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REVIEW PAPER

Recent Advances in Small Clusters and Polymetallic Assemblies Based on Transition Metals and Dithiocarboxylate Zwitterions Derived from *N*-Heterocyclic Carbenes

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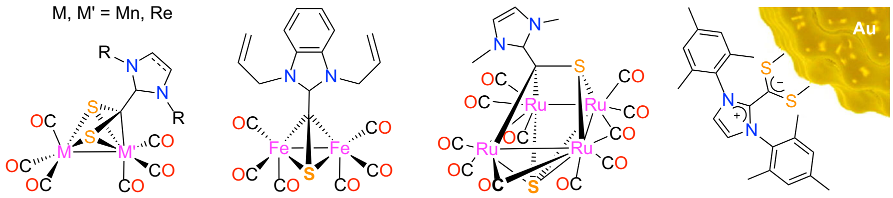
Abstract *N*-Heterocyclic carbenes (NHCs) react readily with carbon disulfide to form stable, crystalline, zwitterionic adducts. In this review, we outline the various strategies that were applied to synthesize transition metal clusters based on such NHC·CS_2 ligands. We also briefly survey their most salient structural features and catalytic properties. Because this research field is still in its infancy, only a limited number of structures containing metals from Group 7 (Mn and Re) and 8 (Fe and Ru) have been described so far. Homo- and heterobimetallic manganese and rhenium carbonyl clusters with the generic formula $[MM'(CO)_6(\mu\text{-}\kappa^2\text{-}S,S'\text{-}\kappa^3\text{-}S,C,S'\text{-}S_2C{\cdot}NHC)]$ ($MM' = Mn_2$, MnRe, or Re_2) were most thoroughly investigated. Isolated examples of dinuclear iron and tetranuclear ruthenium compounds, in which the dithiocarboxylate unit underwent fragmentation, were also reported. Other related polymetallic entities recently elaborated through the use of azolium-2-dithiocarboxylate zwitterions and Group 11 metals (Cu and Au) include copper-based coordination polymers, gold nanoparticles, and self-assembled monolayers.

Graphical Abstract



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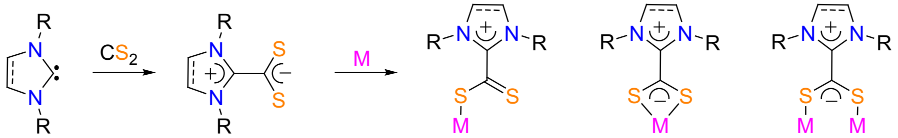
Keywords Carbonyl compounds · Coordination chemistry · Group 7 metals · Group 8 metals · Group 11 metals · Nanoparticles

Introduction

Since their discovery by Arduengo in 1991 [1, 2], *N*-heterocyclic carbenes (NHCs) have been embraced worldwide by organic and organometallic chemists who have taken advantage of these highly tunable, stable, divalent carbon species to develop countless applications in molecular science and catalysis [3]. Indeed, over the past 25 years, NHCs have emerged as powerful nucleophilic organocatalysts for fine organic synthesis [4] and polymer chemistry [5, 6]. They also behave as strong σ-donating and moderate π-accepting ligands toward the whole spectrum of metals, whether these elements belong to the main groups [7, 8], the transition families [8–13], or the lanthanides and actinides [14]. Although most of the complexes investigated so far are monometallic species, several examples of metal clusters featuring NHC ligands have been reported in the literature [15–20]. In particular, transition metal carbonyl clusters (mostly those of ruthenium and osmium) have attracted a great deal of attention [21].

Due to their high nucleophilicity, NHCs react readily with a wide range of neutral electrophiles to afford either ylide or zwitterionic products [22]. Among the various allenes and heteroallenes that have already been employed as substrates for these reactions, carbon disulfide is probably the most promising candidate to generate new ligand systems. Indeed, azolium-2-dithiocarboxylate betaines are non-labile, crystalline adducts [23] that form strong M–S bonds and can exhibit various binding modes (Scheme 1). Compared to other 1,1-dithiolate ligands, such as dithiocarbamate ($R_2NCS_2^-$) [24] and xanthate anions ($ROCS_2^-$) [25], or trialkylphosphonium-dithiocarboxylate zwitterions ($R_3P^+CS_2^-$) [26], whose coordination chemistry has been extensively studied for many years, the NHC·CS_2 inner salts have received much less attention thus far. Early work in this field dates back to the 1980s when Borer et al. [27, 28] showed that 1,3-dimethylimidazolium-2-dithiocarboxylate (IMe·CS_2) formed stable, albeit poorly characterized, complexes with a range of transition metal halides or nitrates. It was not until 2009 that the molecular structure of a monometallic ruthenium–arene complex featuring a NHC·CS_2 chelate was firmly established by Delaude and coworkers using X-ray diffraction analysis [29]. Following these seminal contributions, other ruthenium(II), osmium(II), and palladium(II) compounds were obtained, in which the κ^2-*S,S′* chelating mode of the dithiocarboxylate moiety was further evidenced [30–32].



Scheme 1 Formation of NHC·CS_2 zwitterions and some of their known binding modes to metal centers

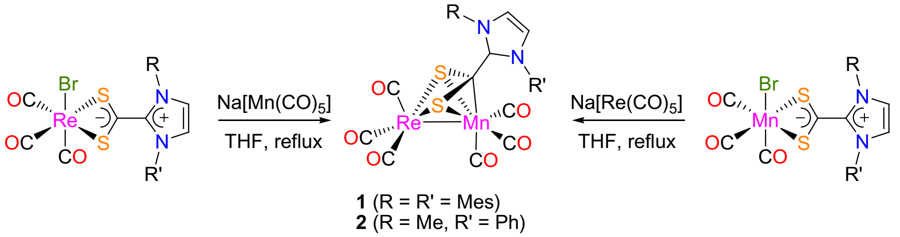
Contrastingly, recourse to various gold(I) precursors afforded either monometallic products featuring a κ^1-*S* binding mode or bimetallic compounds with a μ_2-κ^1-*S*,κ^1-*S*′ bridging unit [33].

Within the last few years, the coordination chemistry of dithiocarboxylate ligands derived from NHCs has been successfully extended to the preparation of small metal clusters. Although this research is still in its infancy and only a handful of reports are available to date, significant advances that came to light recently encouraged us to highlight the main achievements already accomplished in this largely uncharted territory. Thus, in this short review, we present the various strategies that were applied to synthesize transition metal clusters based on NHC·CS_2 ligands, and we briefly discuss the most salient structural features and catalytic properties of these compounds. To the best of our knowledge, only clusters containing metals from Group 7 (Mn and Re) and 8 (Fe and Ru) were investigated so far. They are surveyed in the two following sections. Other related polymetallic entities recently elaborated through the use of azolium-2-dithiocarboxylate zwitterions include nanoparticles, monolayers, and coordination polymers derived from Group 11 metals (Cu and Au). These applications are summarized in a third section.

Manganese and Rhenium Clusters

In 2014, Liu, Li, and coworkers isolated and characterized two heterobimetallic carbonyl clusters with the generic formula [MnRe(CO)$_6$(μ-κ^2-*S*,*S*′-κ^3-*S*,*C*,*S*′-S_2C·NHC)], in which an imidazolium-2-dithiocarboxylate unit acted as a chelate toward the rhenium center and as a pseudoallylic ligand toward the manganese atom [34]. Compounds **1** and **2** were obtained by reacting monometallic precursors of the type [MBr(CO)$_3$(κ^2-*S*,*S*′-S_2C·NHC)] (M = Mn or Re) with either sodium pentacarbonylrhenate or manganate in dry tetrahydrofuran (THF) at reflux temperature (Scheme 2). Their solid-state structures were determined by using X-ray crystallography. It is noteworthy that the isomers that would result from the coordination of the central carbon atom of CS_2^- to rhenium instead of manganese were not detected.

Complex **1** was further reacted with Li[BHEt$_3$] and CH_3I to afford the hydrido-bridged derivative [MnRe(CO)$_6$(μ-H){μ-κ^2-*S*,*S*′-κ^2-*C*,*S*′-CH_3SC(S)·IMes}] (**3**) [34]. This transformation most likely involved the intermediacy of an anionic



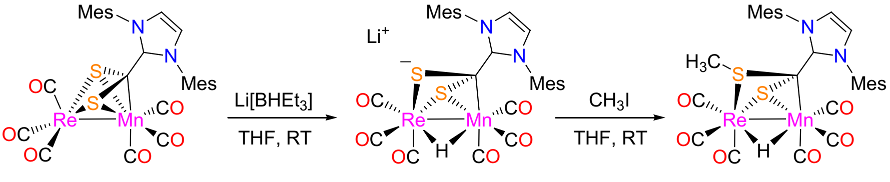
Scheme 2 Synthesis of heterobimetallic Mn/Re carbonyl clusters **1** and **2**

hydridocarbonyl species, which was readily alkylated with iodomethane to afford the final neutral product (Scheme 3). Complex **3** was fully characterized using various analytical techniques and its X-ray crystal structure was solved. Cyclic voltammetry experiments showed that this compound could catalyze the electrochemical reduction of acidic protons into dihydrogen, and might therefore serve as a model for the active site of [FeFe] hydrogenases [35–37].

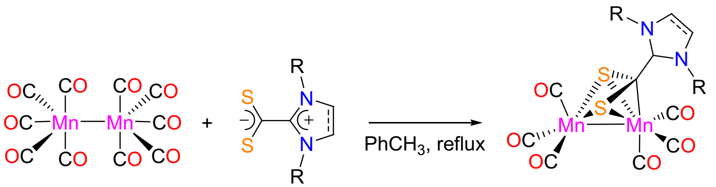
In 2016, Delaude et al. [38] elected a set of five representative imidazolium- and imidazolinium-2-dithiocarboxylate zwitterions to thoroughly investigate the coordination chemistry of these ligands with Group 7 metal–carbonyl sources. In a first series of experiments, the NHC·CS$_2$ betaines were reacted with an equimolar amount of [Mn$_2$(CO)$_{10}$] to afford homobimetallic clusters of general formula [Mn$_2$(CO)$_6$(μ-κ^2-*S*,*S*′-κ^3-*S*,*C*,*S*′-S$_2$C·NHC)]. Preparation of the dimanganese complexes **4**–**6** starting from aromatic imidazolium inner salts bearing cyclohexyl (ICy·CS$_2$), mesityl (IMes·CS$_2$), or 2,6-diisopropylphenyl substituents on their nitrogen atoms (IDip·CS$_2$) required 1 h of reaction in refluxing toluene. Under the same experimental conditions, it took 4 h to achieve the full coordination of imidazolinium-based ligands SIMes·CS$_2$ and SIDip·CS$_2$ onto products **7** and **8** (Scheme 4).

As an alternative to the one-step procedure outlined in Scheme 4, Delaude et al. [38] also investigated the assembly of higher nuclearity materials from mononuclear manganese building blocks. They showed that [MnBr(CO)$_3$(S$_2$C·IMes)] and [MnBr(CO)$_3$(S$_2$C·IDip)] reacted with Na[Mn(CO)$_5$] generated in situ by treating [Mn$_2$(CO)$_{10}$] with an excess of sodium amalgam in dry THF to afford the binuclear hexacarbonyl complexes **5** and **6** in moderate yields (Scheme 5). The overall transformation can be viewed as a nucleophilic substitution of Br$^-$ by [Mn(CO)$_5$]$^-$ accompanied by the formation of a metal–metal bond. Such a coupling process involves the comproportionation of Mn(+I) and Mn(−I) precursors into two Mn(0) centers. From a practical point of view, it should be pointed out that this multistep synthetic route required more time, reagents, and solvents, and afforded less pure products than the direct reaction of [Mn$_2$(CO)$_{10}$] with NHC·CS$_2$ ligands.

The molecular structures of complexes **4**, **6**, **7**, and **8** were determined by X-ray crystallography [38]. In each cluster, the two manganese atoms were unsymmetrically bridged by the CS$_2$ moiety of the imidazol(in)ium-2-dithiocarboxylate ligand, which was bonded through each sulfur atom to both metallic centers, while its central carbon atom was linked to only one of them. In addition, the Mn–Mn distances were consistent with the presence of single intermetallic bonds. Further

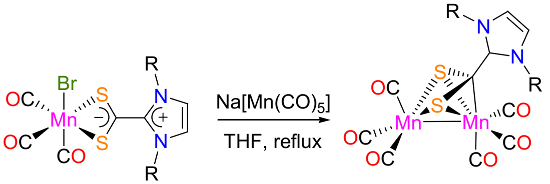


Scheme 3 Synthesis of heterobimetallic Mn/Re hydridocarbonyl cluster **3**



4 (NHC = ICy)
5 (NHC = IMes)
6 (NHC = IDip)
7 (NHC = SIMes)
8 (NHC = SIDip)

Scheme 4 Direct synthesis of homobimetallic manganese carbonyl clusters **4–8**



5 (R = Mes)
6 (R = Dip)

Scheme 5 Indirect synthesis of homobimetallic manganese carbonyl clusters **5** and **6**

evidence of a κ^3-*S*,*C*,*S′* coordination mode for the dithiocarboxylate unit came from ^{13}C NMR spectroscopy, which showed a dramatic shielding of the CS$_2$ carbon nucleus when the free NHC·CS$_2$ ligands or their monometallic chelates were converted into bimetallic clusters (Table 1).

In 2016, Delaude and coworkers extended their research on binuclear manganese clusters to the dirhenium analogues [39]. Substitution of [Re$_2$(CO)$_{10}$] for [Mn$_2$(CO)$_{10}$] in the direct reaction path presented in Scheme 4 did not lead to satisfactory results. In this case, the indirect route involving the comproportionation of monometallic Re(+I) and Re(−I) carbonyl compounds into a single Re(0) homobimetallic product turned out to be more widely applicable and more efficient. Thus, five representative [ReBr(CO)$_3$(S$_2$C·NHC)] complexes were reacted with the pentacarbonylrhenate anion generated in situ by reducing [Re$_2$(CO)$_{10}$] with an excess of sodium amalgam. The two steps were initially performed in dry THF at room temperature (Scheme 6). Under these conditions, chelated precursors featuring the imidazolium-based ligands ICy·CS$_2$, IMes·CS$_2$, and IDip·CS$_2$ cleanly reacted to afford dinuclear octacarbonyl complexes [Re$_2$(CO)$_8$(μ-κ^1-*S*,κ^1-*S′*-S$_2$C·NHC)] (**9–11**) in moderate to satisfactory yields. Heating a suspension of [Re$_2$(CO)$_8$(S$_2$C·IMes)] (**10**) or [Re$_2$(CO)$_8$(S$_2$C·IDip)] (**11**) in petroleum ether (PE) at 130 °C afforded the corresponding [Re$_2$(CO)$_6$(μ-κ^2-*S*,*S′*-κ^3-*S*,*C*,*S′*-S$_2$C·NHC)] clusters **12** and **13** in good yields. Under identical conditions, [Re$_2$(CO)$_8$(S$_2$C·ICy)] (**9**) decomposed into unidentified products. Attempts to minimize unwanted thermal degradation by performing its decarbonylation in THF at 60 °C were not successful.

When monometallic chelates possessing imidazolinium pendant groups served as starting materials, reactions with Na[Re(CO)$_5$] carried out in THF at room temperature led to complex mixtures of products, most likely because partial decarbonylation had already taken place in addition to comproportionation [39]. The full process could be driven to completion simply by performing the reaction

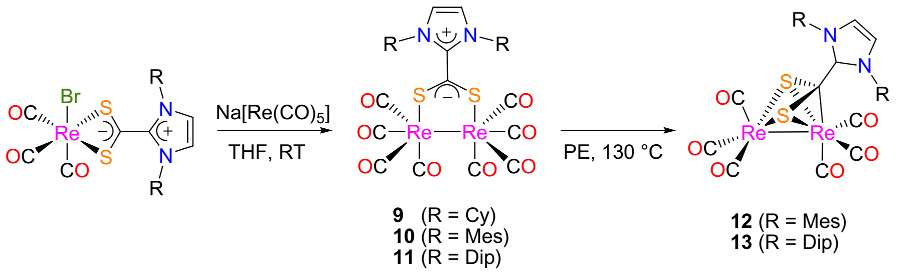
Table 1 Influence of the coordination mode on the ^{13}C NMR chemical shift of the dithiocarboxylate unit of various NHC·CS$_2$ ligands in mono- and bimetallic manganese–carbonyl complexes and clusters

Zwitterion	δ CS$_2$ (ppm) of the free ligand[a]	δ CS$_2$ (ppm) in [MnBr(CO)$_3$(S$_2$C·NHC)] complexes[b]	δ CS$_2$ (ppm) in [Mn$_2$(CO)$_6$(S$_2$C·NHC)] clusters **4–8**[b]
ICy·CS$_2$	226.0	221.6	89.3
IMes·CS$_2$	221.6[c]	215.5	87.6
IDip·CS$_2$	219.7	214.5	87.3
SIMes·CS$_2$	222.7	216.4	85.9
SIDip·CS$_2$	219.8	215.0	85.4

[a] Data recorded in CDCl$_3$ at 298 K, see Ref. [23]

[b] Data recorded in CD$_2$Cl$_2$ at 298 K, see Ref. [38]

[c] Data recorded in [D$_6$]DMSO

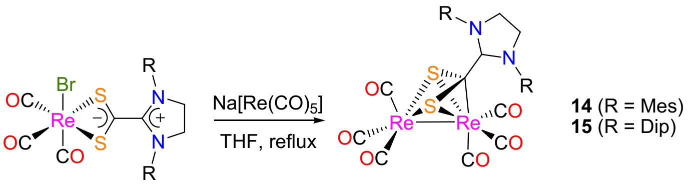


Scheme 6 Multistep synthesis of homobimetallic rhenium carbonyl clusters **12** and **13**

under reflux conditions, thereby leading to the isolation of pure clusters **14** and **15** in 35 and 56% yields, respectively (Scheme 7).

The ^{13}C NMR chemical shift of the dithiocarboxylate moiety remained roughly unchanged whether this unit acted as a chelating ligand in mononuclear [ReBr(CO)$_3$(S$_2$C·NHC)] complexes or as a bridge in binuclear species **9–11** (Table 2). Further comparison with the δ CS$_2$ values recorded for the free NHC·CS$_2$ zwitterions (cf. Table 1) revealed that they were not significantly altered upon coordination to rhenium in the κ^2-*S*,*S*′ or μ–κ^1-*S*,κ^1-*S*′ modes. Contrastingly, binding the central carbon atom of CS$_2^-$ to achieve a κ^3-*S*,*C*,*S*′ hapticity in clusters **12–15** led to a dramatic shielding of this nucleus, as already evidenced for related manganese–carbonyl species **4–8**.

Crystals of dirhenium compounds **12**, **13**, and **15** suitable for X-ray diffraction analysis were grown by slow diffusion of *n*-hexane into cold dichloromethane solutions. Their molecular structures were similar to those determined previously for analogous Mn/Re (**1**, **2**) and Mn/Mn derivatives (**4**, **6**, **7**, **8**). Remarkably, the S–C–S bite angles measured in all these homo- and heterobimetallic clusters (104°–107°) were significantly smaller than those recorded in mononuclear [MBr(CO)$_3$(S$_2$C·NHC)] chelates (M = Mn, Re; 114°–118°) and in bridged dimers **9–11** (130°) [34, 38, 39]. Considering that the free azolium-2-dithiocarboxylate



Scheme 7 Synthesis of homobimetallic rhenium carbonyl clusters **14** and **15**

Table 2 Influence of the coordination mode on the ^{13}C NMR chemical shift of the dithiocarboxylate unit of various NHC·CS_2 ligands in mono- and bimetallic rhenium–carbonyl complexes and clusters

Zwitterion	δ CS_2 (ppm) in $[ReBr(CO)_3(S_2C{\cdot}NHC)]$ complexes[a]	δ CS_2 (ppm) in $[Re_2(CO)_8(S_2C{\cdot}NHC)]$ dimers **9–11**[a]	δ CS_2 (ppm) in $[Re_2(CO)_6(S_2C{\cdot}NHC)]$ clusters **12–15**[a]
ICy·CS_2	225.9[b]	216.7	
IMes·CS_2	220.4[b]	212.2[b]	79.3
IDip·CS_2	219.4	213.7[b]	79.0
SIMes·CS_2	221.6		79.2
SIDip·CS_2	217.7		79.0[b]

[a] Data recorded in CD_2Cl_2 at 298 K, see Ref. [39]

[b] Data recorded at 273 K

zwitterions exhibit a bite angle of ca. 130° [23], the CS_2 unit of these ligands displays a remarkable flexibility, which also allowed significant twists of the thiometallated rings in order to preserve a staggered arrangement of the carbonyl groups in bimetallic systems.

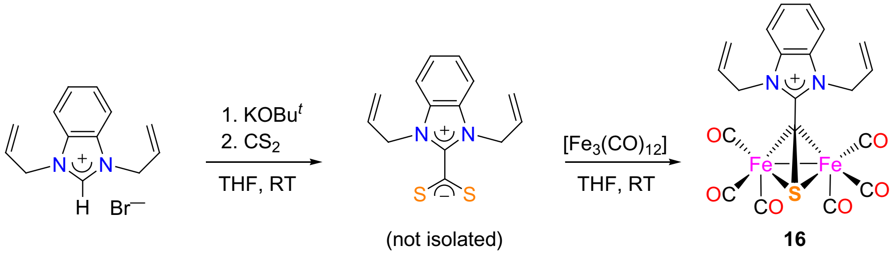
Iron and Ruthenium Clusters

In 2015, the group of Shi reported the synthesis and characterization of a diiron carbonyl cluster upon reaction of 1,3-diallylbenzimidazolium-2-dithiocarboxylate (BAll·CS_2) with $[Fe_3(CO)_{12}]$ in THF at room temperature [40]. The zwitterionic ligand was generated in situ by deprotonating the corresponding benzimidazolium bromide with potassium *tert*-butoxide, followed by trapping the free carbene with an excess of carbon disulfide (Scheme 8). The possible interference of these non-innocent reagents in the subsequent complexation reaction was not detailed. Yet, after chromatographic purification, the unusual product $[Fe_2(CO)_6(\mu\text{-}\kappa^2\text{-}C,\kappa^2\text{-}S\text{-}SC{\cdot}BAll)]$ (**16**), in which only one sulfur atom subsisted, was isolated in low yield. A small amount of $[Fe_3(CO)_9S_2]$ was also eluted. Crystal structure determination showed that the NHC-CS ligand acted as a symmetrical bridge via its carbon and sulfur atoms to afford a tetrahedral $CSFe_2$ cluster. Cyclic voltammograms of compound **16** were recorded in the presence of acetic acid. An efficient production of dihydrogen ensued, thereby suggesting a potential application of this cluster in electrocatalysis.

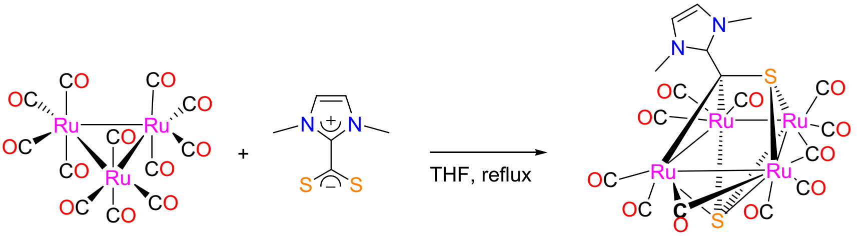
The dissociation of an NHC·CS_2 ligand upon coordination to a Group 8 metal-carbonyl source had already been disclosed by Cabeza et al. [41]. Thus, the reaction of $[Ru_3(CO)_{12}]$ with 1,3-dimethylimidazolium-2-dithiocarboxylate (IMe·CS_2) in THF at reflux temperature went through various intermediates that were detected by IR spectroscopy, but not identified, to ultimately afford tetranuclear complex **17** in 13% yield (Scheme 9). X-Ray diffraction analysis allowed to formulate this compound as $[Ru_4(\mu\text{-}CO)_2(CO)_9(\mu_4\text{-}S)(\mu_4\text{-}\kappa^2\text{-}C,S\text{-}SC\text{-}IMe)]$ as it evidenced the presence of a Ru_4 square core, capped on both sides by μ_4-S and μ_4-SC·NHC fragments that formally resulted from the cleavage of the dithiocarboxylate moiety of the betaine reagent. A bridging and a semibridging carbonyl ligand completed the molecular assembly. Of note, when a similar reaction was carried out starting from the zwitterionic adduct of *N*-methylthiazolylidene and phenylisothiocyanate (a NHC·RNCS inner salt), a second, closely related tetranuclear cluster with μ_4-S and μ_4-NC·NHC vertices was isolated and fully characterized [41].

Copper and Gold Polymetallic Assemblies

In 2015, Neuba, Wilhelm, and coworkers reported the synthesis of two linear coordination polymers by reacting copper(I) chloride or bromide with 1,3-dibenzylimidazolinium-2-dithiocarboxylate (SIBn·CS_2) in acetonitrile at room temperature [42]. Compounds **18** and **19** were stable only in the solid state where they crystallized isostructurally to form one-dimensional, infinite polymeric chains consisting of alternating trigonal planar CuX (X = Cl, Br) and CS_2^- units bearing orthogonal imidazolinium pendant groups (Scheme 10). Their photocatalytic activity was probed in the thiol–ene reaction of thiophenol with styrene (Scheme 11). Reactions carried out in acetonitrile under heterogeneous conditions afforded the expected 2-phenethyl(phenyl)thioether in up to 60% yield after 40 h of irradiation at room temperature. No conversion was recorded in dichloromethane, most likely because dissolution of the $[CuX(S_2C\cdot SIBn)]_n$ chains in this solvent led to their depolymerization. As a matter of fact, ESI–MS and NMR analyses of samples dissolved in DMSO or methanol confirmed the formation of mononuclear



Scheme 8 Synthesis of homobimetallic iron carbonyl cluster **16**

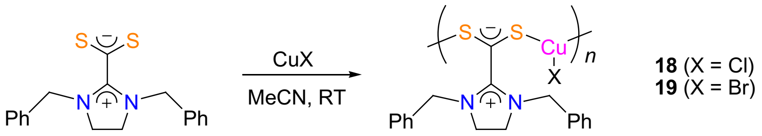


Scheme 9 Synthesis of tetranuclear ruthenium carbonyl cluster **17**

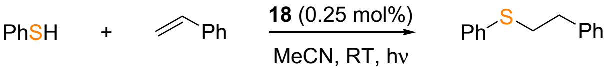
complexes of the type $[Cu(S_2C{\cdot}SIBn)_2]^+[CuX_2]^-$ instead of the polymeric materials under homogeneous conditions.

In 2010, Wilton-Ely and coworkers [33] devised an efficient strategy for the preparation of gold nanoparticles using 1,3-dimesitylimidazolium-2-dithiocarboxylate ($IMes{\cdot}CS_2$) to protect the metal surface. Citrate-stabilized gold nanoparticles were first generated from $HAuCl_4$ according to standard procedures [43]. Next, a solution of $IMes{\cdot}CS_2$ in dichloromethane/methanol was added to the reaction mixture, leading to the instant formation of a sulfur-functionalized protective monolayer (Scheme 12). The zwitterionic ligand in excess was washed away with dichloromethane and the displaced citrate salts were removed by washing with water. Transmission electron microscopy (TEM) showed that the nanoparticles obtained (**NP1**) had an average diameter of 11.5 ± 1.2 nm. A more direct method was also investigated to form nanoparticles of smaller size from $HAuCl_4$, tetraoctylammonium bromide (TOAB), $NaBH_4$, and $IMes{\cdot}CS_2$. Removal of the betaine in excess proved, however, more complicated in this case, because of its similar solubility to the nanoparticles. Eventually, pure gold nanoparticles of average diameter 2.6 ± 0.3 nm with extensive interparticle agglomeration (**NP2**) were isolated, as shown by TEM imaging.

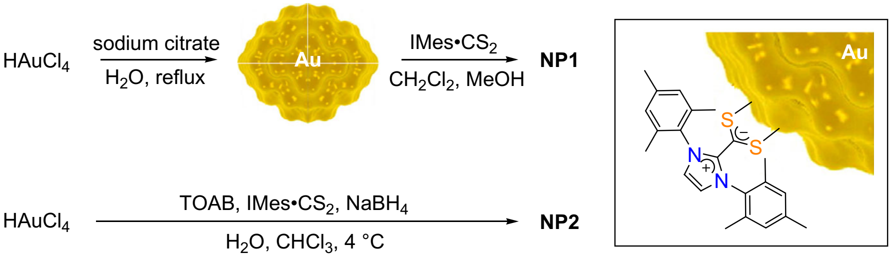
In 2012, Siemeling et al. [44] investigated the chemisorption of four $NHC{\cdot}CS_2$ zwitterions on solid gold surfaces. The *N*-heterocyclic carbenes used to generate dithiocarboxylate adducts in this study were 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDip), 1,3-diisopropylimidazol-2-ylidene (IPr), 1,3-dibenzylimidazol-2-ylidene (IBn), and 1,3-diethylbenzimidazol-2-ylidene (BEt). Adsorption of the betaines on gold substrates was carried out in dichloromethane at room temperature and was monitored in real time by optical second harmonic generation (SHG). The resulting thin films were further characterized by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS) in the case of $IDip{\cdot}CS_2$ and $IPr{\cdot}CS_2$. Altogether, these advanced



Scheme 10 Synthesis of copper(I) coordination polymers **18** and **19**



Scheme 11 Photocatalytic thiol–ene reaction with coordination polymer **18**



Scheme 12 Synthesis of gold nanoparticles **NP1** and **NP2**

analytical tools revealed the formation of almost contamination-free, self-assembled monolayers, which exhibited a remarkable degree of orientational order.

Conclusion and Perspectives

Recent developments in the coordination chemistry of azolium-2-dithiocarboxylate ligands have allowed significant advances in the synthesis of small clusters and polymetallic assemblies based on these zwitterions. Homo- and heterobimetallic carbonyl clusters derived from Group 7 transition metals (Mn and Re) have been most investigated so far, but isolated reports also provided examples of dinuclear iron and tetranuclear ruthenium compounds, in which the dithiocarboxylate unit underwent fragmentation. This could lead to potential applications in C–S bond activation. Presently, however, the catalytic properties of the carbonyl clusters already isolated remain largely unexplored with the exception of two succinct electrochemical studies, suggesting their ability to promote the electrocatalytic reduction of protons into dihydrogen. Scattered research on the formation of copper-based coordination polymers, gold nanoparticles, and self-assembled monolayers add to the diversity of polymetallic assemblies obtained from NHC·CS_2 betaines and could provide valuable materials for heterogeneous catalysis.

The different behaviors exhibited by imidazolium and imidazolinium dithiocarboxylates during the preparation of homobimetallic rhenium carbonyl clusters (cf. Schemes 6 and 7) and the sharp distinction in terms of steric and electronic properties between NHC and phosphine-based zwitterions [23], and clusters derived thereof [34], demonstrated that the positively-charged fragment had a considerable influence on the reactivity of the adjacent dithiocarboxylate unit, although there is no direct electronic communication between them. In their future endeavors to design tailored clusters for catalytic or other applications, scientists should therefore take advantage of the huge library of *N*-heterocyclic carbenes already synthesized to fine-tune the stereoelectronic properties of their target compounds.

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