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Toward N-heterocyclic carbene stabilized zinc sulfides

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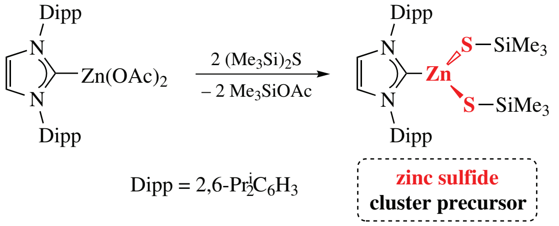
A series of N-heterocyclic carbene (NHC) supported group 12 acetate complexes were prepared and their use as building blocks toward soluble group 12 sulfide precursors was explored. The highly moisture-sensitive NHC-ligated zinc dithiolato complex [(IPr)Zn(SSiMe$_3$)$_2$] was also synthesized [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], and its partial hydrolysis gave the dianionic zinc sulfide cluster [Zn$_3$(μ$_3$-S)(μ$_2$-SSiMe$_3$)$_3$(SSiMe$_3$)$_3$]$^{2-}$, which contained a rare example of a Zn$_3$S structural motif. This preliminary observation indicates that the future growth of related metallosulfide clusters from [(IPr)Zn(SSiMe$_3$)$_2$] should be possible.



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The group 12 elements zinc, cadmium and mercury are generally sourced from their metal sulfide ores: ZnS (sphalerite), CdS (greenockite) and HgS (cinnabar).[1] Notably, these metal sulfides are direct band gap semiconductors and as such have garnered significant interest in the realm of materials science,[2] and in the case of Cu-doped ZnS, long-lived phosphorescence is possible.[3] Despite the widespread exploration of group 12 sulfide nanoparticles, their syntheses typically rely on high temperature 'hot-injection' protocols and the use of toxic/reactive precursors such as CdMe$_2$.[2(a)] Thus, it would be of value to devise new single-source (molecular) precursors to group 12 chalcogenides that are easier to handle. Given our group's previous use of ligand-stabilized GeH$_2$ complexes for the controlled formation of Ge nanoparticles and films under mild conditions from solution (typically at 100–150 °C),[4] we looked to utilize a similar approach to yield soluble molecular group 12 metal sulfide precursors. Of particular relevance to this study, several group 12 complexes containing metal-sulfide bonds [M(SR)$_2$]$_x$ (M = Zn, Cd, Hg; R = alkyl or aryl groups) involving bulky thiolato ligands have been prepared,[5] while neutral donor-stabilized binary metal sulfides have yet to be isolated. We were also encouraged by a report from the Corrigan group, wherein the N-heterocyclic carbene ligand, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), was used to prepare a series of novel luminescent clusters of the general formula [(IPr)$_4$Au$_4$E$_4$Ch$_4$] (E = Ag or Au; Ch = S, Se, Te).[6] Given the aforementioned use of the IPr ligand to prepare metallochalcogen clusters,[6] we decided to make group 12 metal sulfides [(IPr)M(S)]$_x$ (M = Zn, Cd, Hg) a synthetic target. This communication documents our initial efforts in this regard.

It was reasoned that the desired group 12 sulfide complexes [(IPr)M(S)]$_x$ (M = Zn, Cd, Hg) could be synthesized by first preparing [(IPr)M(SSiMe$_3$)$_2$], followed by the addition of [(IPr)MX$_2$] (with concomitant Me$_3$SiX elimination; X = halide). A related 2014 study by Maron, Okuda and coworkers communicated the preparation of the NHC-stabilized thiolate-bridged cationic cluster [(IMes)$_2$Zn$_2$(μ-SPh)$_3$]$^+$ by addition of PhSSPh to the dicationic cluster [(IMes)$_3$Zn$_3$H$_4$(THF)]$^{2+}$.[7] We began our own investigations by first surveying the reaction of known IPr-supported zinc dihalide compounds [(IPr)ZnX$_2$] (X = Cl, I)[8] with the sulfur atom sources (Me$_3$Si)$_2$S and Li[SSiMe$_3$].[9] Unfortunately, product mixtures were obtained in all cases, with no evidence for the formation of the desired zinc(II) thiolato complex [(IPr)Zn(SSiMe$_3$)$_2$] by ^{1}H NMR spectroscopy. We then turned to the previously reported[10] IPr-ligated zinc dihydride dimer [(IPr)ZnH(μ-H)]$_2$ and explored its reactivity with (Me$_3$Si)$_2$S. Analysis of the ^{1}H NMR spectrum revealed the sluggish formation of a new product, exhibiting resonances that corresponded to a new IPr species with two NMR equivalent -SiMe$_3$ groups (δ = 0.33 ppm), consistent with the formation of the target complex [(IPr)Zn(SSiMe$_3$)$_2$]. Unfortunately, this reaction was prohibitively slow, even with a tenfold excess of (Me$_3$Si)$_2$S, providing a very low conversion to the desired product (<10% by ^{1}H NMR spectroscopy) after stirring for 16 h. The formation of [(IPr)Zn(SSiMe$_3$)$_2$] was never able to reach completion as competing decomposition of the zinc dihydride precursor occurs at room temperature in solution, leading to the dihydroaminal IPrH$_2$ (ref. 11) and metallic zinc.[10(b)]

Taking inspiration from the previously reported syntheses of [L–Zn(SSiMe$_3$)$_2$] systems (L = tetramethylethylenediamine or 3,5-lutidine) *via* zinc acetate precursors,[12] we looked to use the carbene-substituted adducts [(IPr)M(OAc)$_2$] (M = Zn, Cd, or Hg) to advance our chemistry, however these acetate complexes had yet to be reported in the literature.[†] Fortunately, we found that addition of IPr to the metal acetates M(OAc)$_2$ (M = Zn, Cd, Hg) in toluene afforded complexes [(IPr)Zn(OAc)$_2$] **1**, [(IPr)Cd(OAc)$_2$] **2** and [(IPr)Hg(OAc)$_2$] **3** in high yields

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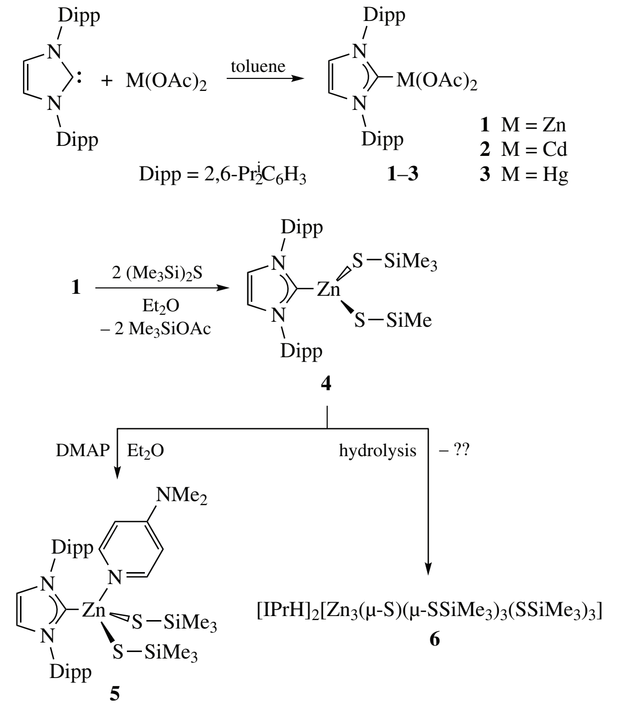
[†] A structurally related carbene-zinc carboxylate [(IMes)Zn(O$_2$CBu^t)$_2$] [IMes = (HCNMes)$_2$C; Mes = 2,4,6-Me$_3$C$_6$H$_2$] was reported recently.[13]



Scheme 1

(Scheme 1, top) as sparingly soluble white solids. Despite repeated attempts to crystallize **1–3**, we could not obtain crystals of sufficient quality for X-ray crystallography, however each species gave NMR spectra consistent with the assigned chemical formula, while compounds **1** and **3** also gave satisfactory elemental analyses. Interestingly, $^4J_{\text{H–Hg}}$ coupling (32.2 Hz in CDCl$_3$) could be discerned in the ^{1}H NMR spectrum of complex **3**, corresponding to coupling between an olefinic C–H proton in the carbene ligand backbone and the Hg center; similar $^4J_{\text{H–Hg}}$ coupling was found in [(IPr)HgCl$_2$(HgCl$_2$)$_2$].[14] Of added note, compounds **1–3** are highly thermally stable (>250 °C) and should serve as excellent building blocks to group 12 clusters in the future.[15]

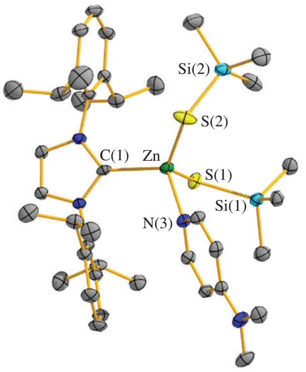


Figure 1 Molecular structure of [(IPr)Zn(SSiMe$_3$)$_2$(DMAP)] **5** with thermal ellipsoids plotted at the 30% probability level. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Zn 2.094(4), Zn–S(1) 2.317(1), Zn–S(2) 2.296(1), Zn–N(3) 2.126(3); S(1)–Zn–S(2) 128.07(5), S(1)–Zn–N(3) 103.62(9), S(1)–Zn–C(1) 100.45(10).

Gratifyingly, we found that the combination of the zinc acetate complex [(IPr)Zn(OAc)$_2$] **1** with two equivalents of (Me$_3$Si)$_2$S resulted in the quantitative formation of the highly moisture-sensitive compound [(IPr)Zn(SSiMe$_3$)$_2$] **4** (see Scheme 1, middle). X-ray crystallography confirmed the expected atomic connectivity and monomeric nature of **4**, however we were unable to grow crystals of suitable quality for a more complete analysis of the bonding situation in this thermally stable solid (mp 138–142 °C). Colorless X-ray quality crystals of compound [(IPr)Zn(SSiMe$_3$)$_2$(DMAP)] **5** (Figure 1)[‡] were obtained by layering a solution of **4** in fluorobenzene with a fluorobenzene solution of 4-dimethylaminopyridine (DMAP), followed by cooling to –30 °C. Despite growing X-ray quality crystals, contamination of the bulk product with free IPr was consistently found. The zinc center in **5** adopts an expected distorted tetrahedral coordination geometry with a C$_{\text{IPr}}$–Zn bond length [2.094(4) Å] in the range of typical four-coordinate IPr-bound zinc species (*cf.* 2.042(2) Å in [(IPr)ZnI$_2$(THF)])[8(b)] as well as a N$_{\text{DMAP}}$–Zn distance of 2.126(3) Å. The Zn–S lengths in **5** average to 2.306(1) Å and lie in the range of Zn–S single bonds [2.184(5)–2.371(5) Å] found in Bochmann's zinc(II) thiolate dimer [Zn(SMes*)(μ-SMes*)]$_2$ (Mes* = 2,4,6-Bu$^t_3$C$_6$H$_2$).[5(a)] While compound **4** is stable for several days in solution, we found that **5** would decompose in C$_6$D$_6$ at room temperature to give free IPr and unidentified insoluble precipitate(s) (*ca.* 30% decomposition after 1 h).

In an attempt to crystallize complex **4**, a saturated toluene solution of this species was layered with hexanes and stored at –30 °C overnight, yielding a few small colorless crystals. X-ray crystallographic analysis revealed the crystals to be the dianionic zinc sulfide cluster salt [IPrH]$_2$[Zn$_3$(μ$_3$-S)(μ$_2$-SSiMe$_3$)$_3$(SSiMe$_3$)$_3$] **6** (Figure 2).[‡] This species was likely formed by the partial hydrolysis of **4** with adventitious water and was obtained in subsequent attempts to crystallize **4** (albeit inconsistently and in very small yield). This cluster features an unusual Zn$_3$S capping motif with μ$_3$-S bonding [atom S(7) in Figure 2] and suggests that **4** may indeed act as a molecular precursor to other molecular zinc sulfide clusters under the appropriate reaction conditions; a search of the Cambridge Structural Database (CSD) revealed that the dianion in **6** is the first tri-zinc cluster with a capping μ$_3$-sulfide. Related salts containing the homoleptic zincate [Zn(SSiMe$_3$)$_3$]$^-$ anion

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[‡] Crystals of compound **5** were grown by storing a fluorobenzene solution at –30 °C for three weeks. Crystals of compound **6** were grown by storing a toluene solution of **4** layered with hexanes at –30 °C overnight.

Crystal data for **5**. C$_{46}$H$_{69}$FN$_4$S$_2$Si$_2$Zn, M = 882.72, triclinic, space group $P\bar{1}$, 173.15 K, a = 10.100(3), b = 12.363(4) and c = 21.191(7) Å, α = 89.824(5)°, β = 85.218(5)°, γ = 69.150(5)°, Z = 2, V = 2463.2(14) Å^3, d_{calc} = 1.190 g cm^{-3}, F(000) = 944. Colorless block-shaped crystal with dimensions 0.29×0.14×0.12 mm was selected and intensities of 18595 reflections were measured using a Bruker D8/APEX II CCD diffractometer (ω scans, λ[MoKα] = 0.71073 Å, μ = 0.670 mm^{-1}, $2\theta_{\text{max}}$ = 51.65°). After merging of equivalents and absorption correction, 9384 independent reflections (R_{int} = 0.0637) were used for the structure solution and refinement. Final R factors: R_1 = 0.0687 [6330 reflections with $I > 2\sigma(I)$], wR_2 = 0.2017 (all reflections), GOF = 0.993.

Crystal data for **6**. C$_{79}$H$_{136}$N$_4$S$_7$Si$_6$Zn$_3$, M = 1730.98, monoclinic, space group $P2_1/c$, 173.15 K, a = 15.6474(3), b = 20.7512(3) and c = 30.1314(5) Å, β = 92.7671(9)°, Z = 4, V = 9772.3(3) Å^3, d_{calc} = 1.177 g cm^{-3}, F(000) = 3696. Colorless crystal fragment with dimensions 0.42×0.09×0.07 mm was selected and intensities of 69438 reflections were measured using a Bruker D8/APEX II CCD diffractometer (ω and ϕ scans, λ[CuKα] = 1.54178 Å, μ = 3.248 mm^{-1}, $2\theta_{\text{max}}$ = 150.07°). After merging of equivalents and absorption correction, 19762 independent reflections (R_{int} = 0.0392) were used for the structure solution and refinement. Final R factors: R_1 = 0.0363 [16044 reflections with $I > 2\sigma(I)$], wR_2 = 0.0956 (all reflections), GOF = 1.040.

The structures were solved by intrinsic phasing and refined by full-matrix least-squares on F^2 in anisotropic approximation. All calculations were carried out with SHELXT[17] (structure solution) and SHELXL[18] (structure refinement) programs. Molecular graphics were drawn using Diamond.[19]

CCDC 2047363 and 2047364 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

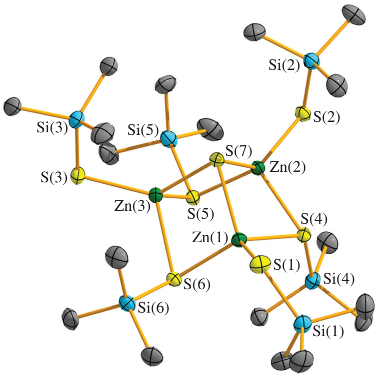

Figure 2 Molecular structure of the dianionic cluster $[Zn_3(\mu_3\text{-}S)(\mu_2\text{-}SSiMe_3)_3(SSiMe_3)_3]^{2-}$ in **6** with thermal ellipsoids plotted at the 30% probability level. All H atoms and the two $[IPrH]^+$ counterions have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–S(4) 2.4289(6), Zn(1)–S(6) 2.4025(6), Zn(3)–S(5) 2.4655(6), Zn(3)–S(6) 2.4710(6), Zn(2)–S(4) 2.4221(6), Zn(2)–S(5) 2.4371(6), Zn(2)–S(7) 2.3572(6); S(1)–Zn(1)–S(4) 114.70(3), S(4)–Zn(1)–S(6) 108.22(2), S(4)–Zn(1)–S(7) 93.63(2).

were recently reported by Sundermeyer and coworkers.[16] Our attempts to prepare a carbene-supported binary zinc sulfide $[(IPr)Zn(\mu\text{-}S)]_x$ by combining $[(IPr)Zn(SSiMe_3)_2]$ **4** with an equimolar amount of $[(IPr)Zn(OAc)_2]$ **1** failed, instead affording free IPr in solution and an insoluble white precipitate (presumably zinc sulfide).

We then attempted to form the heavy element analogues of **4**, $[(IPr)Cd(SSiMe_3)_2]$ and $[(IPr)Hg(SSiMe_3)_2]$ starting from the precursors **2** and **3** (see Scheme 1), respectively. Upon addition of $(Me_3Si)_2S$ to a slurry of **2** in toluene, the reaction mixture became mostly clear with the deposition of a fine white precipitate; ^1H NMR analysis of the recovered soluble fraction revealed the exclusive presence of the free carbene IPr. When $(Me_3Si)_2S$ was added to a slurry of the Hg complex **3**, a dense orange solid formed, which became black after a few minutes of stirring; again, the only soluble species present according to ^1H NMR analysis was free IPr. This observation may be ascribed to the weaker nature of coordinative/dative NHC → Cd/Hg interactions in comparison to zinc,[20] whereby NHC dissociation in the heavier element systems leads to irreversible $[M(SSiMe_3)_2]_x$ aggregate formation (and/or decomposition). While late-transition metal NHC complexes are amenable to C_{NHC}–M bond cleavage in the presence of sulfur-containing reagents,[21] we did not observe the formation of any NHC–S coupling products (*e.g.* NHC=S) by ^1H NMR spectroscopy.

In conclusion, we have reported a series of N-heterocyclic carbene-supported group 12 acetates. The zinc(II) acetate adduct $[(IPr)Zn(OAc)_2]$ was found to be an effective building block[13] for the formation of carbene-bound zinc dithiolato complexes. While only on a small scale, the formation of the trimetallic zinc-sulfur cluster $[Zn_3(\mu_3\text{-}S)(\mu_2\text{-}SSiMe_3)_3(SSiMe_3)_3]^{2-}$ was obtained *via* the hydrolysis of **4**, showing promise that related clusters might be accessed in the future from the reported zinc dithiolato complexes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.03.009.

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