bromoarenes with *t*-butyl acrylate. The related chloroarene substrates had moderate yields after 24 h under the same conditions.

2.4. Thiophene-tethered NHCs

Thiophene-tethered 1-(2-thienylmethyl)-3-methylbenzimidazolium bromide (**74**) was synthesized in a two-step synthesis from 2-thiophenemethanol by bromination of the hydroxyl function with phosphorus tribromide followed by *N*-alkylation with 1-methylbenzimidazole [27]. The corresponding palladium bromide complexes (**75**) were synthesized by reaction of palladium acetate with two equivalents of **74** (Scheme 15). The two rotamers, **75a** and **75b**, have the thiophene pendant on the opposite side of the palladium square planar plane, *cis*-anti (**75a**), and on the same side, *cis*-syn (**75b**). The *cis*-anti complex **75a** is obtained in a 3.5 to 1 ratio over **75b** presumably due to steric interactions of the thiophene pendants. The rotameric mixture is readily interconverted at elevated temperature, as measured by ^{1}H NMR spectroscopy, where the thermodynamically favoured *cis*-anti conformer **75a** was formed. The *trans*-isomer of **75** was not observed. The rotameric mixture of **75** showed high activity for the Suzuki–Miyaura reaction in the C–C cross-coupling of activated *para*-substituted bromobenzenes with phenyl boronic acids to biaryls in aqueous solution at room temperature after 8 h. Deactivated *para*-substituted bromobenzene substrates required elevated temperatures to obtain the biaryl products in quantitative yields. **75** is also catalytically active with chloroarene substrates resulting in low yields of 9 and

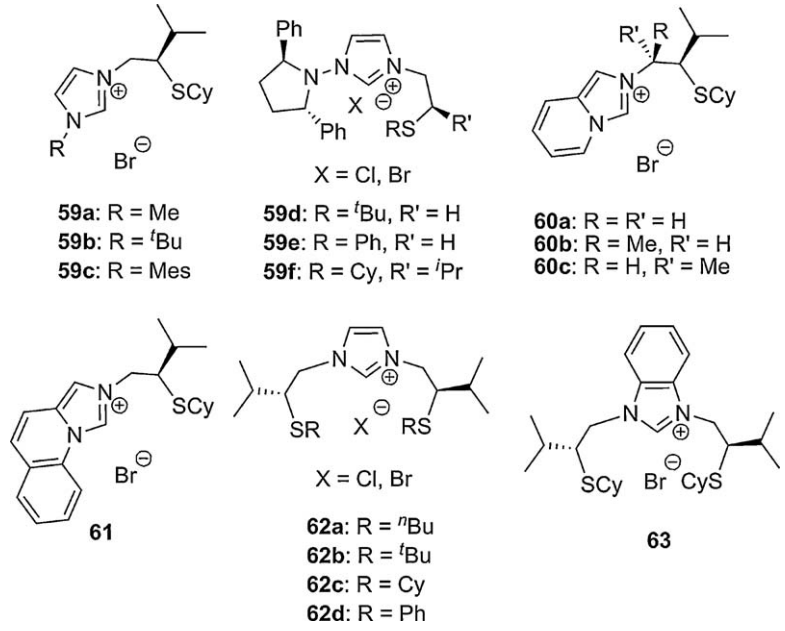
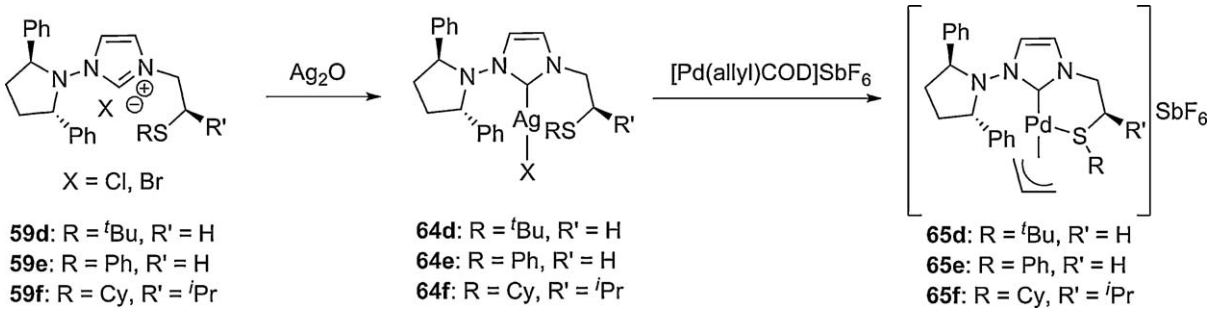


Fig. 7. Overview of chiral S–NHC ligand precursors [37–39].

14% for *para*-chlorobenzaldehyde and *para*-chloroacetophenone after 21 h at 85 °C [27].

McGuinness et al. [31] reported the thiophene-tethered C–S–C pincer ligand (**77**) that was obtained by a copper iodide catalyzed arylation of imidazole with 2,5-diiodothiophene forming the neutral, thiophene bridged intermediate **76** (Scheme 16). **77** was generated by standard *N*-alkylation reaction with isopropyl bromide in refluxing DMF. The corresponding chromium complex **78** was obtained by reaction of the imidazolium salt (**77**) with chromium trichloride *tris*-(tetrahydrofuran) complex (Fig. 10). The related chromium complex **79** is obtained by the reaction with 1-isopropyl-3-thienylimidazolium bromide, which was synthesized from 2-iodothiophene analogously to **77**. **79** is an active ethylene polymerization catalyst. With the addition of cocatalyst methyl aluminum oxide (MAO), 77% polyethylene and 23% oligoethylene is produced with a low TON of 1030. Unfortunately, **78** is not active for ethylene polymerization catalysis. It is hypothesized that the central thiophene group in the pincer ligand of **78** is an effective catalyst poison of the hexacoordinated chromium centre [31].

The thiophene bridged *bis*-imidazolium bromides (**80a**–**c**, Fig. 11), homologous to **77**, were reported by Cavell and co-workers in 2005 [32]. Compounds **80a**–**c** were prepared by nucleophilic sub-



Scheme 13. Synthesis of chiral Pd–(S–NHC) complexes (**65d**–**f**) [37].

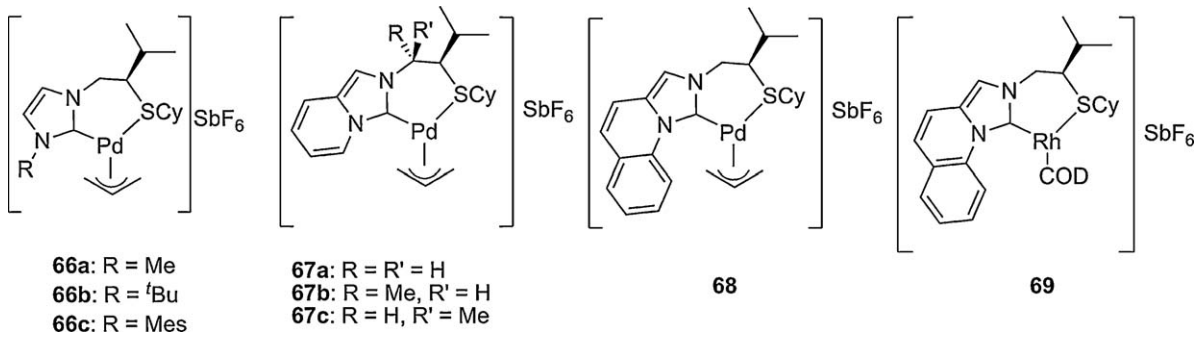
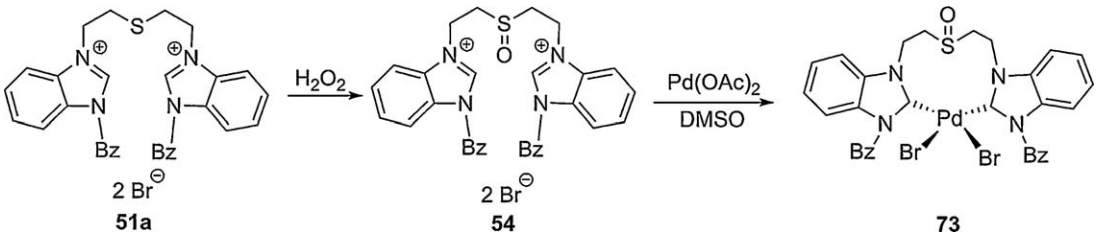
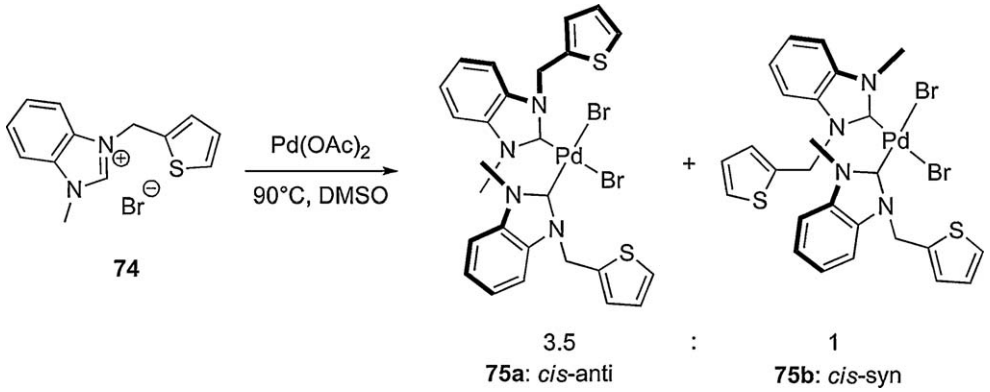


Fig. 8. Chiral Pd and Rh complexes containing chelating S–NHC ligands [37,38].



Scheme 14. Synthesis of sulfoxide-functionalized NHC palladium complex (**73**) [30].



Scheme 15. Rotameric mixture of palladium complexes (**75a**, **b**) with thiophene-tethered NHC ligands [27].

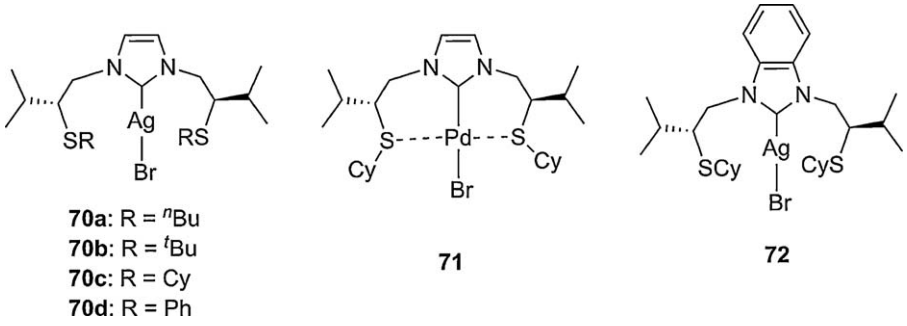
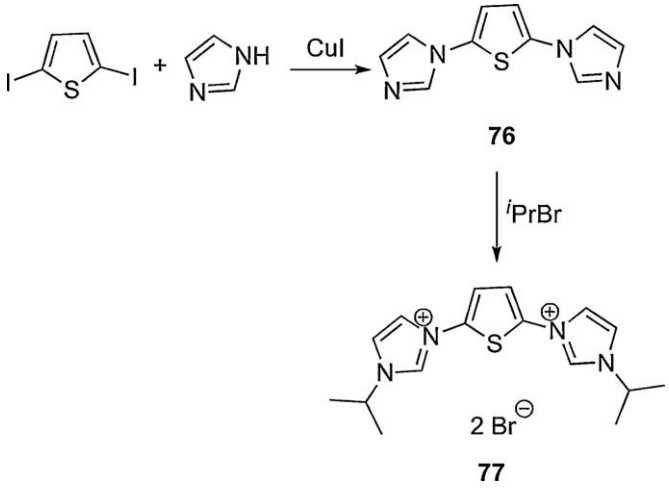


Fig. 9. Chiral silver and palladium complexes with C_2 symmetric S–NHC–S pincer ligands [39].



Scheme 16. Synthesis of thiophene bridged *bis*-imidazolium C–S–C pincer ligand precursor **77** [31].

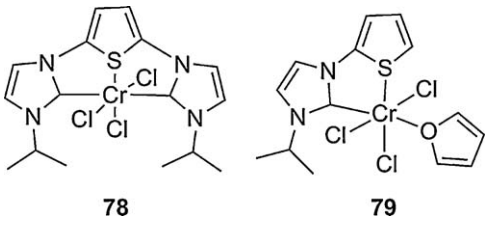


Fig. 10. Chromium complexes with thiophene-tethered NHC ligands [31].

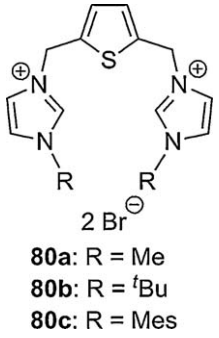
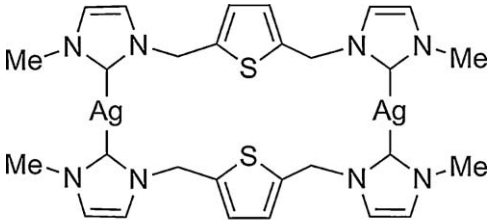


Fig. 11. Thiophene bridged *bis*-imidazolium NHC ligands [32].



81

Fig. 12. Thiophene-functionalized Ag–NHC dimer **81** [32].

stitution of 2,5-*bis*-(bromomethyl)thiophene with two equivalents of the respective 1-methyl-, 1-*tert*-butyl- and 1-mesityl-imidazole reagent in moderate to high yields. Reaction of **80** with silver oxide in dichloromethane–methanol solvent precipitates highly insoluble silver complexes, characterized by mass spectrometry and ^{1}H NMR. Treatment of this silver complex with silver tetrafluoroborate produces a *bis*-silver bridged complex dimer (**81**), obtained for the *N*-methyl ligand (**80a**), which possesses a zig-zag conformation as shown in Fig. 12. The imidazolium S–NHC precursors **80a–c** were tested as ligands with Pd(dba)$_2$ in the presence of potassium *t*-butoxide for the catalytic aryl amination of *para*-bromotoluene with morpholine as a benchmark reaction but showed poor catalytic activity. The palladium complexes with ligands **80a–c** were not isolated.

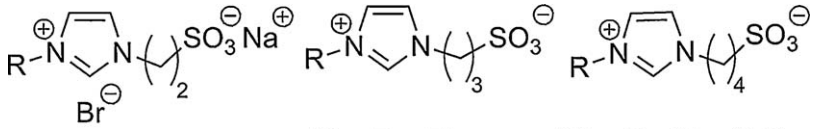
2.5. Sulfonate-tethered NHCs

A limited number of alkyl sulfonate-tethered imidazolium and imidazolinium salts (Fig. 13) have been reported in the literature despite the fact that the first sulfonate-tethered imidazolium salts (**82**, **84a** and **86**) were reported by Herrmann et al. [59] as early as 1996. Sulfonate groups can only coordinate to a metal via a terminal oxygen donor and therefore do not form a S-metal bond. Nevertheless, sulfonates are classified as a sulfur functional group and are reviewed herein due to their inherent properties they add to the NHC. These imidazolium salts are mainly employed as ionic liquids. The functionalization with sulfonate groups has the advantage of providing an anionic group within the ionic liquid generating a zwitterion that does not require a separate anionic counterion. The sulfonate groups are alkyl sulfonate groups with various tether lengths, mainly ethylene, 1,3-propylene and 1,4-butylene bridged systems (Fig. 13). The synthesis of these sulfonate tethered groups with C3 and C4 bridge is conveniently conducted in high yields by ring opening reaction of 1,3-propane sultone (**87**)and 1,4-butane sultone (**88**), respectively, with imidazole at high temperatures resulting (Scheme 17) [36,59–61]; alternatively, a haloalkyl sulfonate can be used as *N*-alkylation agent [59]. Disubstituted sulfonated tethered groups at both *N*-termini (**86**) have also been reported [59].

The imidazolinium sulfonate zwitterion (**85**) and triflate imidazolium salt (**84c**) have been successfully employed by Davis and co-workers [62] as Brønsted acid catalysts and ionic liquid medium solvent for Fisher esterifications, alcohol dehydrodimerizations and pinacol/benzopinacole rearrangement reactions. The *n*-butyl imidazole (**83b**) has been used as ionic zwitterionic liquid for anhydrous proton transport studies [63]. Ethyl and vinyl analogs (**83a**, **c**) have been successfully incorporated in polymers and used as ionic liquids [64].

The sulfonate-tethered imidazolium and imidazolinium salts (**82–86**) can be used as ionic liquids. In addition, anionic functional groups tethered to organic compounds solubilize hydrophobic ligands and allows the use of the respective metal complexes as catalysts in aqueous solutions. Shaughnessy and co-workers [60] reported the silver (**89–91**) and palladium (**92**) alkyl sulfonate containing NHC complexes where the alkyl sulfonate groups increase solubility in water (Fig. 14) so that the respective Pd and Rh complexes can be used for potential catalytic transformations in aqueous conditions. The silver complexes (**89**, **90**) were synthesized with ligand precursors **83b**, **d** and **e** using the silver oxide route. **89** is unstable, particularly when exposed to light, and a Ag mirror precipitates out as the complex decomposes. Palladium iodide complex (**92**), which has a *trans* configuration, has been made by the direct reaction of the imidazolium compound **83d** with palladium acetate with potassium *t*-butoxide and sodium iodide in low yield [60].

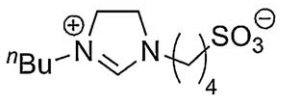
Gebbink and co-workers [36] published the synthesis and characterization of the anionic alkyl sulfonate tethered imidazolium compound **84c** via the 1,4-butane sultone route. **84c** was then reacted with silver oxide forming the homoleptic (NHC)$_2$–Ag$_2$ complex, **91**, in which one silver ion is complexed linearly by the two NHC functional groups and the neutral charge is balanced by a second silver ion. A coordination of the sulfonate groups to the Ag centre was not observed. **91** was then used in the transmetallation reaction with AuCl(thp)$_4$ and [RhCl(COD)]$_2$ in the presence of PPh$_4$Cl or *n*-Bu$_4$NCl as the chloride sources forming **93** and **94**, respectively, in high yields (Fig. 14). The gold and rhodium



82a: R = Me
82b: R = ^{n}Bu

83a: R = Et
83b: R = ^{n}Bu
83c: R = vinyl
83d: R = Mes
83e: R = DIPP

84a: R = Me; NaBr
84b: R = ^{n}Bu; HOTf
84c: R = Mes



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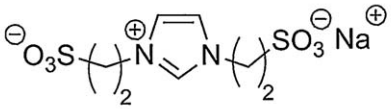

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Fig. 13. Overview of sulfonate-functionalized imidazolium and imidazolinium compounds [36,59–61,63].

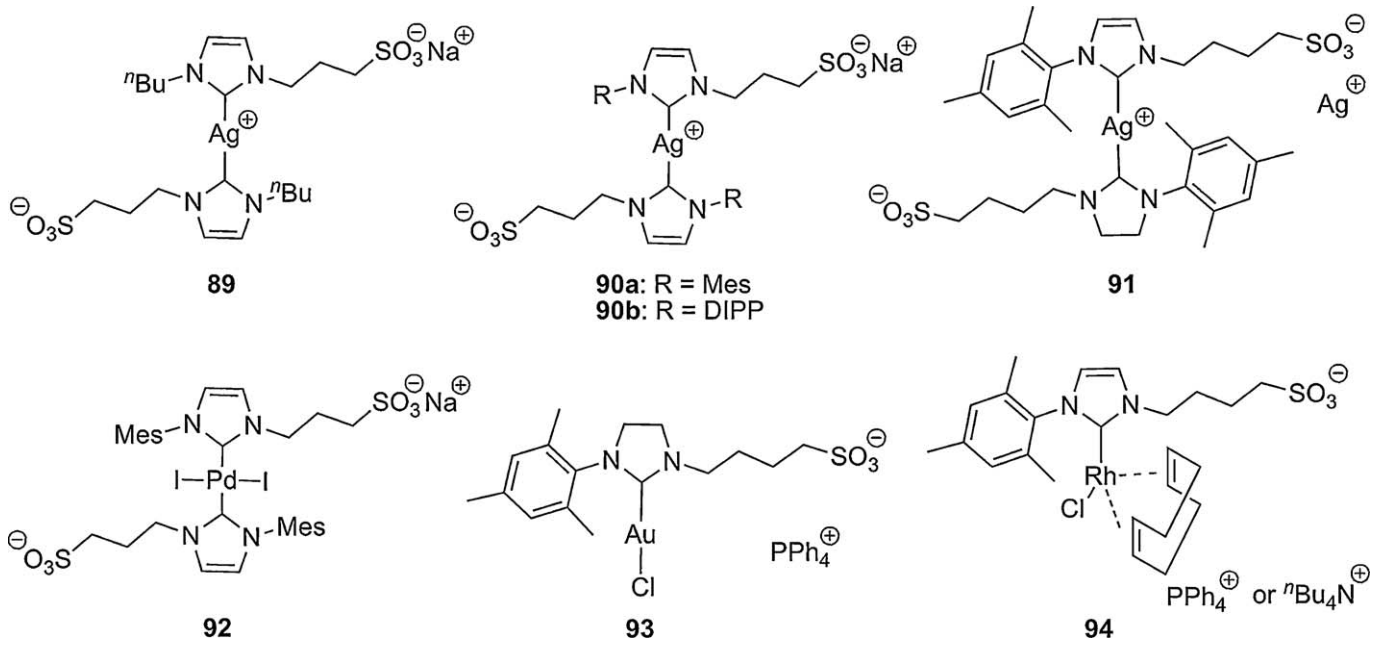
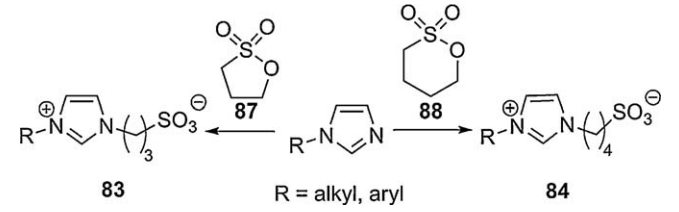


Fig. 14. Sulfonate-tethered NHC complexes with silver (I), gold (I) and rhodium (I) centres [36,60].

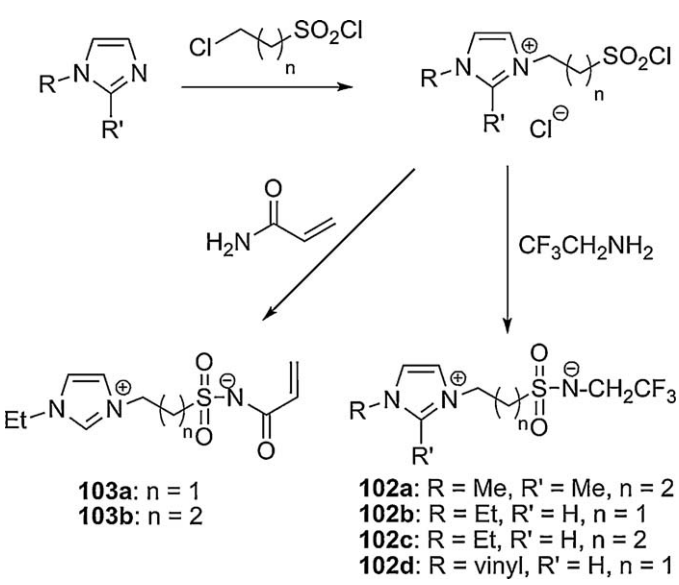
complexes (**93**, **94**) were successfully incorporated and immobilized in non-covalent bonding in a dentritic framework containing cationic ammonium groups. These dentritic metal complexes contain eight gold or rhodium centres each and were characterized by NMR spectroscopy and mass spectrometry. The rhodium complex (**94**) and the rhodium immobilized dentrimer show catalytic activity in the hydrosilylation of cyclohexanone with diphenylsilane. The dentrimer has a slightly smaller activity compared to the non-immobilized rhodium complex (**94**).

Santini and co-workers [61] reported the water-soluble dimeric silver–NHC complexes (**95**) (Fig. 15). The *bis*-1,2,4-trialzolium (**96a**) and *bis*-imidazolium (**96b**) based ligands have a butyl sulfonate tether and were obtained by the *N*-alkylation of the *bis*-(1,2,4-triazoly-1-yl)methane and *bis*-(imidazole-1-yl)methane with 1,3-propane sultone. **96a** and **96b** form the silver complexes (**95a**, **b**) as water-soluble complexes for potential transmetalation reactions (Fig. 15).

Plenio and co-workers [28] reported aryl sulfonate pendant imidazolinium (**97**) and imidazolium (**98**) ligands for the palladium catalyzed Suzuki–Miyaura reaction in aqueous medium (Fig. 16). The ligands **97** and **98** were tested in the chloroarene C–C cross-coupling reactions with *para*-tolylboronic acid and Na_2PdCl_4



Scheme 17. Synthesis of C3 and C4 tethered sulfonate-functionalized imidazolium salts using sultones [36,60,61].



Scheme 18. Synthesis of sulfonamide-tethered imidazolium compounds [64].

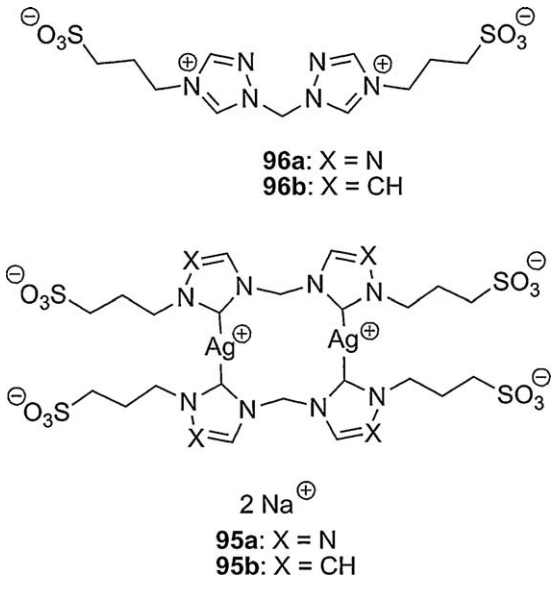
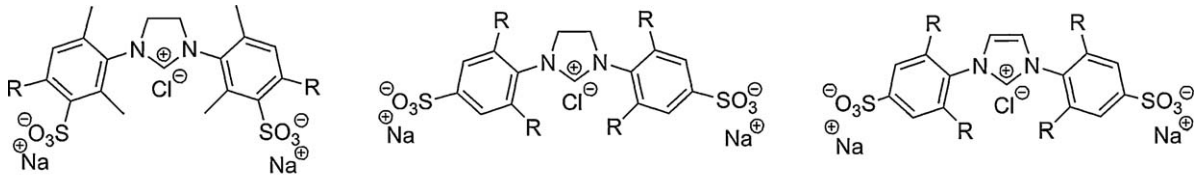
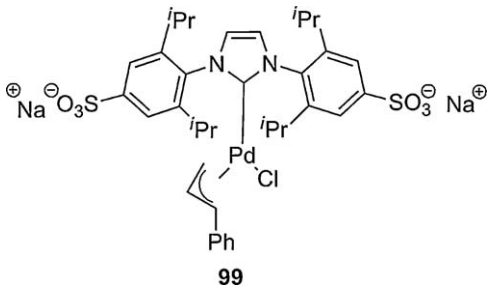


Fig. 15. Sulfonated *bis*-triazolium (**96a**) and *bis*-imidazolium (**96b**) compounds and the related dimeric silver complexes [61].



97a: R = H
97b: R = Me
97c: R = Me
97d: R = ^{i}Pr
98a: R = Me
98b: R = ^{i}Pr

Fig. 16. Imidazolinium (**97**) and imidazolium (**98**) NHCs with aryl sulfonates [28,29].

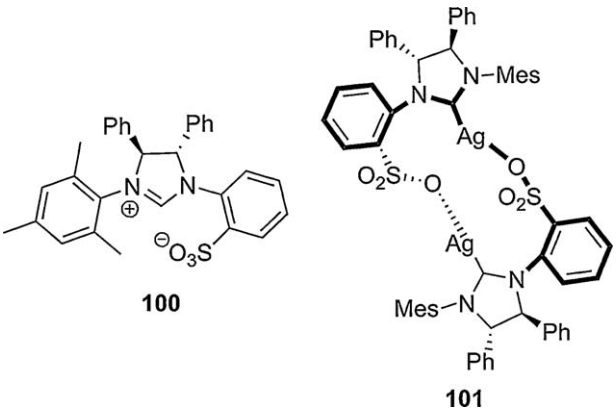


99

Fig. 17. Isolated aryl sulfonate-functionalized NHC–Pd complex **99** [29].

showing outstanding activation of chloroarenes in moderate to high conversions to the biaryl products [28]. It was found that the 2,6-subsituted isopropyl derivatives were more reactive than the methyl analogs. The palladium catalyst was prepared first *in situ* and later isolated as the allylic palladium complex **99** shown in Fig. 17 [29]. Ligands **97**and **98** were loaded with palladium and used successfully for copper free Sonogashira coupling reactions. The isolated Pd complex **99** was also an effective catalyst for aqueous Suzuki–Miyaura reactions and Sonogashira reactions of *N*- and *S*-heterocyclic aryl bromides and chlorides with aryl- and alkylacetylenes [29].

Chiral NHC ligand precursor **100** is a variation of a sulfonated aryl tether and was used to form the chiral, dimeric silver complex (**101**, Fig. 18) [40]. **101** was successfully employed as catalyst

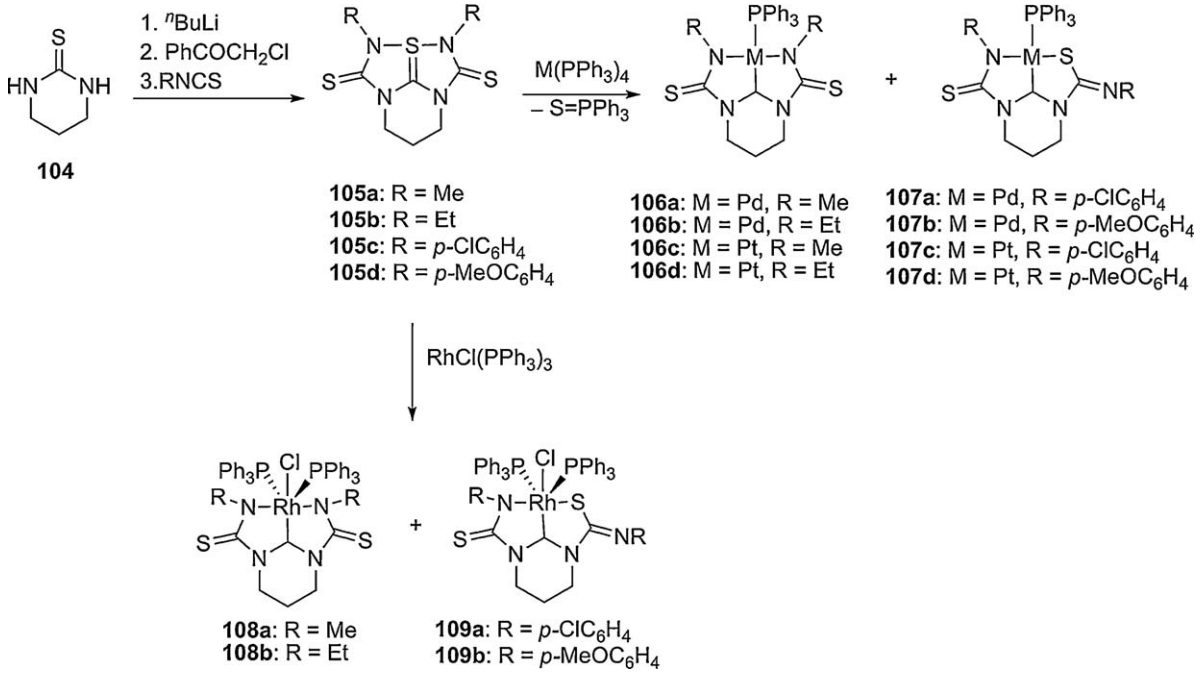


100

101

Fig. 18. Chiral aryl sulfonate imidazolinium compound (**100**) and dimeric Ag complex (**101**) [40].

precursor in the enantioselective catalyzed conjugate additions of γ-keto esters to form chiral all-carbon quaternary centres. **101** performed exceptionally well with Cu and Zn promoted asymmetric conjugate additions. The imidazolinium compound **100** was synthesized in a five-step synthesis from 2-bromobenzenesulfonyl chloride. It is noteworthy that in the silver complex catalyst precursor (**101**) the sulfonate coordinates with a second silver metal, forming a dimeric compound. This is due to the *ortho*-position of the sulfonate group in the benzene ring, as other aryl sulfonate tethers



104

105a: R = Me
105b: R = Et
105c: R = *p*-ClC$_6$H$_4$
105d: R = *p*-MeOC$_6$H$_4$

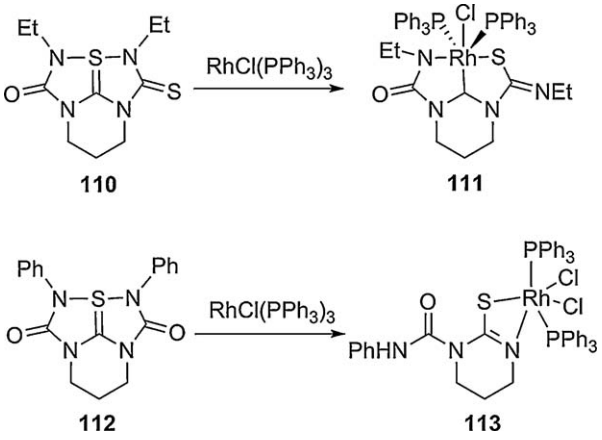
106a: M = Pd, R = Me
106b: M = Pd, R = Et
106c: M = Pt, R = Me
106d: M = Pt, R = Et

107a: M = Pd, R = *p*-ClC$_6$H$_4$
107b: M = Pd, R = *p*-MeOC$_6$H$_4$
107c: M = Pt, R = *p*-ClC$_6$H$_4$
107d: M = Pt, R = *p*-MeOC$_6$H$_4$

108a: R = Me
108b: R = Et

109a: R = *p*-ClC$_6$H$_4$
109b: R = *p*-MeOC$_6$H$_4$

Scheme 19. Sulfurane compounds and their metal complexes (**106**–**109**) [70–72].



Scheme 20. Monooxo (**110**) and dioxo (**112**) ligand analogs of **105** and their rhodium complexes [66].

typically have the sulfonate group in the *meta*- or *para*-position (**97** and **98**).

2.6. Sulfonamide-tethered NHCs

Ohno and co-workers [64] reported the synthesis of sulfonamide-tethered imidazolium zwitterions **102** and **103**. The sulfonamide compounds were synthesized in a two step synthesis from commercially available imidazole compounds, 1-methlyimidazole, 1-ethylimidazole and 1-vinylimidazole by *N*-alkylation reaction with chloro 1-ethanesulfonylchloride and chloro 3-propanesulfonyl chloride (Scheme 18). The sulfonyl chloride functionalities are then reacted with amines or amide to the sulfonamide products. Compounds **102** and **103** have been successfully used in the application of ionic liquids and as monomers for ionic polymers (**103**) [64].

2.7. Tetraazapentalene-based S–NHC compounds

Matsumura and co-workers [65–69] reported the formation of a completely unique sulfur NHC compound; a pincer-type tetrahydropyrimidine-based NHC (**106**–**109**) synthesized via a metallation reaction of 10-S-3 tetraazapentalene **105** through treatment of palladium(0) and platinum(0) triphenylphosphine complexes that can form symmetric S–C–S pincer complexes **106a**–**d** with small alkyl groups (methyl and ethyl) and the asymmetric N–C–S isomers **107a**–**d** [66] where the R groups are aryl (Scheme 19). The same is observed with the formation of the hexacoordinated rhodium complexes **108a**, **b** and **109a**, **b** [67]. The rhodium complex of the monooxo ligand analog (**110**) affords the S–C–N complex **111** while the dioxo ligand derivative (**112**) does not produce the S–NHC carbene complex and instead, an octahedral rhodium complex with N,S bidentate ligand coordination **113** is isolated, as shown in Scheme 20 [66]. The ligands **110** and **112** are synthesized analogously to the ligand **105a**–**d**, but with addition of isocyanates instead of isothiocyanates [66]. The ligand **110** is readily synthesized from cyclic thiourea **104** by deprotonation with two equivalents of *n*-butyl lithium, addition of phenacyl chloride and reaction with thioisocyanate [70–72].

3. Conclusion

Sulfur-functionalized *N*-heterocyclic compounds belong to a new, expanding field of ligands for applications in transition metal chemistry and catalysis. Surprisingly, to date only a few fundamental S–NHCs and their transition metal complexes have been reported. The donor functionalization with various sulfur functionalities opens promising new research directions for hybrid NHCs. The benefit of the S–NHCs is based on the chemical properties of the respective transition metal complexes, in particular the hemilability of sulfur compounds, as well as their easy modifications for tune-ability of the catalytic process applications.

Acknowledgments

The authors gratefully thank the Natural Science and Engineering Research Council of Canada (NSERC), Canada Foundation of Innovation (CFI), Nova Scotia Research and Innovation Trust Fund (NSRIT) and Cape Breton University for financial support.

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