

This is a peer-reviewed, accepted author manuscript of the following item: Saab, M., Nelson, D. J., Tzouras, N. V., Bayrakdar, T. A. C. A., Nolan, S. P., Nahra, F., & van Hecke, K. (2020). Straightforward access to chalcogenoureas derived from *N*-heterocyclic carbenes and their coordination chemistry. *Dalton Transactions*, 49(34), 12068-12081.

<https://doi.org/10.1039/D0DT02558E>

Journal Name

ARTICLE

Straightforward access to chalcogenoureas derived from *N*-heterocyclic carbenes and their coordination chemistry

Received 00th January 20xx,
Accepted 00th January 20xx

Marina Saab,^a David Nelson,^{*b} Nikolaos V. Tzouras,^a Tahani A. C. A. Bayrakdar,^a Steven P. Nolan,^{*a} Fady Nahra^{*a,c} and Kristof Van Hecke^{*a}

DOI: 10.1039/x0xx00000x

Chalcogen-based urea compounds supported by a wide range of *N*-heterocyclic carbenes are synthesised and fully characterised. Coordination of selenoureas is further explored with Group 11 transition metals to form new copper, gold and silver complexes. Single crystal X-ray analyses unambiguously establish the solid-state coordination of these complexes and show that the geometry of a complex is highly influenced by a combination of electronic properties -mainly π -accepting ability- and steric hindrance of the ligands, as well as the nature of the metal, affording a variety of coordination behaviours. In this report, we investigate these phenomena using several experimental methods.

Introduction

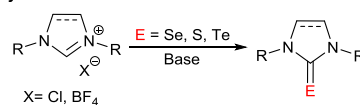
Due to their unique structural properties, reactivity and coordination characteristics, *N*-heterocyclic carbenes (NHCs) have attracted significant attention in the scientific community over the last decades. Their unique properties have made them highly useful in several applications.¹ The quest to better understand these species, more specifically their electronic and steric properties, in order to achieve better ligand designs and ultimately more efficient catalysts, have been a major driving force for the current research in this field.²⁻⁴

Our interest lies in better understanding the π -accepting ability of commonly used NHCs and its influence on their coordination behaviour with transition metals as well as the reactivity of NHC-based complexes in catalysis. To this end, our approach has been based on synthesising NHC-derived selenoureas, analysing these by ⁷⁷Se NMR spectroscopy,^{5,6} and investigating trends in their coordination chemistry to transition metals such as copper, silver and gold.^{7,8} In addition to revealing the π -accepting ability of the parent NHC,⁹⁻¹² selenoureas have themselves found applications in coordination chemistry with several transition metals.¹³⁻¹⁵ Other chalcogen-based derivatives, such as thio- and telluroreas, have also made an impact in this field,¹³⁻¹⁷ although the tellurium analogues are far less common.¹⁴ NHC-based seleno- and thioureas can typically be synthesised either by deprotonating the corresponding imidazolium salts using a strong base (e.g. KO^tBu, NaH), or by adding elemental selenium or sulfur to a free NHC species.^{14,15} Some reports have used K₂CO₃ in methanol yielding lower

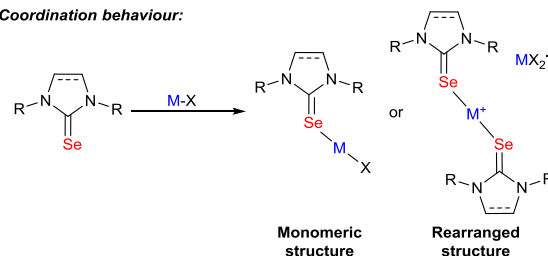
yields, as it generates the strong base KOMe *in situ*.¹⁸ It should be noted that in all approaches, a significant excess of elemental chalcogen is needed. NHC-derived telluroreas, on the other hand, are more scarcely reported, owing to the lower reactivity of elemental tellurium and its more metallic character when compared to selenium and sulfur.¹⁴⁻¹⁶

We have recently developed a systematic approach to the synthesis of NHC-based compounds by means of weak bases such as K₂CO₃ and NEt₃. In a recent report, we accessed [S(IPr)] and [Se(IPr)] compounds (IPr = *N,N'*-bis[2,6-(di-isopropyl)-phenyl]imidazol-2-ylidene) using NEt₃ as the base.¹⁹ In this report, the synthesis of various NHC-based seleno-, thio- and telluroreas is investigated, using two different weak bases (K₂CO₃ and NEt₃) (Scheme 1). We have also built on our previous work concerning the coordination of transition metals to selenoureas.^{7,8} The coordination library of the latter to copper, gold and silver is investigated and compared in more details, providing a better picture of underlying trends (Scheme 1). All new species have been characterised by ¹H, ¹³C and ⁷⁷Se NMR spectroscopy, elemental analysis, and X-ray crystallography.

Synthesis:



Coordination behaviour:



Scheme 1. Summary of this work

Based on previous and current work, single-crystal X-ray analysis is crucial for the elucidation of the solid-state behaviour of [Se(NHC)] ligands when coordinated to Group 11 metals;

^a Department of Chemistry, Ghent University, Krijgslaan 281, Building S3, 9000 Ghent, Belgium. Kristof.VanHecke@UGent.be; Steven.Nolan@UGent.be

^b WestCHEM Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL UK. David.Nelson@strath.ac.uk

^c VITO (Flemish Institute for Technological Research), Boeretang 200, 2400 Mol, Belgium. Fady.Nahra@Vito.be

Electronic Supplementary Information (ESI) available: NMR spectra of new compounds and complexes prepared during this study. See

DOI: 10.1039/x0xx00000x

solid state behaviour differs from solution state behaviour depending on the electronic and steric properties of the parent NHC. In this context, we have established that two different structures for Cu(I) and Au(I) complexes of these ligands can be obtained in the solid-state: i) the (expected) monomeric [MCl(L)] or ii) rearranged-type [M(L)₂][MCl₂] structures. The coordination chemistry of these ligands with Ag(I) is significantly more complicated; the solid-state behaviour of the obtained silver complexes is much more sensitive to the steric and electronic nature of the ligand, and multiple coordination environments can be observed when different crystals are picked from the same batch of the product. Work by Ritch and co-workers has significantly contributed to the understanding of these silver species.²⁰

Results and discussion

Synthesis of NHC-based seleno-, thio- and telluoureas

A wide range of imidazolium salts having different electronic and steric properties were used in this report; these are shown in Figure 1. Using the weak base approach, we attempted the synthesis of the corresponding seleno-, thio- and telluoureas via deprotonation of the imidazolium salts in the presence of 1.1 to 3 equiv. of elemental chalcogen (Scheme 2). Two different weak bases, namely potassium carbonate (K₂CO₃) and triethylamine (NEt₃), were used for comparison; K₂CO₃ affords a heterogeneous reaction mixture, whilst NEt₃ delivers a homogeneous mixture, more suitable for continuous processing applications. Typically, 1.5 to 3 equiv. of elemental chalcogen were needed to achieve good yields when using the K₂CO₃ route, while only 1.1 equiv. of chalcogen were needed with NEt₃. The attractiveness of these reagents, from a cost and practicality points of view, has been well-highlighted in previous studies.¹⁹

Using these conditions, the syntheses of IPr-based chalcogens ([Se(IPr)], [S(IPr)] and [Te(IPr)]) were attempted initially (Table 1). [Se(IPr)] and [S(IPr)] were successfully accessed in good yields (Table 1, entries 1-2). As for [Te(IPr)],

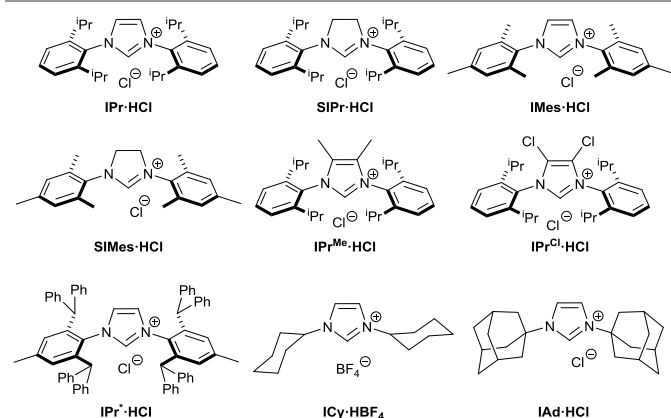
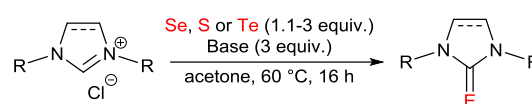


Figure 1. Imidazolium salts used in this work.



Scheme 2. Weak base approach to synthesising chalcogen-based ureas

only K₂CO₃ afforded the desired compound, which was obtained in 78% yield (Table 1, entry 3). Both strategies were then attempted with the other eight imidazolium salts, and good yields of all seleno- and thioureas were obtained with a few exceptions (Table 1, entries 4-20); the triethylamine route did not prove successful with alkyl *N*-substituted compounds (for which the azolium salts have higher pK_a values),²¹ i.e. ICy and IAd, whilst K₂CO₃ performed well for ICy but gave low yield for [Se(IAd)] and no reaction was observed in the case of [S(IAd)] (Table 1, entries 17-20). It should be noted that all potassium carbonate reactions were conducted on a 1-2 g scale while the use of triethylamine was demonstrated on a smaller scale, as proof-of-concept.

Table 1. Syntheses of NHC-based chalcogens using K₂CO₃ and NEt₃^a

Entry	Products	NEt ₃	K ₂ CO ₃
1	[Se(IPr)]	82%	80%
2	[S(IPr)]	99%	>99%
3	[Te(IPr)]	NR	78% ^b
4	[Se(SIPr)]	82%	90% ^c
5	[S(SIPr)]	99%	95% ^b
6	[Te(SIPr)]	NR	NR
7	[Se(IMes)]	82%	94% ^b
8	[S(IMes)]	86%	87% ^b
9	[Te(IMes)]	NR	NR
8	[Se(SIMes)]	65%	71% ^c
9	[S(SIMes)]	71%	86% ^b
10	[Te(SIMes)]	NR	NR
11	[Se(IPr ^{Me})]	75%	71% ^b
12	[S(IPr ^{Me})]	85%	87% ^b
13	[Se(IPr ^{Cl})]	95%	82% ^b
14	[S(IPr ^{Cl})]	98%	92% ^b
15	[Se(IPr [*])]	95%	94% ^c
16	[S(IPr [*])]	91%	95% ^c
17	[Se(ICy)]	NR	87% ^c
18	[S(ICy)]	NR	99% ^c
19	[Se(IAd)]	NR	12% ^c
20	[S(IAd)]	NR	NR

^aReaction conditions: NHC-HX (1 equiv.) + chalcogen (1.1 equiv.) in acetone (0.2 M) at 60 °C for 16 h. ^b1.5 equiv. of chalcogen were used. ^c3 equiv. of chalcogen were used. All yields are isolated yields. NR = no reaction

Despite the successful synthesis of a range of compounds, including [Te(IPr)], no other telluourea compound was afforded using either strategy; no reaction was observed in all

This is a peer-reviewed, accepted author manuscript of the following item: Saab, M., Nelson, D. J., Tzouras, N. V., Bayrakdar, T. A. C. A., Nolan, S. P., Nahra, F., & van Hecke, K. (2020). Straightforward access to chalcogenoureas derived from *N*-heterocyclic carbenes and their coordination chemistry. *Dalton Transactions*, 49(34), 12068-12081.

<https://doi.org/10.1039/D0DT02558E>

Journal Name

ARTICLE

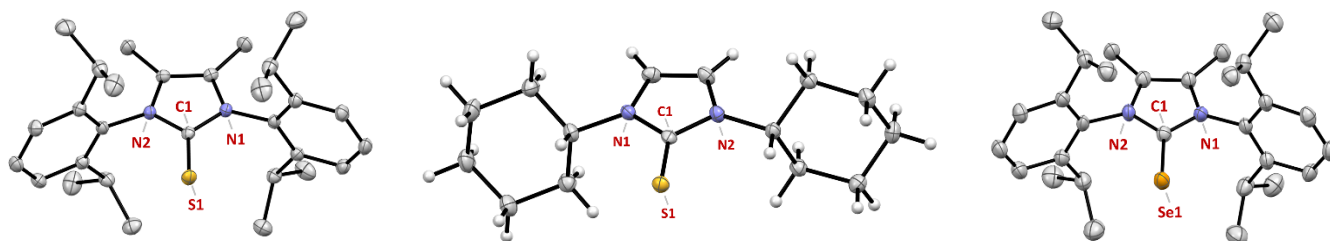
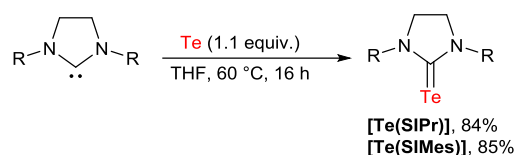


Figure 2. Molecular structures of [S(IPr^{Me})] (left), [S(ICy)] (middle) and [Se(IPr^{Me})] (right) determined by single-crystal X-ray diffraction analysis. Most hydrogen atoms and solvent molecules are omitted for clarity. Thermal displacement ellipsoids are shown at the 50% probability level. Some selected distances for [S(IPr^{Me})], C1-S1 = 1.677(1) Å; for [S(ICy)], C1-S1 = 1.692(2) Å; for [Se(IPr^{Me})], C1-Se1 = 1.842(3) Å.

attempts to access [Te(SIPr)], [Te(IMes)] and [Te(SIMes)] (Table 1, entries 6, 9 and 10). Based on these results, our initial conclusion was to consider the targeted compounds too unstable to be formed. In that context and to test this hypothesis, we attempted to synthesise [Te(SIPr)] and [Te(SIMes)] via the free carbene route. Using 1.1 equiv. of Te and 1 equiv. of the corresponding free carbenes, the desired telluroreas were prepared in 84% and 85%, respectively (Scheme 3). This means that the weak base approach, at least as utilised herein, is not optimal for tellurorea synthesis. Efforts to fully understand and optimise this reaction are ongoing in our laboratories.



Scheme 3. Synthesis of the telluroreas via the free carbene route

X-ray diffraction analysis was also performed on some of the new compounds in order to determine their solid-state structure. Single crystals of previously unreported compounds ([Se(IPr^{Me})], [S(IPr^{Me})] and [S(ICy)]) were grown by vapor diffusion of pentane into a saturated solution of the product in dichloromethane. All molecular structures are illustrated in Figure 2. From the obtained X-ray structures, we note that the C_{carbene}-S bond in the thiourea compounds is not influenced by the substituents on the aryl groups or the ring backbone (when comparing IMes and IPr^{Me}, C1-S1 distance for both is 1.677 Å). It varies more with the *N*-substitution when going from aryl to alkyl groups as shown by the C1-S1 distance of 1.692(2) Å in [S(ICy)], and is in agreement with literature values for similar compounds.²² As for [Se(IPr^{Me})], the C-Se bond (1.842(3) Å) is significantly longer than the C-S bond and is in accordance with previous values.^{5,18} Unfortunately, no suitable crystals could be

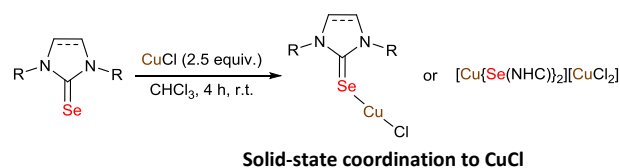
obtained for any of the telluroreas despite numerous attempts.

Coordination of selenoureas to coinage metals (Cu, Ag and Au)

The solid-state behaviour and ⁷⁷Se NMR shift of Cu-, Au- and Ag-coordinated selenoureas are next discussed. It should be noted that multiple crystals from each batch were analysed to confirm the presence of either one or several coordination species. This is especially relevant in the case of Ag-coordinated species as observed previously; as for Cu- and Au-coordinated species, results have consistently afforded only one species with different batches of crystals or different crystals within the same batch.

Copper: As previously observed,⁷ the reaction of CuCl with *N*-alkyl substituted selenoureas remains unsuccessful, and a mixture of unidentified products is obtained. However, *N*-aryl substituted selenoureas readily coordinate to CuCl. X-ray analyses have shown that the copper complexes adopt so far two main coordination motifs leading to different solid-state structures, specifically monomeric [CuCl(L)] complexes or rearranged-type [Cu(L)₂][CuCl₂] structures (Table 2). It should be noted that 2D ¹H DOSY (Diffusion-Ordered NMR Spectroscopy) experiments have always shown that this behaviour is not translated into solution, as only monomeric structures have been observed in solution. Upon reacting CuCl separately with [Se(SIPr)] and [Se(IPr^{Me})], and after work-up, single crystals were grown by vapor diffusion of pentane into a saturated solution of the corresponding products in dichloromethane. All molecular structures are illustrated in Figure 3.

Table 2. Overview of previous and current coordination behaviour of selenoureas to CuCl



[Se(NHC)]	Monomeric	Rearranged	Yield (%)
[Se(IPr)] ^a	[CuCl{Se(IPr)}]	-	81
[Se(IPr*)] ^a	[CuCl{Se(IPr*)}]	-	70
[Se(IMes)] ^a	-	[Cu{Se(IMes)} ₂][CuCl ₂]	90
[Se(SIMes)] ^a	-	[Cu{Se(SIMes)} ₂][CuCl ₂]	86
[Se(SIPr)] ^b	-	[Cu{Se(SIPr)} ₂][CuCl ₂]	86
[Se(IPr ^{Me})] ^c	[CuCl{Se(IPr ^{Me})}]	-	93

Reaction conditions: [Se(NHC)] (1 equiv.) + CuCl (2.5 equiv.) in CHCl₃ for 4 h. All yields are isolated yields. ^aResults taken from reference [7]. ^bReported previously⁷ but crystal structure is not yet reported. ^cNew complex.

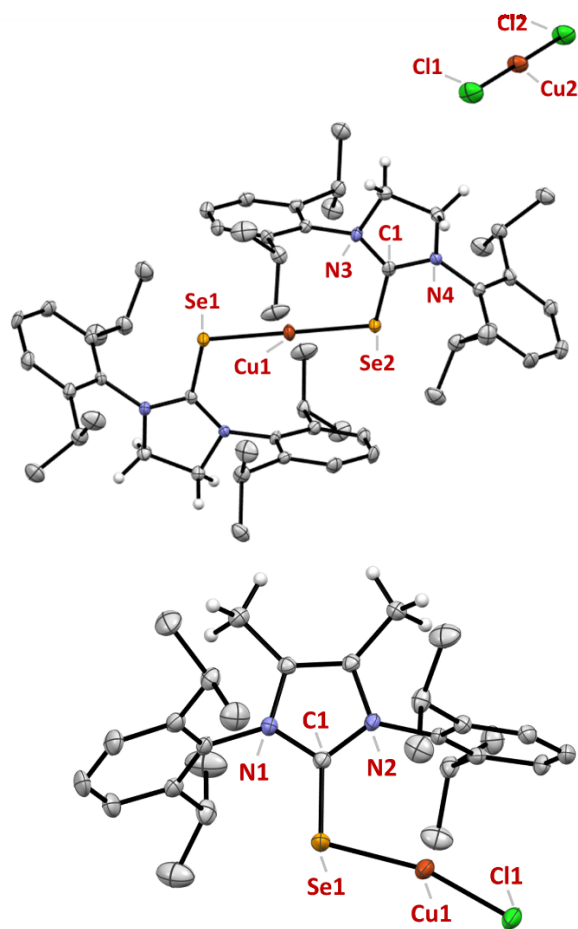


Figure 3. Molecular structures of [Cu{Se(SIPr)}₂][CuCl₂] (top) and [CuCl{Se(IPr^{Me})}] (bottom) determined by single-crystal X-ray diffraction analysis. Most hydrogen atoms and solvent molecules are omitted for clarity. Thermal displacement ellipsoids are shown at the 50% probability level. See Table 5 for selected bond lengths and angles.

X-ray analysis of the two new species clearly highlights the difference in behaviour, as two different types of complexes were obtained (Table 2 and Figure 3); [Se(SIPr)] joins [Se(SIMes)] and [Se(IMes)] in affording a rearranged structure, [Cu{Se(SIPr)}₂][CuCl₂], whilst [Se(IPr^{Me})] joins [Se(IPr)] and [Se(IPr*)] in affording a monomeric one, [CuCl{Se(IPr^{Me})}]. Unfortunately, no clear trend can yet be correlated to the π -accepting ability (or ⁷⁷Se NMR shift) of the corresponding selenourea ligands, since both types of behaviour are manifesting with ligands from across the spectrum. So far, we

can only assert that the monomeric species have only been observed with mid-range π -accepting ligands ($\delta_{\text{Se}} = 90$ -106 ppm). One theory is that the difference in coordination when comparing SIPr- and IPr-based complexes is due to the clear difference in π -accepting ability (190 vs 90 ppm, respectively). However SIMes- and IMes-based complexes both give similar rearranged structures despite their widely different π -accepting abilities (110 vs 27 ppm, respectively) which we propose to be due to the significantly lower steric demand of IMes and SIMes versus IPr and SIPr.

The Se-Cu-Se angle in [Cu{Se(SIPr)}₂][CuCl₂] is 179° (Figure 3), and is in accordance with the analogous structure obtained with [Se(IMes)] (180°). The C-Se-Cu angles (104.8(2)° and 105.9(2)°) are also within range of similar structures (102-105°). The C-Se bonds (1.865(5) and 1.867(5) Å) are within the normal range of similar structures and are only slightly elongated when compared to the C-Se bond in the corresponding free selenourea.⁵ The main structural difference observed for [Cu{Se(SIPr)}₂][CuCl₂], when compared to IMes- and SIMes-rearranged structures, is the significantly elongated Cu-Se bond (2.2814(8)-2.2797(8) Å vs 2.2636(0) Å for IMes and 2.2685(8)-2.2684(8) Å for SIMes), probably due to the additional steric hindrance induced by the SIPr aryl substitution.

As for [CuCl{Se(IPr^{Me})}], the C-Se and Cu-Se bonds are similar to previous IPr- and IPr*-based monomeric structures. The structure also features a bent C-Se-Cu angle (104.22(8)°) within range of previous structures. However, the Se-Cu-Cl angle (164.59(3)°) deviates significantly from a linear geometry and from other monomeric structures (168.21(3)° for IPr and 165.79(3)° for IPr*). This has significant consequences, since now the distance between copper and the *ipso*-carbon on the *N*-aryl substituent (*C*_{*ipso*}-Cu = 2.940(3) Å) is comfortably within the sum of the van der Waals radii (ca. 3.1 Å), thus indicating a possible interaction between the two. Thus far, this phenomenon has only been observed with gold selenourea complexes in this series.

Gold: Coordination to gold has been much more successful. So far, we have only reported gold coordination to *N*-aryl selenoureas.⁸ Herein, we extend the *N*-aryl portfolio to new selenoureas and further include the successful coordination of *N*-alkyl substituted selenoureas to gold(I) chloride using [AuCl(SMe₂)] as the metal precursor (Table 3).

In this manner, *N*-aryl -[Se(IPr^{Me})] and [Se(IPr^{Cl})]- and *N*-alkyl -[Se(ICy)] and [Se(IAd)]- selenoureas were separately reacted with [AuCl(SMe₂)], and after work up, single crystals of the previously unreported compounds were grown by vapor diffusion of pentane into a saturated solution of the corresponding products in dichloromethane (Table 3 and Figure 4). The corresponding structures were identified as monomeric for [AuCl{Se(IPr^{Me})}], [AuCl{Se(IPr^{Cl})}] and AuCl{Se(ICy)}, and as rearranged for [Au{Se(IAd)}₂][AuCl₂] (Figure 4). This represents a clear trend in gold(I) coordination chemistry, as so far only selenoureas with high π -accepting abilities ([Se(SIPr)], [Se(SIPr^{OMe})] and [Se(IAd)] with ⁷⁷Se NMR shift of 190, 185 and 198 ppm, respectively) have led to rearranged structures. In addition, when we previously investigated the coordination of [Se(IPr^{Cl})] to gold chloride, a rearranged structure,

This is a peer-reviewed, accepted author manuscript of the following item: Saab, M., Nelson, D. J., Tzouras, N. V., Bayrakdar, T. A. C. A., Nolan, S. P., Nahra, F., & van Hecke, K. (2020). Straightforward access to chalcogenoureas derived from *N*-heterocyclic carbenes and their coordination chemistry. *Dalton Transactions*, 49(34), 12068-12081.

<https://doi.org/10.1039/D0DT02558E>

Journal Name

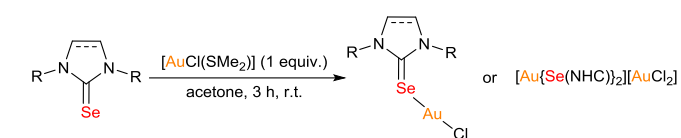
ARTICLE

$[\text{Au}\{\text{Se}(\text{IPr}^{\text{Cl}})\}_2][\text{AuCl}_2]$, was obtained, though it was not suitable for publication at the time and we were never able to reproduce it. As a consequence, this result was omitted from these studies. However, this now offers an insight to the gold trend as we believe that $[\text{Se}(\text{IPr}^{\text{Cl}})]$ is located at the interface of these two behaviours; thus, selenoureas with higher π -accepting abilities ($\delta_{\text{Se}} > 174$ ppm) can be expected to afford rearranged structures when coordinated to gold(I) chloride.

The Se-Au bond in all three monomeric structures is within range (2.35-2.36 Å) of previously reported complexes; 2.3614(5) Å for $[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Me}})\}]$, 2.3646(6) Å for $[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Cl}})\}]$ and 2.3714(6) Å for $[\text{AuCl}\{\text{Se}(\text{ICy})\}]$, with a slight elongation in the

The Au- C_{ipso} distances (3.175(3) Å for $[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Me}})\}]$ and 3.199(3) Å for $[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Cl}})\}]$) are also well within the sum of the van der Waals radii of the two atoms (ca. 3.36 Å), suggesting an interaction as in previous gold complexes. In contrast, $[\text{AuCl}\{\text{Se}(\text{ICy})\}]$ deviates somewhat from the norm. It displays the tightest C-Se-Au angle observed so far (97.38(6)°). The angled bond is also facing forward and not sideways as previously observed, most likely due to the absence of the typical stabilisation brought by the aryl C_{ipso} interaction. Now, the bent structure tries to minimize steric interactions by optimising the torsion angle C4-N-Se-Au (89.4(1)°; C4 is the carbon adjacent to N2). This has significant consequences on the Se-Au-Cl angle which is now closer to linear geometry (177.06(2)°, again due to the absence of the aryl C_{ipso} interaction). Interestingly, new interactions are now observed between Se1 and both H4 and H10 (2.8121 Å and 2.8102 Å, respectively); both lengths are well within the sum of the van der Waals radii of the two atoms (ca. 3.1 Å).

Table 3. Overview of previous and current coordination behaviour of selenoureas to AuCl



[Se(NHC)]	Solid-state coordination to AuCl		
	Monomeric	Rearranged	Yield
$[\text{Se}(\text{IPr})]^{\text{a}}$	$[\text{AuCl}\{\text{Se}(\text{IPr})\}]$	-	99%
$[\text{Se}(\text{SIPr})]^{\text{a}}$	-	$[\text{Au}\{\text{Se}(\text{SIPr})\}_2][\text{AuCl}_2]$	99%
$[\text{Se}(\text{SIPr}^{\text{OMe}})]^{\text{a}}$	-	$[\text{Au}\{\text{Se}(\text{SIPr}^{\text{OMe}})\}_2][\text{AuCl}_2]$	99%
$[\text{Se}(\text{IPr}^*)]^{\text{a}}$	$[\text{AuCl}\{\text{Se}(\text{IPr}^*)\}]$	-	99%
$[\text{Se}(\text{IPr}^{\text{OMe}})]^{\text{a}}$	$[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{OMe}})\}]$	-	99%
$[\text{Se}(\text{IMes})]^{\text{a}}$	$[\text{AuCl}\{\text{Se}(\text{IMes})\}]$	-	99%
$[\text{Se}(\text{SIMes})]^{\text{a}}$	$[\text{AuCl}\{\text{Se}(\text{SIMes})\}]$	-	99%
$[\text{Se}(\text{IPr}^{\text{Me}})]^{\text{b}}$	$[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Me}})\}]$	-	99%
$[\text{Se}(\text{IPr}^{\text{Cl}})]^{\text{c}}$	$[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Cl}})\}]$	-	95%
$[\text{Se}(\text{ICy})]^{\text{b}}$	$[\text{AuCl}\{\text{Se}(\text{ICy})\}]$	-	99%
$[\text{Se}(\text{IAd})]^{\text{b}}$	-	$[\text{Au}\{\text{Se}(\text{IAd})\}_2][\text{AuCl}_2]$	93%

Reaction conditions: $[\text{Se}(\text{NHC})]$ (1 equiv.) + $[\text{AuCl}(\text{SMe}_2)]$ (1 equiv.) in acetone for 3 h. All yields are isolated yields. ^aResults taken from reference [8]. ^bNew complex. ^cReported previously⁸ but crystals were not suitable for publication.

latter case, which is the only *N*-alkyl based selenourea in this monomeric series. The C1-Se bond is also within range for the two *N*-aryl based complexes; however, $[\text{AuCl}\{\text{Se}(\text{ICy})\}]$ presents a longer bond in comparison (1.889(2) vs 1.874(3) Å and 1.868(3) Å).

All three structures feature a bent C-Se-Au angle with some noticeable differences (Figure 4). The *N*-aryl selenoureas, $[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Me}})\}]$ and $[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Cl}})\}]$, display a slightly larger angle than all previous complexes in this series; 106.95(9)° and 107.29(9)°, respectively (vs previous range 103.40°-106.94°). This does not influence the Se-Au-Cl angles which still deviate from a linear geometry in both complexes but remain within range of previously reported monomeric gold structures.

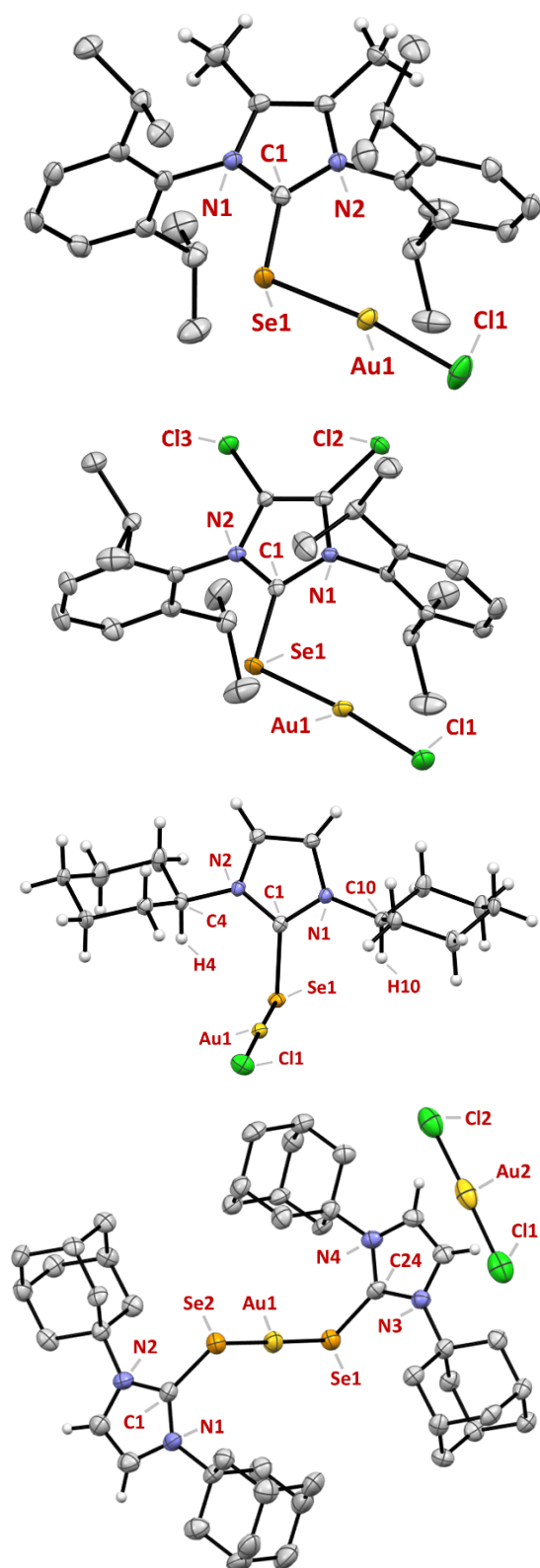


Figure 4. Molecular structures of $[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Me}})\}]$ (top), $[\text{AuCl}\{\text{Se}(\text{IPr}^{\text{Cl}})\}]$ (2nd from top), $[\text{AuCl}\{\text{Se}(\text{ICy})\}]$ (3rd from top) and $[\text{Au}\{\text{Se}(\text{IAd})\}_2][\text{AuCl}_2]$ (bottom) determined by single-crystal X-ray diffraction analysis. Most hydrogen atoms and solvent molecules are omitted for clarity. Thermal displacement ellipsoids are shown at the 50% probability level. See Table 5 for selected bond lengths and angles.

Regarding the rearranged $[\text{Au}\{\text{Se}(\text{IAd})\}_2][\text{AuCl}_2]$ structure, the Se-Au bonds (2.384(1) Å and 2.387(1) Å) are found to be within normal range. Again, elongated C1-Se bonds are found (1.928(7) Å and 1.920(7) Å; longest in the series) along with tighter C-Se-Au angles (100.5(2)° and 100.9(2)°). This seems to be a characteristic of *N*-alkyl based selenoureas. The Se-Cu-Se angle in $[\text{Au}\{\text{Se}(\text{IAd})\}_2][\text{AuCl}_2]$ is quite close to linear geometry (179.34(4)°), and in accordance with previous rearranged structures in this series.

Silver: Coordination to silver has been a much trickier endeavour. Selenourea complexation to silver(I) chloride has displayed a wide range of behaviours in the solid-state, though this series only gave monomeric structures in solution (Table 4). So far, we have identified four types of coordination behaviours: i) *The tri-coordinated trigonal planar cationic* structures, when using relatively small *N*-alkyl based ligands (i.e. ItBu and ICy), affording an $[\text{Ag}\{\text{Se}(\text{ItBu})\}_3]$ core with a $[\text{AgCl}_3]$ counterion or $[\text{Ag}\{\text{Se}(\text{ICy})\}_3]$ core with a chloride counterion. ii) *The di-coordinated trigonal planar neutral* species, when using a larger *N*-alkyl based ligand (i.e. IDD), affording $[\text{AgCl}\{\text{Se}(\text{IDD})\}_2]$. iii) *The di-coordinated linear cationic* structure bearing an outer-sphere chloride counterion, when using a bulky *N*-aryl based ligand (i.e. IPr), affording $[\text{Ag}\{\text{Se}(\text{IPr})\}_2][\text{Cl}]$. iv) *The dimeric* structure with a trigonal planar silver environment, characteristic of a smaller *N*-aryl based ligand (i.e. IMes), affording neutral $[\text{AgCl}\{\mu\text{-Se}(\text{IMes})\}_2]$ species. At this point, it seems that both electronic and steric effects are important and are significantly influencing the coordination patterns (Table 4).

Based on these observations, the reaction of $[\text{Se}(\text{SIMes})]$ with AgCl was attempted, expecting a dimeric structure which was observed after X-ray analysis (Figure 5). In that manner, $[\text{AgCl}\{\mu\text{-Se}(\text{SIMes})\}_2]$ was obtained in a similar structure to the IMes-analogue. The reaction of $[\text{Se}(\text{SIPr})]$ with AgCl was also performed, leading to the expected di-coordinated linear cationic structure, $[\text{Ag}\{\text{Se}(\text{SIPr})\}_2][\text{AgCl}_2]$, similarly to the IPr-analogue. However, this new structure differs from the latter as it possesses an outer sphere $[\text{AgCl}_2]$ counterion. This now puts it in the category of rearranged complexes, still with a linear cationic structure, and the first observed in this series with silver. It should be noted that this structure is now in agreement with the observations made by Ritch and co-workers,²⁰ further adding to the complexity of silver coordination behaviour. The reaction of AgCl with $[\text{Se}(\text{IPr}^{\text{Me}})]$ was also performed and a new complex was obtained as indicated by NMR analysis. Luckily, a ⁷⁷Se NMR shift was observed (4.89 ppm); however, we were not able to grow any suitable crystals for X-ray analysis despite numerous attempts.

The Se-Ag bond (2.4812(5) Å and 2.4816(5) Å) in $[\text{Ag}\{\text{Se}(\text{SIPr})\}_2][\text{AgCl}_2]$ is in the same range as other di-coordinated linear silver complexes in this series, though significantly longer than analogous gold (2.36-2.39 Å) and copper (2.26-2.28 Å) complexes (Figure 5 and Table 5). The C1-Se bond (1.863(5) Å and 1.867(5) Å) is also within the norm and does not vary significantly when comparing different coinage metal complexes. The rearranged species displays a slightly larger C1-Se-Ag angle (105.3(2)° and 104.1(2)°) than all previous linear di-coordinated silver complexes in this series. This does

This is a peer-reviewed, accepted author manuscript of the following item: Saab, M., Nelson, D. J., Tzouras, N. V., Bayrakdar, T. A. C. A., Nolan, S. P., Nahra, F., & van Hecke, K. (2020). Straightforward access to chalcogenoureas derived from N-heterocyclic carbenes and their coordination chemistry. *Dalton Transactions*, 49(34), 12068-12081.

<https://doi.org/10.1039/D0DT02558E>

Journal Name

ARTICLE

not influence the Se-Ag-Se angle, which is still quite close to linear geometry ($178.89(3)^\circ$), and in accordance with previous rearranged structures in this series.

The dimeric $[\text{AgCl}\{\mu\text{-Se}(\text{SImes})\}]_2$ presents some interesting features; each of the Se atoms seems to coordinate to both silver moieties, though not entirely in a symmetrical manner

($2.7067(3) \text{ \AA}$ for Se1-Ag1 and $2.6579(4) \text{ \AA}$ for Se1-Ag2), and not with similar angles ($98.82(7)^\circ$ for C1-Se1-Ag1 and $107.57(7)^\circ$ for C1-Se1-Ag2). Yet, this is still in agreement with previous results obtained with the IMes analogue, and with reports by Ritch and co-workers on similar compounds.

Table 4. Overview of previous and current coordination behaviour of selenoureas to AgCl

[Se(NHC)]	Solid-state coordination to AgCl					Yield (%)
	Dimeric	Rearranged	di-coordinated	Tri-coordinated		
[Se(IPr)] ^a	-	-	[Ag{Se(IPr)} ₂]Cl [Ag{Se(IPr)} ₂][NO ₃] ^b	-	-	89 98
[Se(IMes)] ^a	[AgCl{μ-Se(IMes)}] ₂	-	-	-	-	87
[Se(ItBu)] ^a	-	-	-	[Ag{Se(ItBu)} ₃][0.5{AgCl ₃ }]	-	83
[Se(ICy)] ^a	-	-	-	[Ag{Se(ICy)} ₃]Cl ^c	-	78
[Se(IDD)] ^a	-	-	[AgCl{Se(IDD)}] ₂	-	-	93
[Se(SIPr)] ^d	-	[Ag{Se(SIPr)} ₂][AgCl ₂]	-	-	-	93
[Se(SImes)] ^d	[AgCl{μ-Se(SImes)}] ₂	-	-	-	-	94
[Se(IPr ^{Me})] ^d	No crystals obtained					98

Reaction conditions: [Se(NHC)] (1 equiv.) + AgCl (2 equiv.) in CHCl₃ overnight. All yields are isolated yields. ^aResults taken from reference [7]. ^bAgNO₃ was used instead of AgCl. ^cA different coordination behaviour was observed in the same crystal batch and [(Ag{Se(ICy)}₂)(μ-Se(ICy))][NO₃]₂ was identified by X-ray analysis. ^dNew complexes.

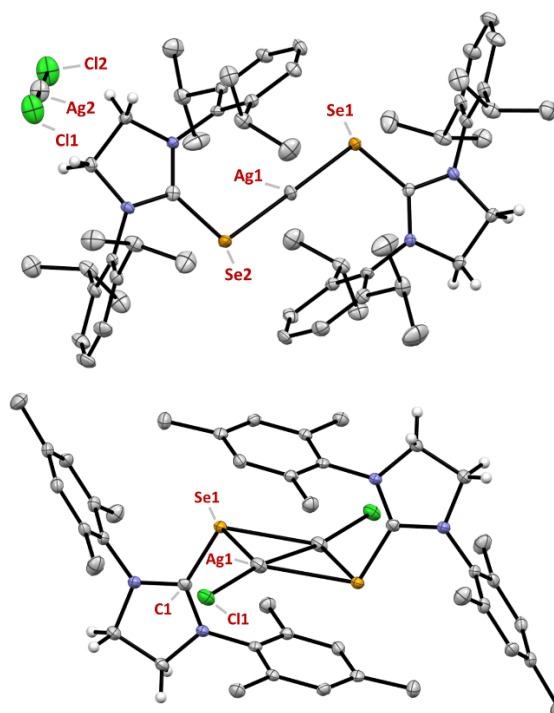


Figure 5. Molecular structures of $[\text{Ag}\{\text{Se}(\text{SIPr})\}_2][\text{AgCl}_2]$ (top) and $[\text{AgCl}\{\mu\text{-Se}(\text{SImes})\}]_2$ (bottom) determined by single-crystal X-ray diffraction analysis. Most hydrogen atoms

and solvent molecules are omitted for clarity. Thermal displacement ellipsoids are shown at the 50% probability level. See Table 5 for selected bond lengths and angles.

Table 5. Selected bond lengths and angles for the newly synthesised complexes

Structure	Se-M dist.	C1-Se dist.	C1-Se-M angles	Se-M-X angle ^a
[Cu{Se(SIPr)} ₂][CuCl ₂]	2.2814(8) 2.2797(8)	1.865(5) 1.867(5)	104.8(2) 105.9(2)	179.28(4)
[CuCl{Se(IPr ^{Me})}]	2.2596(4)	1.865(3)	104.22(8)	164.59(3)
[AuCl{Se(IPr ^{Me})}]	2.3614(5)	1.874(3)	106.95(9)	172.30(3)
[AuCl{Se(IPr ^{Cl})}]	2.3646(6)	1.868(3)	107.29(9)	174.00(3)
[AuCl{Se(ICy)}]	2.3714(6)	1.889(2)	97.38(6)	177.06(2)
[Au{Se(IAd)} ₂][AuCl ₂]	2.384(1) 2.387(1)	1.920(7) 1.928(7)	100.5(2) 100.9(2)	179.34(4)
[Ag{Se(SIPr)} ₂][AgCl ₂]	2.4812(5) 2.4816(5)	1.863(5) 1.867(5)	105.3(2) 104.1(2)	178.89(3)
[AgCl{μ-Se(SIMes)} ₂]	2.7067(3) ^b 2.6579(4) ^c	1.868(3) 1.868(3)	98.82(7) ^d 107.57(7) ^e	123.93(2) 126.93(2)

Distances are in (Å) and angles are in (°). ^aX = Cl or Se depending on coordination. ^bSe1-Ag1 bond distance. ^cSe1-Ag2 bond distance. ^dC1-Se1-Ag1 angle. ^eC1-Se1-Ag2 angle.

⁷⁷Se NMR: Next, we attempted to record the ⁷⁷Se spectra for all newly synthesised coinage-metal selenourea complexes (Figure 6). Of the nine complexes herein reported, only five showed clear signals in the ⁷⁷Se spectrum (two silver and three gold selenourea complexes). The ⁷⁷Se resonances are typically very weak for the coordinated complexes, and extended analyses are required, even on a cryoprobe-equipped spectrometer; the copper and silver complexes were particularly challenging to analyse and, despite numerous attempts, none of the new copper complexes showed any ⁷⁷Se NMR signals. The linear correlation between δ_{Se} for the selenourea ligands and δ_{Se} for the corresponding metal complexes is now updated with the newly obtained values, and the corrected trends are shown in Figure 7.

Conclusions

In summary, we describe in this report the synthesis and characterisation of new chalcogen-based urea compounds bearing a wide range of N-heterocyclic carbenes. A “weak base” approach has been investigated using either NEt₃ or K₂CO₃ as base, and good to excellent yields were obtained overall. Coordination of selenoureas is further investigated with Group

11 transition metals (i.e. copper(I), gold(I) and silver(I)), affording new copper, gold and silver complexes. Single crystal X-ray analysis was used to elucidate the solid-state coordination behaviour of these complexes in an attempt to establish a correlation between the latter and their corresponding electronic and steric properties. We showed that the geometry of a complex is highly influenced by a combination of electronic properties -mainly π-accepting ability- and steric hindrance of the ligands, as well as the nature of the metal, affording a variety of coordination behaviours. Ultimately, we believe that understanding these behaviours, through future in-depth studies, would allow us better prediction tools.

Experimental

NMR spectra were acquired on a Bruker AV3-400 spectrometer equipped with a liquid nitrogen cryoprobe, a Bruker AV400 spectrometer with a BBFO-z-ATMA probe or a Bruker Avance II 500MHz equipped with a 5mm triple channel probe head (TXO type). ¹H NMR spectra were referenced to residual solvent signals and ¹³C{¹H} DEPT Q NMR spectra to the deuterated solvent signal, while chemical shifts are reported in ppm. ⁷⁷Se NMR spectra were referenced to external standards. [¹H, ¹H] COSY, [¹H, ¹³C] HSQC and [¹H, ¹³C] HMBC spectra were used to assign signals. X-ray intensity data were collected at 100 K, on a Rigaku Oxford Diffraction Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using ω scans and Cu Kα (λ = 1.54184 Å) or Mo Kα (λ = 0.71073 Å) radiation. The images were interpreted and integrated with the program CrysAlisPro.²³ Using Olex2,²⁴ the structures were solved by direct methods using the ShelXS/T structure solution program and refined by full-matrix least-squares on F² using the ShelXL program package.^{25,26} Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). Sulfur, selenium, tellurium, AgCl, CuCl, triethylamine and potassium carbonate were obtained from commercial sources and used as supplied. [AuCl(SMe₂)] is prepared according to a known procedure.²⁷ Reagent grade solvents were always used as received unless otherwise stated. When the free carbene route was used for tellourea synthesis, reactions were performed in an Argon-filled glovebox using anhydrous solvents.

ARTICLE

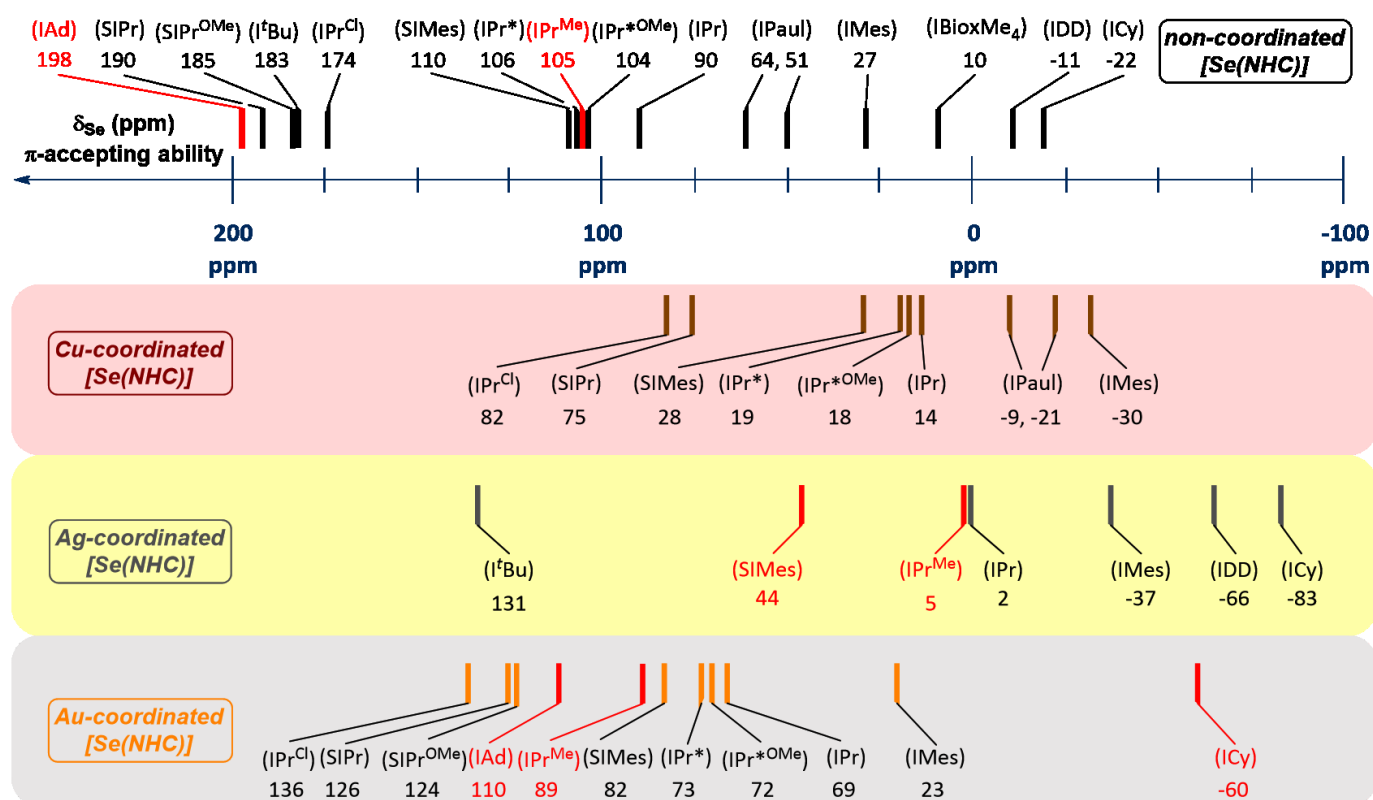


Figure 6. Overview of previous and current (values in red) chemical shifts of selenourea ligands, and their copper, silver, and gold complexes. All NMR data were acquired at 300 K in chloroform-d solution.

ARTICLE

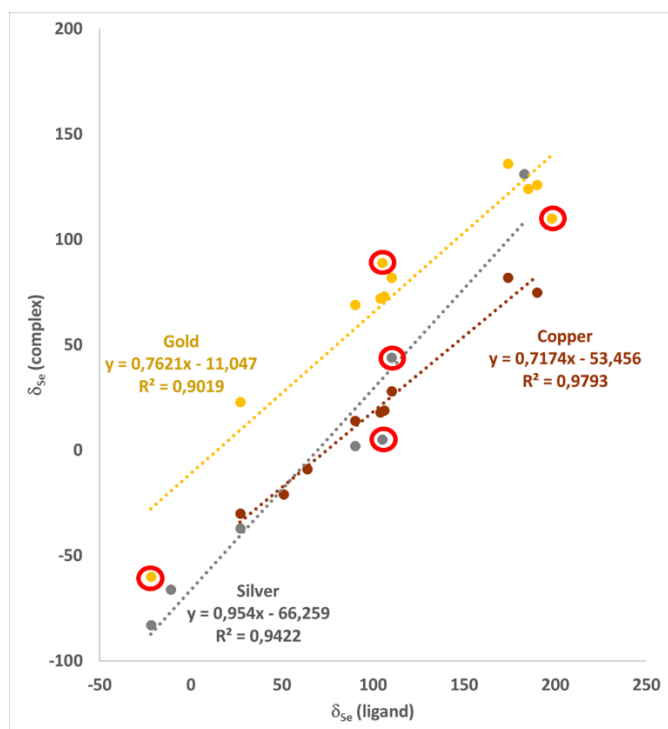


Figure 7. Updated plot of δ_{se} for copper, silver, and gold complexes of selenourea ligands versus δ_{se} of the corresponding ligand. Dots in red circles represent the new additions to this series.

General procedure for the synthesis of chalcogenoureas

[Se(IPr)]

Method 1: IPr-HCl (2 g, 4.70 mmol), K_2CO_3 (1.95 g, 14.12 mmol, 3 equiv.) and selenium (0.408 g, 5.18 mmol, 1.1 equiv.) were mixed together in acetone (20 mL) in a vial provided with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 1.76 g, 3.76 mmol, 80%.

Method 2: IPr-HCl (100 mg, 0.24 mmol), NEt_3 (0.098 mL, 0.71 mmol, 3 equiv.) and selenium (20.4 mg, 0.26 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 90.2 mg, 0.19 mmol, 82%. 1H NMR ($CDCl_3$, 400 MHz): δ_H 7.48 (t, $J = 8$ Hz 2H, Ar CH), 7.31 (d, $J = 7.8$ Hz, 4H, Ar CH), 7.01 (s, 2H, $N(CH)_2N$), 2.69 (sept, $J = 6.9$ Hz, 4H, $CHMe_2$), 1.34 (d, $J = 6.9$ Hz, 12H, CH_3), 1.20 (d, $J = 6.9$ Hz, 12H, CH_3). $^{13}C\{^1H\}$ DEPT Q NMR ($CDCl_3$, 101 MHz): δ_C 162.3 (C=Se), 146.3 (Ar C), 134.5 (Ar C), 130.3 (Ar CH), 124.4 (Ar CH), 121.2

($N(CH)_2N$), 29.1 ($CHMe_2$), 24.5 (CH_3), 23.5 (CH_3). The data obtained matched the reported values.²⁸

[S(IPr)]

Method 1: IPr-HCl (2 g, 4.70 mmol), K_2CO_3 (1.95 g, 14.12 mmol, 3 equiv.) and sulfur (0.166 g, 5.18 mmol, 1.1 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 1.96 g, 4.66 mmol, 99%.

Method 2: IPr-HCl (100 mg, 0.24 mmol), NEt_3 (0.098 mL, 0.071 mmol, 3 equiv.) and sulfur (8.3 mg, 0.259 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 97.9 mg, 0.23 mmol, 99%. 1H NMR ($CDCl_3$, 400 MHz): δ_H 7.46 (t, $J = 8$ Hz, 2H, Ar CH), 7.30 (d, $J = 7.8$ Hz, 4H, Ar CH), 6.84 (s, 2H, $N(CH)_2N$), 2.76 (sept, $J = 6.9$ Hz, 4H, $CHMe_2$), 1.32 (d, $J = 6.9$ Hz, 12H, CH_3), 1.22 (d, $J = 6.9$ Hz, 12H, CH_3). $^{13}C\{^1H\}$ DEPT Q NMR ($CDCl_3$, 101 MHz): δ_C 167.2 (C=S), 146.6 (Ar C), 133.9 (Ar C), 130.1 (Ar CH), 124.3 (Ar CH), 119.1 ($N(CH)_2N$), 29.0 ($CHMe_2$), 24.3 (CH_3), 23.5 (CH_3). The data obtained matched the reported values.²⁹

[Te(IPr)]

IPr-HCl (100 mg, 0.24 mmol), K_2CO_3 (97.6 mg, 0.71 mmol, 3 equiv.) and tellurium (45.0 mg, 0.35 mmol, 1.5 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through Celite using DCM which was then evaporated to yield a greyish powder. Yield: 94.7 mg, 0.18 mmol, 78%. 1H NMR ($CDCl_3$, 400 MHz): δ_H 7.51 (t, $J = 8$ Hz, 2H, Ar CH), 7.32 (d, $J = 7.8$ Hz, 4H, Ar CH), 7.20 (s, 2H, $N(CH)_2N$), 2.59 (sept, $J = 6.9$ Hz, 4H, $CHMe_2$), 1.38 (d, $J = 6.8$ Hz, 12H, CH_3), 1.18 (d, $J = 6.9$ Hz, 12H, CH_3). $^{13}C\{^1H\}$ DEPT Q NMR ($CDCl_3$, 101 MHz): δ_C 146.0 (C=Te), 138.1 (Ar C), 135.6 (Ar C), 130.6 (Ar CH), 124.5 (Ar CH), 123.5 ($N(CH)_2N$), 29.7 ($CHMe_2$), 24.7 (CH_3), 23.5 (CH_3). The data obtained matched the reported values.¹⁸

[Se(SIPr)]

Method 1: SIPr-HCl (2 g, 4.68 mmol), K_2CO_3 (1.94 g, 14.05 mmol, 3 equiv.) and selenium (1.109 g, 14.05 mmol, 3 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through

This is a peer-reviewed, accepted author manuscript of the following item: Saab, M., Nelson, D. J., Tzouras, N. V., Bayrakdar, T. A. C. A., Nolan, S. P., Nahra, F., & van Hecke, K. (2020). Straightforward access to chalcogenoureas derived from N-heterocyclic carbenes and their coordination chemistry. *Dalton Transactions*, 49(34), 12068-12081.

<https://doi.org/10.1039/D0DT02558E>

Journal Name

ARTICLE

silica using DCM which was then evaporated to yield a white powder. Yield: 1.98 g, 4.22 mmol, 90%.

Method 2: SIPr-HCl (100 mg, 0.23 mmol), NEt₃ (0.097 mL, 0.70 mmol, 3 equiv.) and selenium (20.3 mg, 0.26 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 99.7 mg, 0.212 mmol, 82%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.40 (t, *J* = 8 Hz, 2H, Ar CH), 7.24 (d, *J* = 8 Hz, 4H, Ar CH), 4.03 (s, 4H, N(CH₂)₂N), 3.06 (sept., *J* = 6.9 Hz, 4H, CHMe₂), 1.39 (d, *J* = 6.8 Hz, 12H, CH₃), 1.32 (d, *J* = 7 Hz, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 184.3 (C=Se), 147.3 (Ar C), 135.4 (Ar C), 129.5 (Ar CH), 124.6 (Ar CH), 51.5 (N(CH₂)₂N), 29.3 (CHMe₂), 24.9 (CH₃), 24.5 (CH₃). The data obtained matched the reported values.⁹

[S(SIPr)]

Method 1: SIPr-HCl (2 g, 4.68 mmol), K₂CO₃ (1.94 g, 14.05 mmol, 3 equiv.) and sulfur (0.225 g, 7.02 mmol, 1.5 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 1.88 g, 4.45 mmol, 95%.

Method 2: SIPr-HCl (100 mg, 0.234 mmol), NEt₃ (0.097 mL, 0.702 mmol, 3 equiv.) and sulfur (8.3 mg, 0.258 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 108.2 mg, 0.256 mmol, 99%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.39 (t, *J* = 8 Hz, 2H, Ar CH), 7.24 (d, *J* = 7.7 Hz, 4H, ArCH), 4.03 (s, 4H, N(CH₂)₂N), 3.08 (sept., *J* = 6.9 Hz, 4H, CHMe₂), 1.35 (d, *J* = 6.8 Hz, 12H, CH₃), 1.32 (d, *J* = 7 Hz, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 184.5 (C=S), 147.6 (Ar C), 134.9 (Ar C), 129.6 (Ar CH), 124.5 (Ar CH), 50.4 (N(CH₂)₂N), 29.2 (CHMe₂), 24.7 (CH₃), 24.5 (CH₃). The data obtained matched the reported values.³⁰

[Se(IMes)]

Method 1: IMes-HCl (2 g, 5.87 mmol), K₂CO₃ (2.432 g, 17.60 mmol, 3 equiv.) and selenium (0.694 g, 8.80 mmol, 1.5 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield an off-white powder. Yield: 2.114 g, 5.514 mmol, 94%.

Method 2: IMes-HCl (100 mg, 0.293 mmol), NEt₃ (0.122 mL, 0.88 mmol, 3 equiv.) and selenium (25.48 mg, 0.323 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The

solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield an off-white powder. Yield: 92.2 mg, 0.241 mmol, 82%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.02 (s, 4H, Ar CH), 6.96 (s, 2H, N(CH₂)₂N), 2.35 (s, 6H, CH₃), 2.13 (s, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 157.8 (C=Se), 139.6 (Ar C), 135.5 (Ar C), 134.4 (Ar C), 129.4 (Ar CH), 120.3 (N(CH₂)₂N), 21.3 (CH₃), 18.2 (CH₃). The data obtained matched the reported values.⁸

[S(IMes)]

Method 1: IMes-HCl (2 g, 5.87 mmol), K₂CO₃ (2.432 g, 17.60 mmol, 3 equiv.) and sulfur (0.282 g, 8.80 mmol, 1.5 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a greyish powder. Yield: 1.728 g, 5.139 mmol, 87%.

Method 2: IMes-HCl (100 mg, 0.293 mmol), NEt₃ (0.122 mL, 0.880 mmol, 3 equiv.) and sulfur (10.3 mg, 0.322 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a greige powder. Yield: 84.8 mg, 0.252 mmol, 86%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.01 (s, 4H, Ar CH), 6.79 (s, 2H, N(CH₂)₂N), 2.34 (s, 6H, CH₃), 2.15 (s, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 163.6 (C=S), 139.4 (Ar C), 135.9 (Ar C), 133.8 (Ar C), 129.4 (Ar CH), 118.2 (N(CH₂)₂N), 21.3 (CH₃), 18.0 (CH₃). The data obtained matched the reported values.³¹

[Se(SIMes)]

Method 1: SIMes-HCl (2 g, 5.833 mmol), K₂CO₃ (2.418 g, 17.50 mmol, 3 equiv.) and selenium (1.382 g, 17.50 mmol, 3 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield an off-white powder. Yield: 1.596 g, 4.142 mmol, 71%.

Method 2: SIMes-HCl (100 mg, 0.292 mmol), NEt₃ (0.12 mL, 0.875 mmol, 3 equiv.) and selenium (25.3 mg, 0.321 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield an off-white powder. Yield: 73.1 mg, 0.190 mmol, 65%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 6.98 (s, 4H, Ar C-H), 4.00 (s, 4H, N(CH₂)₂N), 2.32 (s, 12H, CH₃), 2.31 (s, 6H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 180.3 (C=S), 138.6 (Ar C), 136.4 (Ar C), 135.1 (Ar C), 129.7 (Ar CH), 48.9 (N(CH₂)₂N), 21.3 (CH₃), 18.0 (CH₃). The data obtained matched the reported values.⁸

[S(SIMes)]

Method 1: SIMes-HCl (2 g, 5.833 mmol), K₂CO₃ (2.418 g, 17.4978 mmol, 3 equiv.) and sulfur (0.280 g, 8.749 mmol, 1.5 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a greyish powder. Yield: 1.698 g, 5.016 mmol, 86%.

Method 2: SIMes-HCl (100 mg, 0.292 mmol), NEt₃ (0.12 mL, 0.875 mmol, 3 equiv.) and sulfur (10.3 mg, 0.321 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a greige powder. Yield: 70.1 mg, 0.207 mmol, 71%. ¹H NMR (CDCl₃, 400 MHz): δ_H 6.97 (s, 4H, Ar CH), 4.00 (s, 4H, N(CH₂)₂N), 2.32 (s, 12H, CH₃), 2.30 (s, 6H, CH₃). ¹³C{¹H} DEPT Q NMR (CDCl₃, 101 MHz): δ_C 181.2 (C=S), 138.4 (Ar C), 136.7 (Ar C), 134.7 (Ar C), 129.6 (Ar CH), 47.7 (N(CH₂)₂N), 21.3 (CH₃), 17.9 (CH₃). The data obtained matched the reported values.³²

[Se(IPr^{Me})]

Method 1: IPr^{Me}-HCl (1.00 g, 2.207 mmol), K₂CO₃ (0.915 g, 6.621 mmol, 3 equiv.) and selenium (0.261 g, 3.310 mmol, 1.5 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 0.969 g, 1.955 mmol, 89%.

Method 2: IPr^{Me}-HCl (20 mg, 0.044 mmol), NEt₃ (0.019 mL, 0.132 mmol, 3 equiv.) and selenium (3.8 mg, 0.049 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 16.4 mg, 0.033 mmol, 75%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.48 (t, J = 8 Hz, 2H, Ar CH), 7.31 (d, J = 7.8 Hz, 4H, Ar CH), 2.61 (sept., J = 6.9 Hz, 4H, CHMe₂), 1.94 (s, 6H, CH₃(imid)), 1.36 (d, J = 6.8 Hz, 12H, CH(CH₃)₂), 1.21 (d, J = 6.9 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} DEPT Q NMR (CDCl₃, 101 MHz): δ_C 159.5 (C=Se), 146.5 (Ar C), 132.8 (Ar C), 130.2 (CCH₃(imid)), 124.5 (Ar CH), 124.3 (Ar CH), 29.2 (CHMe₂), 24.4 (CH₃), 24.0 (CH₃), 10.5 (CH₃(imid)). ⁷⁷Se NMR (CDCl₃, 76MHz): δ_{Se} 105.2. CHN Calculated for C₂₉H₄₀N₂Se: C, 70.28; H, 8.14; N, 5.65. Found: C, 69.78; H, 8.43; N, 5.98.

[S(IPr^{Me})]

Method 1: IPr^{Me}-HCl (1.00 g, 2.207 mmol), K₂CO₃ (0.915 g, 6.621 mmol, 3 equiv.) and sulfur (0.106 g, 3.31 mmol, 1.5 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The reaction was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 0.861 g, 1.92 mmol, 87%.

Method 2: IPr^{Me}-HCl (20.0 mg, 0.044 mmol), NEt₃ (0.019 mL, 0.132 mmol, 3 equiv.) and sulfur (1.6 mg, 0.049 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The

solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 16.8 mg, 0.038 mmol, 85%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.46 (t, J = 8 Hz, 2H, Ar CH), 7.30 (d, J = 7.7 Hz, 4H, Ar CH), 2.67 (sept., J = 6.9 Hz, 4H, CHMe₂), 1.89 (s, 6H, CH₃(imid)), 1.32 (d, J = 6.8 Hz, 12H, CH(CH₃)₂), 1.22 (d, J = 6.7 Hz, 12H, CH(CH₃)₂). ¹³C{¹H} DEPT Q NMR (CDCl₃, 101 MHz): δ_C 165.2 (C=S), 146.9 (Ar C), 132.2 (Ar C), 130.0 (CCH₃(imid)), 124.6 (Ar CH), 121.9 (Ar CH) 29.1 (CHMe₂), 24.4 (CH₃), 23.9 (CH₃), 10.28 (CH₃(imid)). CHN Calculated for C₂₉H₄₀N₂S: C, 77.63; H, 8.99; N, 6.24. Found: C, 77.51; H, 8.81; N, 6.24.

[Se(IPr^{Cl})]

Method 1: IPr^{Cl}-HCl (1.00 g, 2.025 mmol), K₂CO₃ (0.839 g, 6.074 mmol, 3 equiv.) and selenium (0.239 g, 3.037 mmol, 1.5 equiv.) were mixed together in acetone (9 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 0.891 g, 1.660 mmol, 82%.

Method 2: IPr^{Cl}-HCl (100 mg, 0.205 mmol), NEt₃ (0.084 mL, 0.607 mmol, 3 equiv.) and selenium (17.6 mg, 0.222 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 104.2 mg, 0.194 mmol, 95%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.54 (t, J = 7.8 Hz, 2H, Ar CH), 7.34 (d, J = 7.8 Hz, 4H, Ar CH), 2.62 (sept., J = 6.9 Hz, 4H, CHMe₂), 1.35 (d, J = 6.8 Hz, 12H, CH₃), 1.26 (d, J = 6.9 Hz, 12H, CH₃). ¹³C{¹H} DEPT Q NMR (CDCl₃, 101 MHz): δ_C 162.2 (C=Se), 146.9 (Ar C), 131.4 (Ar CH), 131.2 (Ar C), 124.6 (Ar CH), 115.5 (N(CCl₂)₂N), 29.6 (CHMe₂), 24.0 (CH₃), 24.0 (CH₃). The data obtained matched the reported values.⁸

[S(IPr^{Cl})]

Method 1: IPr^{Cl}-HCl (1 g, 2.024 mmol), K₂CO₃ (0.839 g, 6.072 mmol, 3 equiv.) and sulfur (0.0974 g, 3.037 mmol, 1.5 equiv.) were mixed together in acetone (20 mL). The reaction was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 0.8612 g, 1.919 mmol, 87%.

Method 2: IPr^{Cl}-HCl (100 mg, 0.205 mmol), NEt₃ (0.084 mL, 0.6073 mmol, 3 equiv.) and sulfur (7.2 mg, 0.225 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 98.1 mg, 0.200 mmol, 98%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.52 (t, J = 7.8 Hz, 2H, Ar CH), 7.33 (d, J = 7.8 Hz, 4H, Ar CH), 2.67 (sept., J = 6.8 Hz, 4H, CHMe₂), 1.31 (d, J = 6.8 Hz, 12H), 1.27 (d, J = 6.9 Hz, 12H). ¹³C{¹H} DEPT Q NMR (CDCl₃, 101 MHz): δ_C 166.3 (C=S), 147.2 (Ar C), 131.0 (Ar C), 130.6 (Ar CH), 124.5 (Ar CH), 113.6 (N(CCl₂)₂N), 29.5 (CHMe₂), 24.0(CH₃), 24.0 (CH₃). CHN Calculated for C₂₇H₃₄N₂Cl₂S: C, 66.24; H, 7.00; N, 5.72. Found: C, 66.24; H, 7.14; N, 6.35.

This is a peer-reviewed, accepted author manuscript of the following item: Saab, M., Nelson, D. J., Tzouras, N. V., Bayrakdar, T. A. C. A., Nolan, S. P., Nahra, F., & van Hecke, K. (2020). Straightforward access to chalcogenoureas derived from N-heterocyclic carbenes and their coordination chemistry. *Dalton Transactions*, 49(34), 12068-12081.

<https://doi.org/10.1039/D0DT02558E>

Journal Name

ARTICLE

[Se(IPr*)]

Method 1: IPr*·HCl (1.00 g, 1.05 mmol), K₂CO₃ (0.437 g, 3.16 mmol, 3 equiv.) and selenium (0.249 g, 3.16 mmol, 3 equiv.) were mixed together in acetone (20 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 0.982 g, 0.989 mmol, 94%.

Method 2: IPr*·HCl (100 mg, 0.105 mmol), NEt₃ (0.044 mL, 0.316 mmol, 3 equiv.) and selenium (9.2 mg, 0.116 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 99.3 mg, 0.100 mmol, 95%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.39–7.37 (m, 8H, Ar C-H), 7.22–7.08 (m, 20H, Ph), 6.85–6.81 (m, 12H, Ar CH), 5.42 (s, 4H, CH(Ph)₂), 5.37 (s, 2H, N(CH₂)₂N), 2.22 (s, 6H, Me). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 161.0 (C=S), 143.5 (Ar C), 142.9 (Ar C), 141.7 (Ar C), 139.6 (Ar C), 134.0 (Ar C), 130.5 (Ar C), 130.2 (Ar CH), 129.5 (Ar CH), 128.3 (Ar CH), 128.2 (Ar CH), 126.6 (Ar CH), 126.4 (Ar CH), 121.0 (CH_{imid}), 51.9 (CHPh₂), 22.0 (CH₃). The data obtained matched the reported values.⁵

[S(IPr*)]

Method 1: IPr*·HCl (1.00 g, 1.05 mmol), K₂CO₃ (0.437 g, 3.16 mmol, 3 equiv.) and sulfur (0.101 g, 3.16 mmol, 3 equiv.) were mixed together in acetone (5 mL) in a vial equipped with a stirring bar. The reaction was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 0.945 g, 0.999 mmol, 95%.

Method 2: IPr*·HCl (100 mg, 0.105 mmol), NEt₃ (0.044 mL, 0.316 mmol, 3 equiv.) and sulfur (3.7 mg, 0.116 mmol, 1.1 equiv.) were mixed together in acetone (1 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 90.5 mg, 0.096 mmol, 91%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.32 (d, *J* = 7.2 Hz, 8H, Ar CH), 7.22–7.1 (m, 24H, Ar CH), 6.86–6.83 (m, 12H, Ar CH), 5.46 (s, 4H, CH(Ph)₂), 5.29 (s, 2H, N(CH₂)₂N), 2.22 (s, 6H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 165.6 (C=S), 143.7 (Ar C), 142.9 (Ar C), 141.8 (Ar C), 139.4 (Ar C), 133.3 (Ar C), 130.4 (Ar C), 130.1 (Ar CH), 129.5 (Ar CH), 128.4 (Ar CH), 128.2 (Ar CH), 126.5 (Ar CH), 126.4 (Ar CH), 118.9 (CH_{imid}), 51.8 (CHPh₂), 22.0 (CH₃). The data obtained matched the reported values.³³

[Se(ICy)]

ICy·HBF₄ (1.00 g, 3.12 mmol), K₂CO₃ (1.30 g, 9.37 mmol, 3 equiv.) and selenium (0.740 g, 9.37 mmol, 3 equiv.) were mixed together in acetone (14 mL) in a vial equipped with a stirring

bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 0.846 g, 2.72 mmol, 87%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 6.88 (s, 2H, N(CH₂)₂N), 4.88 (tt, 2H, *J* = 11.8, 3.8 Hz, NCH), 2.12–2.08 (m, 4H, CH₂), 1.88–1.84 (m, 4H, CH₂), 1.76–1.73 (m, 2H, CH₂), 1.53–1.36 (m, 8H, CH₂), 1.24–1.14 (m, 2H, CH₂). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 Hz): δ_C 153.3 (C=Se), 115.8 (N(CH₂)₂N), 58.0 (NCH), 32.7 (CH₂), 25.5 (CH₂), 25.5 (CH₂). The data obtained matched the reported values.⁶

[S(ICy)]

ICy·HBF₄ (1.00 g, 3.12 mmol), K₂CO₃ (1.30 g, 9.37 mmol, 3 equiv.) and sulfur (0.300 g, 9.37 mmol, 3 equiv.) were mixed together in acetone (13.6 mL) in a vial equipped with a stirring bar. The reaction was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a white powder. Yield: 0.86 g, 3.2 mmol, 99%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 6.72 (s, 2H, N(CH₂)₂N), 4.88 (tt, 2H, *J* = 11.8, 3.8 Hz, NCH), 2.08–2.05 (m, 4H, CH₂), 1.87–1.83 (m, 4H, CH₂), 1.75–1.72 (m, 2H, CH₂), 1.51–1.34 (m, 8H, CH₂), 1.24–1.12 (m, 2H, CH₂). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 160.0 (C=S), 113.8 (N(CH₂)₂N), 55.9 (NCH), 32.6 (CH₂), 25.6 (CH₂), 25.6 (CH₂). **HRMS** *m/z* calcd for C₁₅H₂₄N₂S (M+H⁺) 265.17; found 265.1741.

[Se(IAd)]

IAd·HCl (2.00 g, 5.36 mmol), K₂CO₃ (2.22 g, 16.09 mmol, 3 equiv.) and selenium (1.270 g, 16.09 mmol, 3 equiv.) were mixed together in acetone (24 mL) in a vial equipped with a stirring bar. The mixture was stirred at 60 °C for 16 h. The solvent was evaporated and the residue was filtered through silica using DCM which was then evaporated to yield a brown powder. Yield: 0.2673 g, 0.643 mmol, 12%. **¹H NMR** (300 MHz; CDCl₃): δ_H 6.98 (s, 2H, CH_{imid}), 2.76 (m, 12H, CH₂), 2.21 (s, 6H, CH), 1.74 (dd, *J* = 12.1 Hz, 12H, CH₂). **¹³C{¹H} DEPT Q NMR** (101 MHz, CDCl₃): δ_C 148.0 (C=Se), 115.6 (CH_{imid}), 62.1 (CN), 40.2 (CH₂), 36.1 (CH₂), 30.3 (CH). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} 198.3. The data obtained matched the reported values.⁶

General procedure for the synthesis of telluroreas *via* free NHCs

[Te(SIPr)]

A vial equipped with a stirring bar was charged with free SIPr (100 mg, 0.256 mmol) and elemental tellurium (32.6 mg, 0.256 mmol) in THF (10 mL) under argon. The reaction was stirred at room temperature for 16 h. The reaction was then filtered through Celite using DCM which was then evaporated to yield a greige powder. Yield: 103 mg, 0.198 mmol, 77%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.43 (t, *J* = 8 Hz, 2H, Ar CH), 7.27 (d, *J* = 8 Hz, 4H, Ar CH), 4.04 (s, 4H, N(CH₂)₂N), 3.02 (sept., *J* = 6.8 Hz, 4H, CHMe₂), 1.44 (d, *J* = 6.8 Hz, 12H, CH₃), 1.31 (d, *J* = 7.0 Hz, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 168.2 (C=Te),

147.0 (Ar C), 136.4 (Ar C), 129.7 (Ar CH), 124.7 (Ar CH), 52.6 (N(CH₂)₂N), 29.4 (CHMe₂), 25.2 (CH₃), 24.6 (CH₃). **CHN** Calculated for C₂₁H₂₆N₂Te: C, 62.58; H, 7.39; N, 5.41. Found: C, 62.63; N, 5.21; H, 7.82.

[Te(SIMes)]

A vial equipped with a stirring bar was charged with free SIMes (100 mg, 0.326 mmol) and elemental tellurium (41.6 mg, 0.326 mmol) in THF (10 mL) under argon. The reaction was stirred at room temperature for 16 h. The reaction was then filtered through Celite using DCM which was then evaporated to yield a grey powder. Yield: 106 mg, 0.244 mmol, 75%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 6.99 (s, 4H, Ar CH), 4.01 (s, 4H, N(CH₂)₂N), 2.30 (s, 6H, CH₃), 2.32 (s, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 163.0 (C=Te), 138.9 (Ar C), 136.2 (Ar C), 136.0 (Ar C), 129.8 (Ar CH), 50.0 (N(CH₂)₂N), 21.3 (CH₃), 18.4 (CH₃). **CHN** Calculated for C₂₁H₂₆N₂Te: C, 58.11; H, 6.04; N, 6.45. Found: C, 58.05; H, 6.44; N, 6.57.

General procedure for the Cu(I)-coordination to selenoureas

[Cu{Se(SIPr)}₂][CuCl₂]

This complex was synthesised according to a previously reported procedure.⁷

[CuCl{Se(IPr^{Me})}]

A vial equipped with a stirring bar was charged with [Se(IPr^{Me})] (20 mg, 0.040 mmol) and CuCl (8 mg, 0.081 mmol, 2.0 equiv.) in chloroform (1 mL). The reaction was stirred at room temperature overnight. Afterwards, the solvent was evaporated and the residue was filtered through Celite using DCM which was then evaporated to yield a white powder. Yield: 93%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.65 (t, *J* = 7.8 Hz, 2H, Ar CH), 7.41 (d, *J* = 7.8 Hz, 4H, Ar CH), 2.44 (sept., *J* = 6.6 Hz, 4H, CHMe₂), 1.99 (s, 6H, CH_{3(imid)}), 1.38 (d, *J* = 6.7 Hz, 12H, CH₃), 1.22 (d, *J* = 6.9 Hz, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 126 MHz): δ_C 152.9 (C=Se), 145.8 (Ar C), 131.9 (Ar CH), 130.9 (CCH_{3(imid)}), 126.8 (Ar C), 125.8 (Ar CH), 29.3 (CHMe₂), 24.6 (CH₃), 24.0 (CH₃), 10.4 (CH_{3(imid)}).

General procedure for the Ag(I)-coordination to selenoureas

[Ag{Se(SIPr)}₂][AgCl₂]

A vial equipped with a stirring bar was charged with [Se(SIPr)] (100 mg, 0.213 mmol) and AgCl (61 mg, 0.426 mmol, 2.0 equiv.) in chloroform (2 mL). The reaction was stirred at room temperature overnight. Afterwards, the solvent was evaporated and the residue was filtered through Celite using DCM which was then evaporated to yield a white powder. Yield: 121.9 mg, 93%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.47 (t, *J* = 7.7 Hz, 2H, Ar CH), 7.28 (d, *J* = 7.8 Hz, 4H, Ar CH), 4.09 (s, 4H, NCH₂), 2.91 (m, 4H, CHMe₂), 1.37 (d, *J* = 6.8 Hz, 12H, CH₃), 1.31 (d, *J* = 6.9 Hz, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 181.4 (C=Se, determined by HSQC), 146.8 (Ar C), 130.7 (Ar C), 125.4 (Ar CH), 52.0 (N(CH)₂N), 29.3 (CHMe₂), 24.9 (CH₃), 24.7 (CH₃). **CHN** Calculated for C₅₄H₇₆Ag₂Cl₂N₄Se₂: C, 52.91; H, 6.25; N, 4.57. Found: C, 53.21; H, 6.49; N, 4.62.

[AgCl{μ-Se(SIMes)}]₂

A vial equipped with a stirring bar was charged with [Se(SIMes)] (100 mg, 0.259 mmol) and AgCl (74 mg, 0.519 mmol, 2.0 equiv.) in chloroform (2.5 mL). The reaction was stirred at room temperature overnight. Afterwards, the solvent was evaporated and the residue was filtered through Celite using DCM which was then evaporated to yield a white powder. Yield: 137 mg, 94%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.02 (s, 4H, Ar CH), 4.05 (s, 4H, N(CH₂)₂N), 2.34 (s, 6H, CH₃), 2.27 (s, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 177.8 (C=Se), 140.0 (Ar C), 135.9 (Ar C), 133.8 (Ar C), 130.4 (Ar CH), 49.3 (N(CH₂)₂N), 21.4 (CH₃), 17.9 (CH₃). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} 42.0. **HRMS** *m/z* calcd for C₄₂H₅₂AgN₄Se₂⁺ [M – (AgCl₂)]⁺ 879.16; found 879.1569.

[AgCl{Se(IPr^{Me})}]

A vial equipped with a stirring bar was charged with [Se(IPr^{Me})] (100 mg, 0.202 mmol) and AgCl (57.8 mg, 0.404 mmol, 2.0 equiv.) in chloroform (1.9 mL). The reaction was stirred at room temperature overnight. Afterwards, the solvent was evaporated and the residue was filtered through Celite using DCM which was then evaporated to yield a white powder. Yield: 126 mg, 98%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.60 (t, *J* = 7.1 Hz, 2H, Ar CH), 7.38 (d, *J* = 7.7 Hz, 4H, Ar CH), 2.42 (sept., *J* = 8 Hz, 2H, CHMe₂), 1.98 (s, 6H, CH₃), 1.34 (d, *J* = 6.8 Hz, 12H, CHCH₃), 1.20 (d, *J* = 6.9 Hz, 12H, CHCH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 186.9 (C=Se), 145.9 (Ar C), 131.7 (Ar CH), 125.5 (Ar CH), 29.2 (CHMe₂), 24.6 (CH₃), 24.0 (CH₃), 10.4 (CH₃). **⁷⁷Se NMR** (CDCl₃, 76MHz): δ_{Se} 5.26. **CHN** Calculated for C₂₉H₄₀AgClN₂Se: C, 54.52; H, 6.31; N, 4.38. Found: C, 55.17; H, 6.74; N, 4.43.

General procedure for the Au(I)-coordination to selenoureas

[AuCl{Se(IPr^{Me})}]

A vial equipped with a stirring bar was charged with [Se(IPr^{Me})] (100 mg, 0.202 mmol) and [AuCl(SMe₂)] (59.43 mg, 0.202 mmol, 1 equiv.) in acetone (1 mL). The reaction was stirred at room temperature for 3 h. Afterwards, the solvent was evaporated and the residue was filtered through Celite using DCM which was then evaporated to yield a white powder. Yield: 148.8 mg, 99%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.64 (t, *J* = 7.8 Hz, 2H, Ar CH), 7.39 (d, *J* = 7.8 Hz, 4H, Ar CH), 2.41 (sept., *J* = 6.8 Hz, 2H), 2.00 (s, 6H, CH₃), 1.40 (d, *J* = 6.8 Hz, 12H, CH₃), 1.21 (d, *J* = 6.9 Hz, 12H, CH₃). **¹³C{¹H} DEPT Q NMR** (CDCl₃, 101 MHz): δ_C 147.5 (C=Se), 145.8 (Ar C), 131.8 (Ar CH), 131.0 (Ar C), 127.5 (Ar C), 125.5 (Ar CH), 29.3 (CHMe₂), 24.5 (CH₃), 24.1 (CH₃), 10.3 (CH₃). **⁷⁷Se NMR** (CDCl₃, 76MHz): δ_{Se} 88.9. **CHN** Calculated for C₂₉H₄₀AuClN₂Se: C, 47.84; H, 5.54; N, 3.85. Found: C, 47.39; H, 5.57; N, 3.92.

[AuCl{Se(IPr^{Cl})}]

This complex was synthesised according to a previously reported procedure.⁸

[AuCl{Se(ICy)}]

A vial equipped with a stirring bar was charged with [Se(ICy)] (100 mg, 0.321 mmol) and [AuCl(SMe₂)] (94.6 mg, 0.321 mmol, 1 equiv.) in acetone (1.4 mL). The reaction was stirred at room temperature for 3 h. Afterwards, the solvent was evaporated

This is a peer-reviewed, accepted author manuscript of the following item: Saab, M., Nelson, D. J., Tzouras, N. V., Bayrakdar, T. A. C. A., Nolan, S. P., Nahra, F., & van Hecke, K. (2020). Straightforward access to chalcogenoureas derived from N-heterocyclic carbenes and their coordination chemistry. *Dalton Transactions*, 49(34), 12068-12081.

<https://doi.org/10.1039/D0DT02558E>

Journal Name

ARTICLE

and the residue was filtered through Celite using DCM which was then evaporated to yield a white powder. Yield: 177 mg, 99%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.13 (s, 2H, N(CH)₂N), 4.98 (ddd, *J*=15.4, 7.8, 3.8 Hz, 2H, N-CH), 2.21-2.16 (m, 4H, CH₂), 1.94-1.87 (m, 4H, CH₂), 1.81-1.77 (m, 2H, CH₂), 1.56 – 1.47 (m, 8H, CH₂), 1.27-1.17 (m, 2H, CH₂). ¹³C{¹H} DEPT Q NMR (CDCl₃, 101 MHz): δ_C 139.1 (C=Se), 118.6 (CH_{imid}), 59.8 (NCH), 31.2 (CH₂), 25.4 (CH₂), 25.1 (CH₂). ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se}-60.4. CHN Calculated for C₁₅H₂₄AuClN₂Se: C, 33.13; H, 4.45; N, 5.15. Found: C, 33.42; H, 4.65; N, 5.46.

[Au{Se(IAd)}₂][AuCl₂]

A vial equipped with a stirring bar was charged with [Se(IAd)] (100 mg, 0.241 mmol) and [AuCl(SMe₂)] (70.9 mg, 0.241 mmol, 1 equiv.) in acetone (1.1 mL). The reaction was stirred at room temperature for 3 h. Afterwards, the solvent was evaporated and the residue was filtered through Celite using DCM which was then evaporated to yield a brown powder. Yield: 144.9 mg, 93%. ¹H NMR (400 MHz; CDCl₃): δ_H 7.24 (s, *J*=5.9 Hz, 2H, CH_{imid}), 2.76 (d, *J*=2.5 Hz, 12H, CH₂), 2.30 (br. s, 6H, CH), 1.76 (m, 6H, CH₂), 1.75 (m, 6H, CH₂). ¹³C{¹H} DEPT Q NMR (101 MHz, CDCl₃): δ_C 132.6 (C=Se), 118.6 (CH_{imid}), 65.5 (CN), 41.4 (CH₂), 35.7 (CH₂), 30.3 (CH). ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se} 110.7. HRMS *m/z* calcd for C₄₆H₆₄AuN₄Se₂⁺ [M – (AuCl₂)]⁺ 1029.31; found 1029.3170.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

DJN thanks the University of Strathclyde for a Chancellor's Fellowship (2014-18) and Mr Craig Irving and Dr John Parkinson for assistance with NMR spectroscopy facilities. S.P.N. thanks the Special Research Fund (BOF) of Ghent University (Doctoral Scholarship 01D14919, as well as starter and senior research grants) for support. Umicore AG is thanked for gifts of materials. KVH, FN and MS thank the Hercules Foundation (project AUGE/11/029) and the Special Research Fund (BOF) – UGent (project 01N03217) for funding.

Notes and references

§ Crystallographic data underpinning this study can be downloaded from the Cambridge Structural Database (CSD) via the following link: [https://www.ccdc.cam.ac.uk/structures/\(CCDC 1997588-1997598\)](https://www.ccdc.cam.ac.uk/structures/(CCDC 1997588-1997598)). See supporting information for more details.

- 1 M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485-496.

- 2 H. Clavier and S. P. Nolan, *Chem. Commun.*, 2010, **46**, 841-861
- 3 D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723-6753.
- 4 H. V. Huynh, *Chem. Rev.*, 2018, **118**, 9457-9492.
- 5 D. J. Nelson, A. Collado, S. Manzini, S. Meiries, A. M. Z. Slawin, D. B. Cordes and S. P. Nolan, *Organometallics*, 2014, **33**, 2048-2058.
- 6 S. V. C. Vummaleti, D. J. Nelson, A. Poater, A. Gomez-Suarez, D. B. Cordes, A. M. Z. Slawin, S. P. Nolan and L. Cavallo, *Chem. Sci.*, 2015, **6**, 1895-1904.
- 7 F. Nahra, K. Van Hecke, A. R. Kennedy and D. J. Nelson, *Dalton Trans.*, 2018, **47**, 10671-10684.
- 8 D. J. Nelson, F. Nahra, S. R. Patrick, D. B. Cordes, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2014, **33**, 3640-3645.
- 9 A. Liske, K. Verlinden, H. Buhl, K. Schaper and C. Ganter, *Organometallics*, 2013, **32**, 5269-5272.
- 10 K. Verlinden, H. Buhl, W. Frank and C. Ganter, *Eur. J. Inorg. Chem.*, 2015, **2015**, 2416-2425.
- 11 H. Buhl, K. Verlinden, C. Ganter, S. B. Novaković and G. A. Bogdanović, *Eur. J. Inorg. Chem.*, 2016, **2016**, 3389-3395.
- 12 Y. Koto, F. Shibahara and T. Murai, *Org. Biomol. Chem.*, **2017**, **15**, 1810-1820.
- 13 (a) A. Molter and F. Mohr, *Coord. Chem. Rev.*, 2010, **254**, 19-45; (b) M. T. Aroz, M. C. Gimeno, M. Kulcsar, A. Laguna, and V. Lippolis, *Eur. J. Inorg. Chem.*, 2011, 2884-2894.
- 14 J. S. Ritch, *Phys. Sci. Rev.* 2018, **4**. doi: 10.1515/psr-2017-0128.
- 15 A. Doddi, M. Peters and M. Tamm, *Chem. Rev.*, 2019, **119**, 6994-7112.
- 16 J. E. McDonough, A. Mendiratta, J. J. Curley, G. C. Fortman, S. Fantasia, C. C. Cummins, E. V. Rybak-Akimova, S. P. Nolan and C. D. Hoff, *Inorg. Chem.*, 2008, **47**, 2133-2141.
- 17 N. Nakata, F. Kawachi, S. Takahashi and A. Ishii, *N. J. Chem.*, 2019, **43**, 10894-10898.
- 18 K. Srinivas, P. Suresh, C. N. Babu, A. Sathyanarayana and G. Prabusankar, *RSC Adv.*, 2015, **5**, 15579-15590.
- 19 N. V. Tzouras, F. Nahra, L. Falivene, L. Cavallo, M. Saab, K. Van Hecke, A. Collado, C. J. Collett, A. D. Smith, C. S. J. Cazin and S. P. Nolan, *Chem. Eur. J.*, 2020, **26**, 4515-4519.
- 20 J. H. Perras, S. M. J. Mezibroski, M. A. Wiebe and J. S. Ritch, *Dalton Trans.*, 2018, **47**, 1471-1478.
- 21 E. M. Higgins, J. A. Sherwood, A. G. Lindsay, J. Armstrong, R. S. Massey, R. W. Alder and A. C. O'Donoghue, *Chem. Commun.*, 2011, **47**, 1559-1561.
- 22 M. K. Denk, S. Gupta, J. Brownie, S. Tajammul and A. J. Lough, *Chem. Eur. J.*, 2001, **7**, 4477-4486.
- 23 Rigaku Oxford Diffraction, (2018), CrysAlisPro Software system, Rigaku Corporation, Yarnton, UK.
- 24 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.

- 25 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.
- 26 G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3-8.
- 27 K. C. Dash and H. Schmidbaur, *Chem. Ber.*, 1973, **106**, 1221-1225.
- 28 I. Abdellah, B. Cassirame, S. Condon, J. Y. Nedelec and C. Pichon, *Current topics in electrochemistry*, 2011, **16**, 81-91.
- 29 S. P. Wei, X. G. Wei, X. Y. Su, J. S. You and Y. Ren, *Chem. Eur. J.*, 2011, **21**, 5965-5971.
- 30 M. Paas, B. Wibbeling, R. Frohlich and F. E. Hahn, *Eur. J. Inorg. Chem.*, 2006, 158-162.
- 31 T. K. Das and A. T. Biju, *Eur. J. Inorg. Chem.*, 2017, 4500-4506.
- 32 D. Yang, Y. C. Chen and N. Y. Zhu, *Org. Lett.*, 2004, **6**, 1577-1580.
- 33 N. Parvin, S. Pal, S. Khan, S. Das, S. K. Pati and H. W. Roesky, *Inorg. Chem.*, 2017, **56**, 1706-1712.