

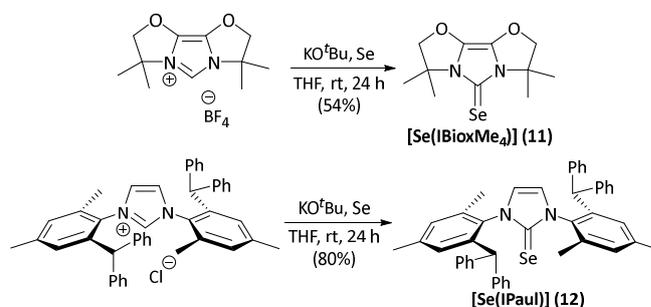
Figure 2. Previously-reported selenourea ligands used for this study.

Results and Discussion

Synthesis of Ligands

This work was carried out with the selenourea ligands (**1** – **10**) depicted in Figure 2. These are based on the widely-used NHC ligands IPr (**1**),^{16, 17} IPr^{Cl} (**2**), SIPr (**3**), IMes (**4**), SIMes (**5**), IPr* (**6**),¹⁸ IPr*OMe (**7**), ItBu (**8**),¹⁹ ICy (**9**), and IDD (**10**).²⁰ The selenourea ligands were prepared using previously-reported synthetic routes, either from the free carbene plus excess selenium, or from the imidazolium salt plus potassium *tert*-butoxide and excess selenium.^{10–12, 15} All ligands are stable at room temperature under air, and were worked-up and stored without any special precautions to eliminate air or moisture. The ⁷⁷Se NMR chemical shifts were checked *versus* literature values, and found to be within 2 ppm in each case. While it is known that δ_{Se} can be a function of concentration, we did not control this factor when preparing NMR samples. Instead, we used samples that were as concentrated as possible throughout this work, in order to overcome the relatively low sensitivity of this nuclide.²¹ The chemical shift range for ⁷⁷Se is sufficiently wide, and the known range of δ_{Se} for selenourea ligands covers a significant part of this range, so that small differences in δ_{Se} do not affect the validity of our conclusions.

Two new selenoureas were prepared from Glorius's IBioxMe₄ ligand (**11**)²² and from the recently-reported IPaul ligand (**12**),²³ and characterised by methods including NMR spectroscopy (Scheme 1). The IPaul derivative exists as a mixture of two rotamers, with δ_{Se} values (51, 64 ppm) lying midway between those for IMes (27 ppm) and IPr* (106 ppm), consistent with the structure of IPaul as an IMes/IPr* hybrid. For **11**, δ_{Se} is rather low (10 ppm), potentially as a result of the resonance donating properties of the oxygen atoms attached to C⁴ and C⁵ of the imidazol-2-ylidene core.



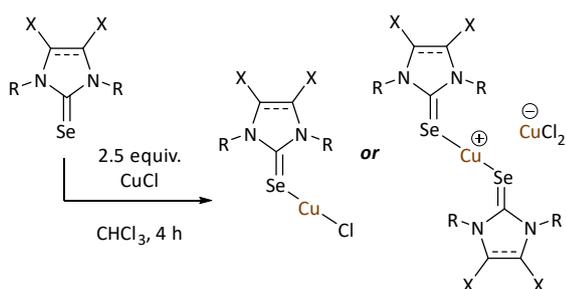
Scheme 1. Synthesis of ligands **11** and **12**, from IBioxMe₄ and IPaul, respectively.

Synthesis of Copper(I) Complexes

Selenoureas based on benzimidazole and imidazole scaffolds have previously been coordinated to copper, yielding complexes with a number of different geometries. Kimani has studied the coordination of 1,3-dimethyl-1,3-dihydro-2*H*-imidazole-2-selenone (**13**) with Cu(OTf)₂ to yield [Cu(**13**)₄][OTf]₂ with concomitant formation of [**13**]₂ (with a Se–Se bond) in a process that uses **13** as a reductant as well as a ligand.²⁴ The reaction of **13** with CuX (X = Cl, Br, I) has also been probed, leading to the isolation of [Cu₄X₄(**13**)₄] (X = Br, I) and [CuX(**13**)₂] (X = Cl, Br, I) depending on the choice of solvent.²⁵ Singh used 1,3-dibutyl-1,3-dihydro-2*H*-benzo[*d*]imidazole-2-selenone (**14**) to prepare [CuBr(**14**)₂] and [CuI(**14**)₂];²⁶ lower δ_{Se} values were reported for each selenourea upon coordination to a metal centre. Selenoureas have been coordinated to copper scaffolds including those supported by tris(pyrazolyl)borate ligands²⁷ and complexes supported by soft scorpionate ligands.²⁸ Dimeric copper complexes, with one or two bridging selenourea ligands, have also been disclosed.²⁹ However, in the majority of these examples, the *N*-substituents are rather small primary alkyl groups. A search of the Cambridge Structural Database (CSD; March 2018) reveals few examples with bulkier selenoureas:

Roesky reported [CuBr(**6**)],³⁰ while Prabusankar has used [Cu(L)₂]X complexes (L = **1** or **4**; X = BF₄ or ClO₄) as catalysts for the hydroboration of alkynes.³¹ Here, we have deployed compounds with a range of steric profiles including derivatives of bulky-yet-flexible carbenes such as IPr* (i.e. **6**, **7** and **12**).

The ligands were systematically exposed to 2.5 equiv. copper(I) chloride in chloroform (Scheme 2; Table 1). Excess copper(I) chloride was used to promote the formation of simple [CuCl(L)] complexes, rather than species with multiple selenoureas coordinated to one copper centre. The copper(I) products listed in Table 1 were fully characterised by ¹H, ¹³C{¹H}, and ⁷⁷Se NMR spectroscopy (*vide infra*), and several examples were characterised by elemental analysis.



Scheme 2. Synthesis of copper complexes; see Table 1 for yields.

Table 1: Outcomes from synthetic experiments with copper chloride.

Ligand	Product (Solid State)	Yield
1	[CuCl(1)]	81%
2	[CuCl(2)] ^a	47%
3	[CuCl(3)] ^a	86%
4	[Cu(4) ₂][CuCl ₂]	90%
5	[Cu(5) ₂][CuCl ₂]	86%
6	[CuCl(6)]	70%
7	[CuCl(7)] ^a	64%
8	- ^b	-
9	- ^b	-
10	- ^b	-
11	- ^b	-
12	[CuCl(12)] ^a	79%

a) Formulated based on crystallographic data for complexes of **1** and **6**; see Figure 3 and text. b) No tractable product was obtained.

The ligands used in this work are far bulkier than **13**, and so it was expected that this would preclude the formation of [CuCl(L)₂] or metal cluster complexes. The reactions of bulkier selenoureas such as **1** and **6** quickly produced the copper complexes, which could be isolated as bench-stable pale solids after filtration through celite, removal of the solvent *in vacuo*, and washing with alkanes. These compounds were characterised by X-ray diffraction of crystals obtained by the slow diffusion of hexane into a concentrated DCM or chloroform solution of the complex (Figure 3). Attempts to prepare crystals from THF solutions led to the precipitation of green or blue powders, suggestive of disproportionation processes to form copper(II).

Surprisingly, a search of the CSD revealed that no [CuCl(L)]-type complexes with selenoureas have been submitted to the

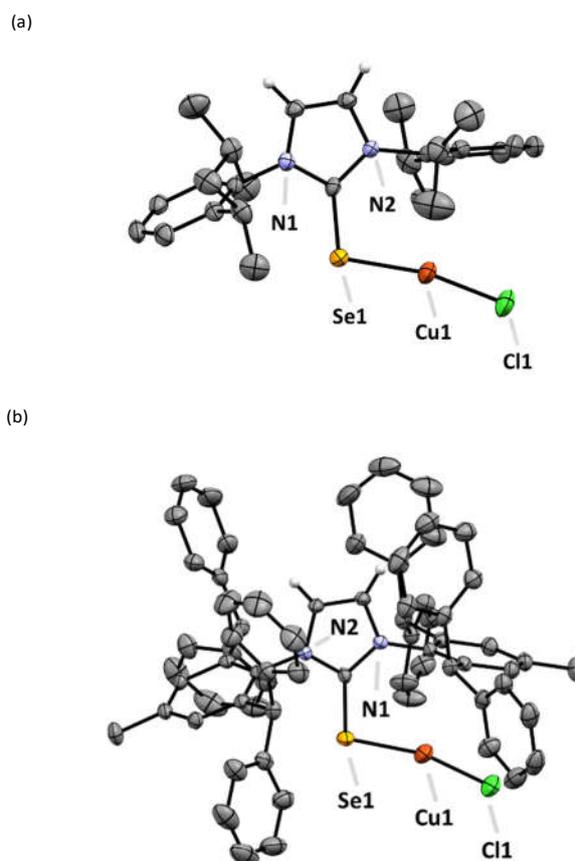


Figure 3. Molecular structures of [CuCl(L)] complexes (L = (a) **1**, (b) **6**) determined by X-ray crystal diffraction analysis. Most hydrogen atoms are omitted for clarity. Thermal displacement ellipsoids are shown at the 50% probability level.

database; the closest analogue is Roesky's [CuBr(**6**)] complex.³⁰ Complexes derived from ligands **1** and **6** feature a bent C-Se-Cu angle (103.71(9)° and 104.66(7)°, respectively).³² The Se-Cu-Cl angles deviate slightly from a linear geometry (168.21(3)° and 165.79(3)°, respectively), but the distance between copper and the *ipso*-carbon on the *N*-aryl substituents is greater than the sum of van der Waals radii, therefore excluding any possible interaction between the two.

The results of reactions with selenoureas derived from *N,N'*-dialkylimidazol-2-ylidenes were rather different. The reactions of **8** - **11** produced mixtures of unidentified products. The dark colours of the resulting solutions suggest that copper(II) complexes may have formed, but attempts to crystallise and characterise these species were not successful.

The reaction of **4** with CuCl produced an off-white compound that appeared by ¹H NMR to be a single compound, with broad peaks in both the ¹H and ⁷⁷Se NMR spectra ($\omega_{1/2}$ = *ca.* 4 Hz and *ca.* 650 Hz, respectively). X-ray crystallographic analysis revealed that in the solid state this complex adopts an ion pair arrangement, consisting of a cationic Cu^I centre ligated by two selenourea ligands and a [CuCl₂]⁻ counterion (Figure 4). The ⁷⁷Se signal of a sample of this complex did not resolve into two signals upon cooling to -50 °C. Variable temperature ¹H NMR studies between 27 and -43 °C resolved two overlapping signals (*meta* Ar C-H, C⁴-H/C⁵-H on the heterocyclic core) but did

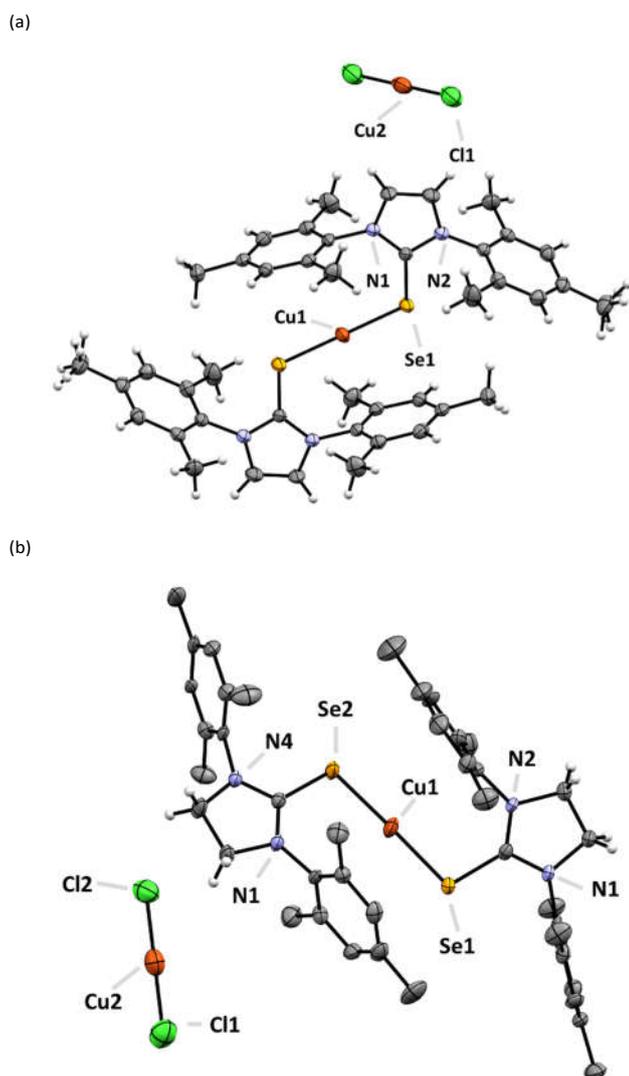


Figure 4. Molecular structures of (a) $[\text{Cu}(\mathbf{4})_2][\text{CuCl}_2]$ and (b) $[\text{Cu}(\mathbf{5})_2][\text{CuCl}_2]$, as determined by X-ray crystallographic analysis. Both copper atoms in (a) sit on crystallographic centres of symmetry. Most hydrogen atoms are omitted for clarity. Thermal displacement ellipsoids are shown at the 50% probability level.

not lead to any splitting of the methyl signals. The isolation of crystals of $[\text{Cu}(\mathbf{4})_2][\text{CuCl}_2]$ is therefore likely due to ligand rearrangement processes during crystallisation. NMR spectra of the reaction of **5** (derived from SIMes) with CuCl yielded similarly broad ^1H and ^{77}Se NMR spectra ($\omega_{1/2} = ca.$ 15 Hz and 235 Hz, respectively); X-ray crystallographic data confirmed that **5** leads to the same solid state structure (Figure 4(b)). The Se-Cu-Se angle in $[\text{Cu}(\mathbf{4})_2][\text{CuCl}_2]$ is 180° due to the space group symmetry, while for $[\text{Cu}(\mathbf{5})_2][\text{CuCl}_2]$ the angle is $168.65(4)^\circ$. The C-Se-Cu angles are in a similar range to those noted above ($105.15(8)^\circ$ for $[\text{Cu}(\mathbf{4})_2][\text{CuCl}_2]$; $103.06(14)^\circ$ and $102.65(14)^\circ$ for $[\text{Cu}(\mathbf{5})_2][\text{CuCl}_2]$). Table 2 records some key parameters for these structures.

The X-ray data are informative, but do not necessarily reflect the solution state behaviour of these complexes. The use of Diffusion-Ordered NMR Spectroscopy (DOSY) has emerged as a valuable and informative way to probe the solution state

Table 2: Key structural parameters for the solid state structures of copper complexes.

Structure	Cu-Se distance(s)	Se-C distance(s)	C-Se-Cu angle(s)
$[\text{CuCl}(\mathbf{1})]$	2.2563(7)	1.857(2)	103.72(9)
$[\text{CuCl}(\mathbf{6})]$	2.2440(5)	1.846(3)	104.66(8)
$[\text{Cu}(\mathbf{4})_2][\text{CuCl}_2]$	2.2636	1.867(3)	105.14
		1.867(3)	
$[\text{Cu}(\mathbf{5})_2][\text{CuCl}_2]$	2.2685(8)	1.848(4)	103.1(1)
	2.2684(8)	1.851(4)	102.6(1)

behaviour and properties of a very wide range of compounds, including main group and transition metal complexes.³³ Using most modern NMR apparatus – i.e. where the probe is equipped with gradients – it is possible to measure the diffusion coefficient for analytes within a sample. This ability to measure the diffusion coefficient of solutes then allows for the accurate estimation of molecular weights,^{34, 35} and so DOSY has been applied to fundamental challenges such as discerning the aggregation behaviour of organolithium reagents in solution.³⁶ As a result of ongoing research in this field by various leading groups, it is possible to achieve accurate molecular weight estimation using samples containing one of a number of specific, readily-available standards for which external calibration curves have been constructed.^{37, 38}

Previous 2D ^1H DOSY NMR studies of analogous gold-based systems showed that complexes that gave $[\text{Au}(\text{L})_2][\text{AuCl}_2]$ structures in the solid state were monomeric $[\text{AuCl}(\text{L})]$ species in solution.¹⁵ 2D ^1H DOSY NMR studies of the copper complexes of **3** and **5** ($[\text{CuCl}(\mathbf{3})]$ and $[\text{Cu}(\mathbf{5})_2][\text{CuCl}_2]$ as determined by X-ray analysis) were conducted using Stalke's method of external calibration, with tetraphenyl-naphthalene as an internal standard in a CDCl_3 solution at 300K.³⁸ The molecular weight of copper complex of **3** was determined to be 570 g/mol using the dissipated spheres and ellipsoids (DSE) curve (*versus* 568.68 g/mol expected for $[\text{CuCl}(\mathbf{3})]$; <1% error). Similarly, the molecular weight of the copper complex of **5** was determined to be 483 g/mol using the enlarged disc (ED) curve (*versus* 484.42 g/mol expected for $[\text{CuCl}(\mathbf{5})]$; <1% error). These two calibration curves, and alternative calibration curves such as compact spheres (CS) or the curve based on all data (Merge), did not correlate well with $[\text{Cu}(\text{L})_2][\text{CuCl}_2]$ (error >10% in all cases). Based on these data, it is proposed that, like the gold analogues, the complexes are monomeric in solution but that their crystallisation behaviour leads to $[\text{CuCl}(\text{L})]$ or $[\text{Cu}(\text{L})_2][\text{CuCl}_2]$ complexes depending on the ligand structure. Ligands **4** and **5** have somewhat flat aryl *N*-substituents, which may allow the two ligands to approach sufficiently closely to form $[\text{Cu}(\text{L})_2][\text{CuCl}_2]$. Visualisation of the packing in the crystal structure shows that the mesityl rings of adjacent complexes stack together.

Our previous study of Au^I complexes resulted in the isolation of $[\text{Au}(\text{L})_2][\text{AuCl}_2]$ and $[\text{AuCl}(\text{L})]$ complexes, analogous to the copper species obtained here.¹⁵ However, the former motif was obtained where L = **3** (based on SiPr) and an analogue based on SiPr^{OMe} (1,3-bis(2,6-diisopropyl-4-methoxyphenyl)-4,5-dihydro-

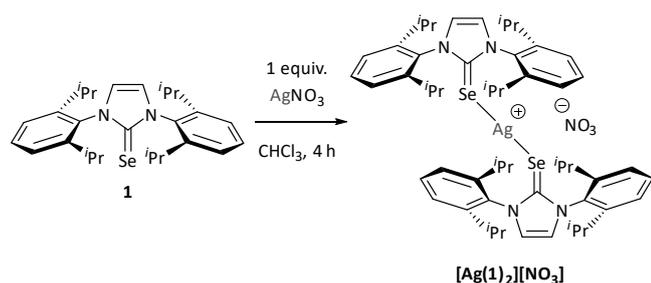
imidazol-2-ylidene).¹⁹ This is in contrast to the copper systems where **4** and **5** lead to rearranged products, but **2** – with the same *N*-aryl substituents as **3** – does not. We previously suggested that the rearrangement may be correlated to the strongly π -accepting nature of SIPr and SIPr^{OMe}, but this explanation does not hold here. Instead, it may be that copper, being smaller than gold, simply cannot accommodate two molecules of ligands with 2,6-diisopropylphenyl *N*-substituents around the metal centre.

Additionally, the ready formation of AuX₂⁻ and CuX₂⁻ counterions has been shown during the direct syntheses of [AuX(NHC)] and [CuX(NHC)] complexes from the corresponding imidazolium salts.^{39, 40}

Synthesis of Silver(I) Complexes

The coordination chemistry of selenoureas with silver has received rather less attention than that of copper. Gimeno has disclosed a tetranuclear silver complex supported by PPh₃ ligands and three bidentate imidazolyl-2-selone ligands,⁴¹ and Thöne has reported [Ag(SeC(NH₂)₂{ μ -SeC(NH₂)₂})₂].⁴² Recently, Ritch reported the coordination chemistry of ligands **1** and **4** with AgOTf and AgNO₃, leading to [Ag(**1**)₂][OTf], [Ag(**1**)₂][Ag(NO₃)₂], and [Ag(μ -X)(**4**)₂] (X = OTf, NO₃).⁴³ These results strongly suggest that the coordination environment of the silver centres is highly sensitive to the substitution pattern of the ligand and to the nature of the silver counterion. In order to study these coordination patterns and to consequently correlate results with those from investigations with other coinage metals (i.e. gold and copper), we systematically examined the coordination chemistry of ligands **1, 4–12**, using silver chloride and silver nitrate.

Initially, a 1:1 mixture of AgNO₃ and **1** were stirred at room temperature in acetone for 3 h (Scheme 3). A single new product was formed as determined by NMR analysis. Single crystals were grown by vapour diffusion of pentane into a saturated solution of the product in DCM. X-ray analysis showed that the product was in fact [Ag(**1**)₂][NO₃] (Scheme 3; Figure 5).



Scheme 3. Reaction of **1** with AgNO₃ to form [Ag(**1**)₂][NO₃].

This is somewhat different to the results of Ritch and co-workers; their report showed that the reaction of **1** with AgNO₃, in methanol solvent rather than in chloroform, yielded [Ag(**1**)₂][Ag(NO₃)₂]. This subtle variation in solvent choice is not trivial; based on our experience, this kind of behaviour is not uncommon, highlighting the highly variable coordination chemistry of these species. It is evident that when handling

these products – and especially in the case of any solid-state analysis – different batches of crystals (using various crystallisation solvents) and even different crystals within the same batch, can show different coordination patterns. This will

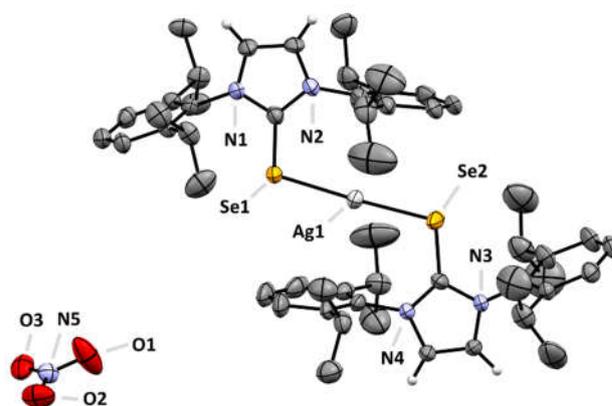


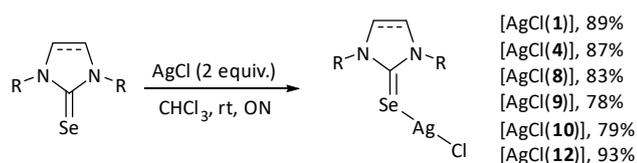
Figure 5. Molecular structure of [Ag(**1**)₂][NO₃], as determined by X-ray crystallographic analysis. Most hydrogen atoms are omitted for clarity. Thermal displacement ellipsoids are shown at the 50% probability level.

also have consequences for the subsequent application of these complexes in fields such as catalysis, since the solid state structure will not necessarily indicate the solution state structure under conditions used for catalysis.

Due to the notorious insolubility of silver chloride, attempts were made to form the AgCl adduct *in situ* by mixing **1** with AgNO₃ and KCl in a 1:1:2 ratio. However, NMR analysis of the resulting product showed only very broad peaks, hinting at different coordination patterns and a possible equilibrium between AgCl and AgNO₃ adducts, demonstrating incomplete anion exchange between the two.

Consequently, a different route was developed; ligand **1** reacts directly with excess AgCl (*ca.* 2 equivalents) in chloroform overnight at room temperature (Scheme 4). After filtration, evaporation of the solvent and washing with diethyl ether, a white powder was obtained. Single crystal X-ray analysis showed a similar structure to that obtained with AgNO₃, albeit with a chloride counterion, [Ag(**1**)₂]Cl (Figure 6 (a)). However, the NMR spectra – especially the ¹H NMR spectrum – of the newly-obtained compound were significantly different from those of [Ag(**1**)₂][NO₃]. This prompted the analysis of these complexes using 2D ¹H DOSY NMR experiments (*vide supra*) to elucidate the structure of the compound in solution. This experiment (in chloroform-*d*) revealed a diffusion coefficient equal to 7.76 × 10⁻¹⁰ m² s⁻¹. Using the correlation proposed by Morris and co-workers,³⁴ the molecular weight of this species can be estimated at 703 g mol⁻¹. By comparing this value with the molecular weights of the mono-coordinated [AgCl(**1**)] (610 g mol⁻¹) and the di-coordinated [Ag(**1**)₂]Cl (1078 g mol⁻¹) or other dimeric species, we can conclude that this species adopts a mono-coordinated structure in solution, i.e. [AgCl(**1**)].

Following this initial result, selenoureas **1, 4, 8, 9, 10** and **12** underwent successful reaction with AgCl, leading to the formation of the corresponding [AgCl(L)] complexes. Ligands **6** and **7** were also tested under similar conditions; however,



Scheme 4. Reactions of AgCl with selenoureas **1**, **4**, **8**, **9**, **10** and **12**.

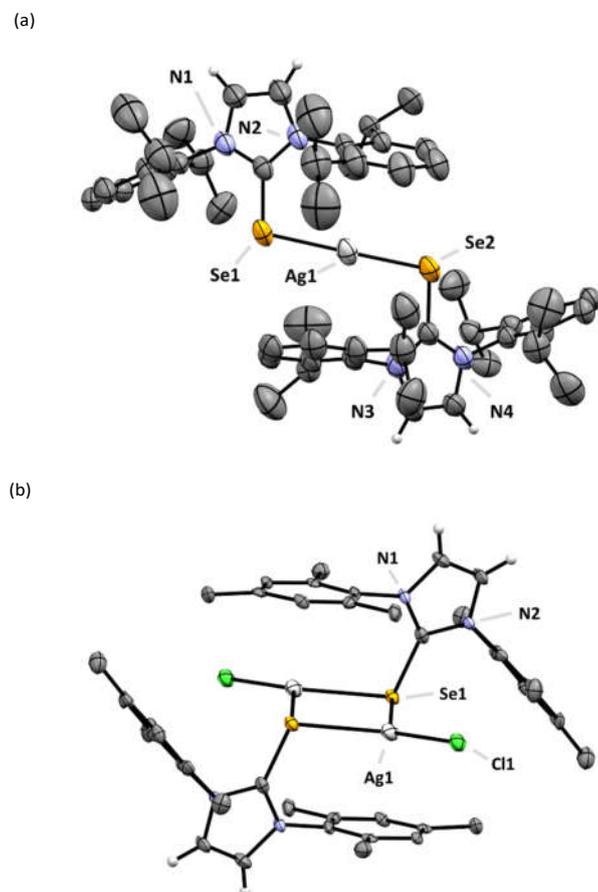


Figure 6. Single crystal X-ray diffraction analyses of silver(I) complexes with *N*-aryl-substituted selenoureas: (a) $[\text{Ag}(\mathbf{1})_2]\text{Cl}$, and (b) $[\text{AgCl}(\mu\text{-}\mathbf{4})_2]$. Most hydrogen atoms are omitted for clarity. Only the cationic fragments are displayed. Thermal displacement ellipsoids are shown at the 50% probability level.

we did not observe any successful coordination and only starting materials were recovered.

Several compounds were characterised by single crystal X-ray diffraction analysis (Figures 6 and 7). It should be noted that the same crystallisation system was used for all complexes; single crystals were grown *via* vapour diffusion of pentane into a saturated DCM solution of the compound. Multiple crystals from each batch were analysed to check for the presence of either one or several species. The two examples in Figure 6 are relatively straightforward, adopting arrangements that are preceded by other work in the field. The dimeric structure of $[\text{Ag}(\mu\text{-Cl})(\mathbf{4})_2]$ is in direct agreement with that reported by Ritch on the reaction of **4** with AgNO_3 and AgOTf .⁴³ The di-coordinated structure $[\text{Ag}(\mathbf{1})_2]\text{Cl}$ deviates somewhat from the expected structure; since it was concluded on the basis of DOSY experiments that this species is most likely mono-coordinated

in solution, one might expect the X-ray structure to be either the monomeric form $[\text{AgCl}(\mathbf{1})]$ or the rearranged structure $[\text{Ag}(\mathbf{1})_2][\text{AgCl}_2]$, by analogy to the work reported here with copper, and previous investigations with gold and silver. This slight difference in coordination could be a direct consequence of the crystallisation method/system; the insolubility of AgCl and its high lattice energy could be a significant driving force in the elimination of AgCl from $[\text{Ag}(\mathbf{1})_2][\text{AgCl}_2]$ during crystallisation in this particular solvent combination. This phenomenon is still under investigation in our laboratories.

Figure 7 displays a variety of coordination geometries for silver(I) with ^tBu-, ICy- and IDD-derived ligands **8**, **9** and **10**, (respectively). In the case of **9**, two structures were obtained from the *same batch of crystalline material*, despite the NMR spectra showing only one species in CDCl_3 solution. Figure 7 (b) displays a complex in which three molecules of **9** have coordinated a trigonal planar silver(I) centre; the Se-Ag-Se angles are in the range 115 – 124° and sum to 360°. Figure 7 (c) displays a closely related structure in which one molecule of **9** acts as a bridging ligand, with an almost-linear Ag1-Se5-Ag2 arrangement (168.13(3)°) and two slightly distorted trigonal planar silver centres. $[(\text{Ag}(\mathbf{9})_2)_2(\mu\text{-}\mathbf{9})][\text{NO}_3]_2$ displays two outer-sphere NO_3^- counterions; since no nitrate-based reagent was added to the synthesis and that the same freshly-bought AgCl batch was used for the synthesis of all complexes, we can only assume that the AgCl reagent is contaminated with trace amounts of AgNO_3 , which is not surprising since commercial AgCl is made from the nitrate counterpart. Each silver centre has two smaller angles and one larger angle; Se1-Ag1-Se2, Se1-Ag1-Se5, Se4-Ag2-Se5, and Se4-Ag2-Se3 are in the range 108 - 116°, while Se2-Ag1-Se5 and Se3-Ag2-Se5 are 134.43(3) and 135.72(3), respectively. A search of the CSD revealed no other structures of this type.

Ligand **8** displayed a similar coordination pattern to **9** as shown by the tri-coordinated structure $[\text{Ag}(\mathbf{8})_3][\text{AgCl}_3]_{0.5}$ in Figure 7 (a). The three molecules of **8** coordinate a trigonal planar silver(I) centre with Se-Ag-Se angles in the range 115 – 124°, summing to 360°. In contrast to **9**, this species presents $0.5[\text{AgCl}_3]^-$ as the outer-sphere counterion instead of the typical Cl⁻; though rare, this counterion is known and has been reported as part of similar phosphine-based structures.⁴⁴ In contrast, IDD-derived ligand **10** showcases a completely different coordination pattern; two molecules of **10** coordinate a trigonal planar silver(I) centre with a covalently-bonded chloride anion. The two selenium atoms form a 130.19(2)° angle with the silver atom (Se1-Ag1-Se2) whilst each selenium-silver-chlorine angle is smaller (Se1-Ag1-Cl, 110.95(2)°; Cl-Ag1-Se2, 118.56(2)°). This structure seems to be half way between the linear di-coordinated geometry obtained with ligand **1** and the tri-coordinated trigonal planar geometry obtained with ligands **8** and **9**. The trigonal planar structures appear to be a trademark of the *N*-alkyl derived selenoureas; however, in the case of **10**, the ligand is far too bulky to allow coordination of a third molecule, and therefore the silver bears only two selenourea ligands and a covalently-bonded chloride in a trigonal planar arrangement. Since no copper or gold complexes with *N*-alkyl derived selenoureas have been observed during our studies, no

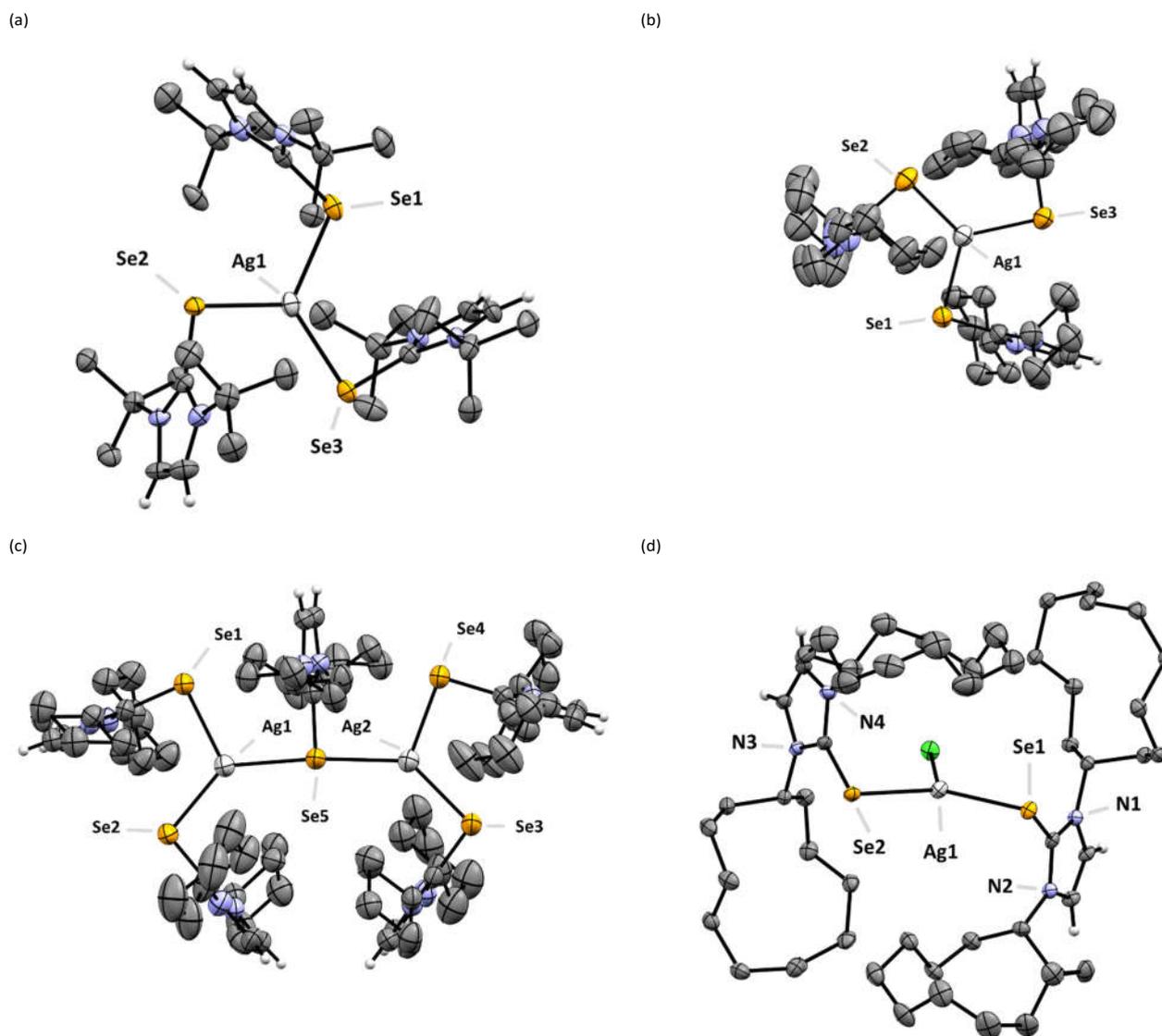


Figure 7. Single crystal X-ray diffraction analyses of silver(I) complexes of *N*-alkyl-substituted selenoureas: (a) $[\text{Ag}(\mathbf{8})_3][0.5\{\text{AgCl}_3\}]$, (b) $[\text{Ag}(\mathbf{9})_3]\text{Cl}$, (c) $[(\text{Ag}(\mathbf{9})_2)_2(\mu\text{-}\mathbf{9})][\text{NO}_3]_2$, and (d) $[\text{AgCl}(\mathbf{10})_2]$. Most hydrogen atoms are omitted for clarity. Only the cationic fragments for (a), (b), and (c) are displayed. Thermal displacement ellipsoids are shown at the 50% probability level.

direct comparison can be made; however, these structures hint at a complementary relationship between the coinage metals where silver appears to be the only metal to support coordination of these highly electron-rich ligands, whilst copper and gold are able to afford monomeric- $[\text{MCl}(\text{L})]$ and rearranged-type $[\text{M}(\text{L})_2][\text{MCl}_2]$ structures in the solid state. Nonetheless, all three metals have one common feature: in solution, they all afford monomeric structures as confirmed by 2D ^1H DOSY NMR experiments on the rearranged structures of the gold and copper complexes as well as all of the silver complexes (see the Supporting Information).

Table 3 collects some key structural parameters for the seven silver-containing crystal structures obtained during the

course of this work.

To further probe the structures of these silver(I) complexes in solution, electrospray ionisation and high-resolution mass spectrometry studies of acetonitrile solutions were conducted. In all cases, the dominant ion (in positive ion mode) was identified as the two-coordinate complex $[\text{Ag}(\text{SeNHC})_2]^+$ along with the protonated free ligand $[\text{SeH}(\text{NHC})]^+$, further suggesting that the solution state structures of these complexes differ significantly not only from their solid state structures but also from one solvent to another. However, we cannot eliminate the possibility that the ionisation process in the mass spectrometer alters the solution composition for the acetonitrile solutions used herein.

Table 3: Key structural parameters for the solid state structures of silver complexes.

Structure	Ag-Se dist.	Se-C dist.	C-Se-Ag angle(s)	Sum of angles at Ag
[Ag(1) ₂][NO ₃]	2.4607(7)	1.865(7)	102.0(2)	-
	2.4554(8)	1.866(7)	103.8(2)	-
[Ag(1) ₂]Cl	2.4577(8)	1.873(8)	104.6(2)	-
	2.4634(8)	1.856(8)	103.8(2)	-
[AgCl(μ-4)] ₂	2.6943(7)	1.871(8)	97.8(2)	-
	2.6921(7)	-	107.3(2)	-
[Ag(8) ₃][0.5{AgCl ₃ }]	2.5747(6)	1.886(4)	105.3(1)	359.99
	2.5479(8)	1.872(5)	99.8(1)	-
[Ag(9) ₃]Cl ^a	2.5704(6)	1.886(4)	97.2(1)	-
	2.5736(8)	1.847(5)	92.7(1)	359.98
[[Ag(9) ₂] ₂ (μ-9)][NO ₃] ₂	2.5480(7)	1.882(6)	95.2(2)	359.99
	2.5703(7)	1.870(6)	94.9(2)	-
[[Ag(9) ₂] ₂ (μ-9)][NO ₃] ₂	2.5384(8)	1.860(8)	94.0(2)	-
	2.5753(8)	1.861(6)	92.0(2)	-
[AgCl(10) ₂]	2.5613(8)	1.876(6)	91.6(2)	-
	2.6001(8)	1.875(5)	91.4(2)	359.62
[AgCl(10) ₂]	2.5488(8)	1.871(5)	99.4(2)	358.98
	2.6249(6)	1.873(6)	92.2(2)	-
[AgCl(10) ₂]	2.6331(6)	1.879(5)	100.5(2)	-
	2.5465(8)	1.888(6)	93.2(2)	-
[AgCl(10) ₂]	2.5925(8)	-	93.9(2)	-
	2.5644(5)	1.871(3)	96.3(1)	359.7
[AgCl(10) ₂]	2.5853(4)	1.872(4)	92.3(1)	-

a) Two independent molecules in the unit cell.

The collection of ⁷⁷Se NMR data for these complexes was often highly challenging. Extended analyses (up to 7 h) on highly concentrated samples using a liquid nitrogen cryoprobe yielded good data for the chloro-based silver complexes of **8** and **9**, and satisfactory data for those of **1**, **4**, and **10**; however, no signals were observed for other complexes, despite the use of saturated solutions. This may be a consequence of the ½ spin of ¹⁰⁷Ag and ¹⁰⁹Ag, which led to no observable J_{Se-Ag}, but may broaden the signal and further decrease the already low signal to noise ratio.

NMR data analysis

The ⁷⁷Se chemical shifts for each complex were recorded and compared with those of the free ligands (**1-12**) and the gold complexes¹⁵ (Figure 8). In most cases, the ⁷⁷Se resonances were very weak, and extended analyses (up to 7 h) were required, even on a cryoprobe-equipped spectrometer; the silver complexes were particularly challenging to analyse (*vide supra*). It has already been shown that there is a linear correlation between δ_{Se} for the selenourea and δ_{Se} for the corresponding gold(I) complex. This work shows that a similar correlation exists for the copper and silver complexes (Figure 9), with a similar gradient but a different intercept for copper and gold. The generally higher chemical shifts for the gold complexes are consistent with the higher electronegativity of this element, compared to silver or copper, which may lead to this greater deshielding behaviour. The plot for the silver complexes has fewer points, and has a single point quite far removed from the others, so this gradient may only be approximate.

Conclusions

This manuscript describes the synthesis and characterisation of a series of new copper and silver complexes, using easy-to-prepare selenourea derivatives of well-known *N*-heterocyclic carbene ligands. All of the complexes are single components in solution; 2D ¹H DOSY NMR studies of selected examples confirm the monomeric nature of these species. However, a variety of structures were obtained from X-ray diffraction analysis, so the solid state structures are a result of crystallisation behaviour, which can be profoundly influenced by factors such as the choice of solvent.

Copper complexes bearing IMes and SIMes derivatives (**4** and **5**), which have flat *N*-aryl substituents, lead to [Cu(L)₂][CuCl₂] complexes in the solid state, while other ligands gave [CuCl(L)] species. No polynuclear species were obtained. This is somewhat similar to the results of our study of gold complexes, where most complexes were of the form [AuCl(L)], with the exception of those of **3** (and a closely related ligand based on SIPr^{OMe}) which led to [Au(L)₂][AuCl₂].

The solid state behaviours of the silver species were far more varied. [Ag(L)₂]X, [AgCl(μ-L)]₂, [Ag(L)₃]X, {[Ag(L)₂]₂(μ-L)}[X]₂, and [AgCl(L)₂] species were all crystallographically characterised, with multiple motifs sometimes obtained from the same sample. The solid state behaviour appears to be highly sensitive to the steric and electronic nature of the ligand; *N*-aryl ligands lead to [Ag(L)₂]X or [AgCl(μ-L)]₂ species, while *N*-alkyl species lead to [Ag(L)₃]X, {[Ag(L)₂]₂(μ-L)}[X]₂, and [AgCl(L)₂] complexes with trigonal planar silver centres. Selenourea derivatives of *t*-Bu (**8**) and ICy (**9**) are sufficiently small to coordinate three ligands to a silver centre. IDD has larger *N*-substituents and so only two molecules of **10** can be accommodated.

Comparisons across different metal systems are hampered by the difficulty in preparing copper, silver, and gold complexes of the same ligands. However, the data presented here allow general trends between metal systems to be identified; with chemical shifts for the complexes of a given ligand decreasing in the order [AuCl(L)] >> [CuCl(L)] > [AgCl(L)].

This work extends the coordination chemistry of NHCs and their derivatives into new areas; further studies of this chemistry are currently underway within our laboratories.

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} NMR spectra to the deuterated solvent signal.⁴⁵ ⁷⁷Se NMR spectra were referenced to external standards. [¹H, ¹H] COSY, [¹H, ¹³C] HSQC, [¹H, ¹³C] HMBC and ¹³C-jmod spectra were used to assign signals. Crystallographic measurements were made with monochromatic radiation using an Oxford Diffraction Xcalibur sealed-tube diffractometer for the Cu complexes and a SuperNova microsource instrument for

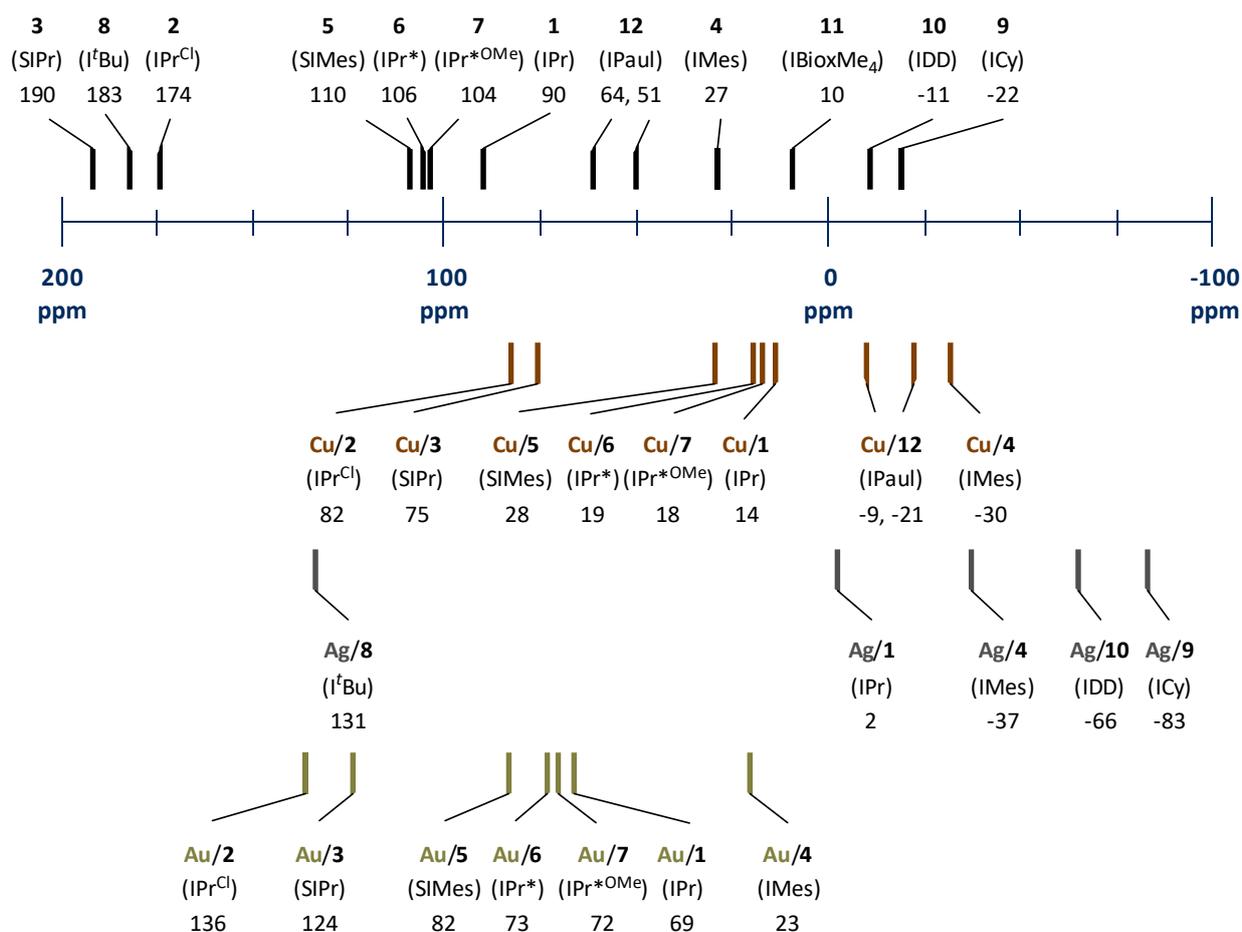


Figure 8. Chemical shifts of selenourea ligands, and their copper, silver, and gold complexes. All NMR data were acquired at 300 K in chloroform-*d* solution.

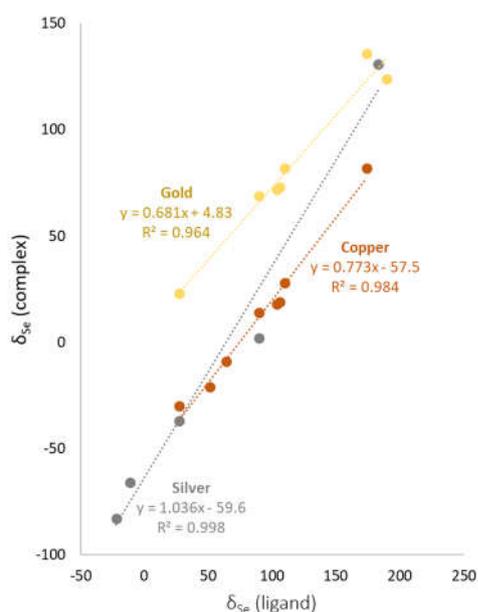


Figure 9. Plot of δ_{Se} for copper, silver, and gold complexes of selenourea ligands versus δ_{Se} of the corresponding ligand.

the Ag complexes. Structures were refined against F^2 to convergence using all unique reflections and Shelxl programs (see Tables S1-S3). Selenium and potassium *tert*-butoxide were obtained from commercial sources and used as supplied. Known selenoureas^{10-12, 15} and IPaul-HCl²³ were prepared using literature methods. Anhydrous THF was obtained from solvent drying apparatus (Innovative Technologies PureSolv). The raw data underpinning this study are available for download *via* the University of Strathclyde PURE system.^{†,§}

Ligand 11. A vial equipped with a stir bar was charged with IBioxMe₄-HBF₄ (104.3 mg, 0.388 mmol), KO^tBu (82.7 mg, 0.738 mmol, 1.9 equiv.), selenium (87.4 mg, 1.106 mmol, 2.9 equiv.), and anhydrous THF (1 mL). The reaction was stirred at room temperature for 20 h. The solvent was evaporated and the residue was dissolved in DCM (5 mL) and passed through a pad of celite, followed by additional DCM (2 x 5 mL). The DCM was evaporated to yield a pale solid which was washed with hexane (2 x 5 mL) and diethyl ether (5 mL) to yield a pale pink solid. Yield: 60.2 mg, 0.210 mmol, 54%. ¹H NMR (CDCl₃, 400 MHz): δ_{H} 4.46 (s, 4H, CH₂O), 1.80 (s, 12H, CH₃). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ_{C} 129.7 (C-Se), 123.5 (backbone C), 88.2 (CH₂O), 62.7

(CMe₂), 24.0 (CH₃). ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se} 10.3. **CHN** Calculated for C₁₁H₁₆ClN₂SeO₂: C, 46.00; H, 5.62; N, 9.75. Found: C, 45.75; H, 5.50; N, 9.63.

Ligand 12. A vial equipped with a stir bar was charged with IPaul·HCl (0.94 g, 1.46 mmol), KO^tBu (0.33 g, 2.95 mmol, 2.0 equiv.), and selenium (0.29 g, 3.67 mmol, 2.5 equiv.). A septum was fitted and anhydrous THF (10 mL) was added. The reaction was stirred at room temperature for 24 h, and the solvent was removed under vacuum. The residue was taken up in bench DCM (10 mL) and filtered through a pad of celite. The pad was washed with further DCM (10 mL). The combined DCM fractions were evaporated under vacuum, washed with pentane (3 x 5 mL), and dried under high vacuum to yield a pale solid. Yield: 0.81 g, 1.17 mmol, 80%. The compound is a mixture of two rotamers with overlapping signals, as has been observed previously for other IPaul complexes;²³ these can be resolved by ⁷⁷Se NMR, and partially resolved by ¹H NMR, but not by ¹³C{¹H} NMR. **Major Rotamer:** ¹H NMR (CDCl₃, 400 MHz): δ_H 7.40–6.92 (m, 20H, Ar CH), 6.78 (d, 2H, *J* = 1.5 Hz, Ar CH), 6.07 (s, 2H, N(CH)₂N), 5.55 (s, 2H, CHPh₂), 2.31 (s, 6H, Me), 2.10 (s, 6H, Me). ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se} 63.9. **Minor Rotamer:** ¹H NMR (CDCl₃, 400 MHz): δ_H 7.40–6.92 (m, 20H, Ar CH), 6.68 (d, 2H, *J* = 1.5 Hz, Ar CH), 5.80 (s, 2H, N(CH)₂N), 5.53 (s, 2H, CHPh₂), 2.31 (s, 3H, Me), 2.18 (s, 3H, Me). ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se} 50.5. **Mixture of Rotamers:** ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ_C 159.3 (C-Se), 158.3 (C-Se), 143.6 (Ar C), 143.4 (Ar C), 142.8 (Ar C), 142.7 (Ar C), 141.8 (Ar C), 141.4 (Ar C), 136.1 (Ar C), 135.9 (Ar C), 130.4 (Ar CH), 130.3 (Ar CH), 130.12 (Ar CH), 130.06 (Ar CH), 129.7 (Ar CH), 129.6 (Ar CH), 129.52 (Ar CH), 129.47 (Ar CH), 128.4 (Ar CH), 128.3 (Ar CH), 126.54 (Ar CH), 126.52 (Ar CH), 120.5 (N(CH)₂N), 120.3 (N(CH)₂N), 51.9 (CHPh₂), 51.8 (CHPh₂), 21.7 (Me), 18.8 (Me), 18.6 (Me).

[CuCl(1)]. A vial was charged with **1** (103.6 mg, 0.222 mmol), copper(I) chloride (47.0 mg, 0.475 mmol, 2.1 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature for 3 h, filtered through celite, and evaporated to yield a white solid. The solid was washed with diethyl ether (2 x 5 mL) and dried under high vacuum to yield a white powder. Yield: 101.4 mg, 0.179 mmol, 81%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.63 (t, 2H, *J* = 8.3 Hz, Ar CH), 7.38 (d, 4H, *J* = 8.3 Hz, Ar CH), 7.19 (s, 2H, N(CH)₂N), 2.46 (sept, 4H, *J* = 6.8 Hz, CHMe₂), 1.35 (d, 12H, *J* = 6.8 Hz, CH₃), 1.19 (d, 12H, *J* = 6.8 Hz, CH₃). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ_C 156.4 (C-Se), 145.5 (Ar C), 132.6 (Ar C), 132.0 (Ar CH), 125.6 (Ar CH), 123.2 (N(CH)₂N), 29.3 (CHMe₂), 24.6 (CH₃), 23.6 (CH₃). ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se} 13.8. **CHN** Calculated for C₂₇H₃₆ClCuN₂Se: C, 57.24; H, 6.41; N, 4.94. Found: C, 56.91; H, 6.29; N, 5.05.

[CuCl(2)]. A vial was charged with **2** (118.8 mg, 0.221 mmol), copper(I) chloride (70.5 mg, 0.712 mmol, 3.2 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature for 4.5 h, filtered through celite, and evaporated to yield a white solid that was washed with diethyl ether and dried under high vacuum. Yield: 65.5 mg, 0.103 mmol, 47%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.69 (t, *J* = 7.8 Hz, 2H, Ar CH), 7.43 (d,

J = 7.8 Hz, 4H, Ar CH), 2.44 (sept., *J* = 7.0 Hz, 4H, CHMe₂), 1.38 (d, *J* = 6.8 Hz, 12H, CH₃), 1.26 (d, *J* = 6.8 Hz, 12H, CH₃). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ_C 156.7 (C-Se), 146.1 (Ar C), 132.8 (Ar C-H), 129.7 (Ar C), 125.9 (Ar C-H), 118.6 (N(CCl)₂N), 29.8 (CHMe₂), 24.2 (CH₃), 24.0 (CH₃). ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se} 82.4.

[CuCl(3)]. A vial was charged with **3** (104.4 mg, 0.222 mmol), copper(I) chloride (64.9 mg, 0.656 mmol, 3.0 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature for 4.5 h, filtered through celite, and evaporated to yield a pale solid that was washed with diethyl ether and dried under high vacuum. Yield: 102.0 mg, 0.179 mmol, 86%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.56 (t, *J* = 7.8 Hz, 2H, Ar CH), 7.34 (d, *J* = 7.8 Hz, 4H, Ar CH), 4.13 (s, 4H, N(CH₂)₂N), 2.91 (sept., *J* = 6.9 Hz, 4H, CHMe₂), 1.43 (d, *J* = 6.8 Hz, 12H, CH₃), 1.33 (d, *J* = 6.8 Hz, 12H, CH₃). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ_H 181.7 (C-Se), 146.5 (Ar C), 133.0 (Ar C), 131.1 (Ar C-H), 125.8 (Ar C-H), 52.4 (N(CH₂)₂N), 29.3 (CHMe₂), 25.0 (CH₃), 24.6 (CH₃). ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se} 74.5.

[Cu(4)₂][CuCl₂]. A vial was charged with **4** (152.3 mg, 0.397 mmol), copper(I) chloride (105.1 mg, 1.06 mmol, 2.7 equiv.), and chloroform (4 mL). The reaction was stirred at room temperature for 4.5 h, evaporated and then re-dissolved in DCM, and filtered through celite. The solution was evaporated to yield a white solid that was washed with diethyl ether and dried under high vacuum. Yield: 172.9 mg, 0.358 mmol, 90%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.11 (s, 2H, N(CH)₂N), 7.05 (s, 4H, Ar CH), 2.37 (s, 6H, CH₃), 2.05 (s, 12H, CH₃). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ_C 141.4 (Ar C), 134.8 (Ar C), 132.5 (Ar C), 130.4 (Ar CH), 122.5 (N(CH)₂N), 21.4 (CH₃), 18.0 (CH₃). The carbon attached to selenium could not be located. ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se} -29.8. **CHN** Calculated for C₂₁H₂₄ClCuN₂Se: C, 52.29; H, 5.01; N, 5.81. Found: C, 51.89; H, 4.94; N, 5.82.

[CuCl(5)]. A vial was charged with **5** (80.5 mg, 0.209 mmol), copper(I) chloride (67.5 mg, 0.682 mmol, 3.3 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature for 4.5 h, filtered through celite, and evaporated to yield a pale solid that was washed with diethyl ether and dried under high vacuum. Yield: 86.6 mg, 0.179 mmol, 86%. ¹H NMR (CDCl₃, 400 MHz): δ_H 7.00 (s, 4H, Ar C-H), 4.07 (s, 4H, N(CH₂)₂N), 2.32 (s, 6H, CH₃), 2.24 (s, 12H, CH₃). ¹³C{¹H} NMR (CDCl₃, 101 MHz): δ_H 177.8 (C-Se), 140.6 (Ar C), 135.6 (Ar C), 133.0 (Ar C), 130.7 (Ar C-H), 49.7 (N(CH₂)₂N), 21.3 (CH₃), 17.8 (CH₃). ⁷⁷Se NMR (CDCl₃, 76 MHz): δ_{Se} 28.3.

[CuCl(6)]. A vial was charged with **6** (202.0 mg, 0.204 mmol), copper(I) chloride (59.7 mg, 0.603 mmol, 2.7 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature for 4.5 h, evaporated and then re-dissolved in DCM, and filtered through celite. The solution was evaporated to yield a white solid that was washed with diethyl ether and dried under high vacuum. Yield: 155.6 mg, 0.143 mmol, 70%. ¹H NMR (CDCl₃, 400 MHz): 7.33–7.21 (m, 20H, Ar CH), 7.20–7.11 (m, 12H, Ar CH), 6.99 (s, 4H, Ar CH), 6.87–6.79 (m, 8H, Ar CH), 5.49 (s, 2H, N(CH₂)₂N), 5.21 (s, 4H, CHPh₂), 2.35 (s, 3H, CH₃). ¹³C{¹H}

NMR (CDCl₃, 101 MHz): 154.8 (C-Se), 142.7 (Ar C), 142.1 (Ar C), 140.8 (Ar C), 132.0 (Ar CH), 131.6 (Ar CH), 130.1 (Ar CH), 129.3 (Ar CH), 128.7 (Ar CH), 128.5 (Ar CH), 127.1 (Ar CH), 126.9 (Ar CH), 122.7 (N(CH₂)₂N), 52.0 (CHPh₂), 22.2 (CH₃). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} 19.4. **CHN** Calculated for C₆₉H₅₆ClCuN₂Se: C, 75.95; H, 5.17; N, 2.57. Found: C, 75.63; H, 5.14; N, 2.50.

[CuCl(7)]. A vial was charged with **8** (198.5 mg, 0.194 mmol), copper(I) chloride (53.8 mg, 0.543 mmol, 2.8 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature for 4.5 h, filtered through celite, and evaporated to yield a white solid that was washed with diethyl ether and dried under high vacuum. Yield: 140.5 mg, 0.125 mmol, 64%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.31–7.18 (m, 20H, Ar CH) 7.16–7.06 (m, 12H, Ar CH), 6.86–6.78 (m, 8H, Ar CH), 6.66 (4H, s, Ar CH), 5.40 (2H, s, N(CH₂)₂N), 5.16 (s, 4H, CHPh₂), 3.64 (s, 6H, OCH₃). **¹³C{¹H} NMR** (CDCl₃, 101 MHz): δ_H 161.4 (Ar C), 155.6 (C-Se), 142.7 (Ar C), 142.4 (Ar C), 142.0 (Ar C), 130.0 (Ar CH), 129.3 (Ar CH), 128.7 (Ar CH), 128.5 (Ar CH), 127.3 (Ar CH), 126.9 (Ar CH), 122.9 (N(CH₂)₂N), 116.5 (Ar CH), 55.6 (OCH₃), 52.2 (CHPh₂). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} 18.3.

[CuCl(12)]. A vial was charged with **12** (142.7 mg, 0.207 mmol), copper(I) chloride (53.6 mg, 0.541 mmol, 2.6 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature for 4.5 h, evaporated and then re-dissolved in DCM, and filtered through celite. The solution was evaporated to yield a white solid that was washed with diethyl ether and dried under high vacuum. Yield: 129.4 mg, 0.164 mmol, 79%. The compound is a mixture of two rotamers with overlapping signals, as has been observed previously for other IPaul complexes;²³ these can be resolved by ⁷⁷Se NMR, and partially resolved by ¹H NMR, but not by ¹³C{¹H} NMR.

Major rotamer: **¹H NMR** (CDCl₃, 400 MHz): 7.41–7.11 and 7.00–6.82 (m, 24H, Ar CH), 6.26 (s, 2H, N(CH₂)₂N), 5.31 (s, 2H, CHPh₂), 2.37 (s, 6H, CH₃), 2.21 (s, 6H, CH₃). *Minor rotamer:* **¹H NMR** (CDCl₃, 400 MHz): 7.41–7.11 and 7.00–6.82 (m, 24H, Ar CH), 5.93 (s, 2H, N(CH₂)₂N), 5.30 (s, 2H, CHPh₂), 2.37 (s, 6H, CH₃), 2.16 (s, 6H, CH₃). *Mixture of rotamers:* **¹³C{¹H} NMR** (CDCl₃, 101 MHz): 153.1 (br., C-Se), 152.0 (br., C-Se), 142.3 (Ar C), 142.15 (Ar C), 142.06 (Ar C), 142.04 (Ar C), 141.54 (Ar C), 141.49 (Ar C), 140.9 (Ar C), 140.6 (Ar C), 135.2 (Ar C), 135.1 (Ar C), 132.3 (Ar C), 131.7 (Ar CH), 131.5 (Ar CH), 130.4 (Ar CH), 130.3 (Ar CH), 129.9 (Ar CH), 129.8 (Ar CH), 129.4 (Ar CH), 128.7 (Ar CH), 128.6 (Ar CH), 127.0 (Ar CH), 122.5 (N(CH₂)₂N), 122.2 (N(CH₂)₂N), 52.1 (CHPh₂), 51.9 (CHPh₂), 21.8 (CH₃), 18.5 (CH₃), 18.4 (CH₃). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} -9.2, -21.1. **CHN** Calculated for C₄₅H₄₀ClCuN₂Se: C, 68.70; H, 5.12; N, 3.56. Found: C, 68.14; H, 5.11; N, 3.52.

[Ag(1)₂][NO₃]. A vial was charged with **1** (25 mg, 0.053 mmol), silver nitrate (9.1 mg, 0.053 mmol, 1.0 equiv.), and acetone (2.5 mL). The reaction was stirred at room temperature for 3 h, then filtered through a microfilter, and evaporated to yield a white solid. The solid was washed with pentane (2 x 5 mL) and dried under high vacuum to yield a white powder. Yield: 29 mg, 98%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.64 (t, 2H, J = 7.8 Hz, Ar CH), 7.43 (d, 4H, J = 7.8 Hz, Ar CH), 7.23 (s, 2H, N(CH₂)₂N), 2.55 – 2.38 (m,

4H, CHMe₂), 1.36 (d, 12H, J = 6.9 Hz, CH₃), 1.20 (d, 13H, J = 6.9 Hz, CH₃). **¹³C{¹H} NMR** (CDCl₃, 101 MHz): δ_C 154.4 (C-Se), 145.5 (Ar C), 132.3 (Ar C), 132.0 (Ar CH), 125.7 (Ar CH), 123.2 (N(CH₂)₂N), 29.4 (CHMe₂), 24.6 (CH₃), 23.6 (CH₃).

[AgCl(1)]. A vial was charged with **1** (50 mg, 0.107 mmol), silver chloride (30.7 mg, 0.21 mmol, 2.0 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature overnight, then filtered through a microfilter, and evaporated to yield a white solid. The solid was washed with diethyl ether (2 x 5 mL) and dried under high vacuum to yield a white powder. Yield: 58.2 mg, 89%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.58 (t, 2H, J = 7.8 Hz, Ar CH), 7.36 (d, 4H, J = 7.8 Hz, Ar CH), 7.15 (s, 2H, N(CH₂)₂N), 2.61 – 2.44 (m, 4H, CHMe₂), 1.34 (d, 12H, J = 6.9 Hz, CH₃), 1.19 (d, 12H, J = 6.9 Hz, CH₃). **¹³C{¹H} NMR** (CDCl₃, 101 MHz): δ_C 157.1 (C-Se, determined by HSQC), 145.8 (Ar C), 133.2 (Ar C), 131.5 (Ar CH), 125.3 (Ar CH), 122.6 (N(CH₂)₂N), 29.3 (CHMe₂), 24.6 (CH₃), 23.7 (CH₃). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} 2.0. **HRMS** m/z calcd. for C₅₄H₇₂AgClN₄Se₂ [M - Cl]⁺ 1043.3133; found 1043.3179. **2D ¹H DOSY NMR** (CDCl₃, 500 MHz): diffusion coefficient = 7.76 x 10⁻¹⁰ m² s⁻¹ (MW = 703 g mol⁻¹).

[AgCl(4)]. A vial was charged with **4** (41 mg, 0.107 mmol), silver chloride (30.7 mg, 0.21 mmol, 2.0 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature overnight, then filtered through a microfilter, and evaporated to yield a white solid. The solid was washed with diethyl ether (2 x 5 mL) and dried under high vacuum to yield a white powder. Yield: 49.1 mg, 87%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.09 (s, 2H, N(CH₂)₂N), 7.08 (s, 4H, Ar CH), 2.39 (s, 6H, CH₃), 2.09 (s, 12H, CH₃). **¹³C{¹H} NMR** (CDCl₃, 101 MHz): δ_C 153.3 (C-Se), 140.9 (Ar C), 135.0 (Ar C), 133.2 (Ar C), 130.2 (Ar CH), 121.6 (N(CH₂)₂N), 21.5 (CH₃), 18.0 (CH₃). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} -37.5. **HRMS** m/z calcd. for C₄₂H₄₈AgClN₄Se₂ [M - Cl]⁺ 875.1255; found 875.1267. **2D ¹H DOSY NMR** (CDCl₃, 500 MHz): diffusion coefficient = 8.51 x 10⁻¹⁰ m² s⁻¹ (MW = 579 g mol⁻¹).

[AgCl(8)]. A vial was charged with **8** (55.5 mg, 0.21 mmol), silver chloride (61.2 mg, 0.42 mmol, 2.0 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature overnight, then filtered through a microfilter, and evaporated to yield a white solid. The solid was washed with pentane (2 x 5 mL) and dried under high vacuum to yield a white powder. Yield: 70.3 mg, 83%. **¹H NMR** (CDCl₃, 400 MHz): δ_H 7.03 (s, 2H, N(CH₂)₂N), 1.90 (s, 18H, CH₃). **¹³C{¹H} NMR** (CDCl₃, 101 MHz): δ_C 147.64 (C-Se), 116.45 (N(CH₂)₂N), 61.36 (C(CH₃)₃), 29.32 (CH₃). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} 131.1. **HRMS** m/z calcd. for C₂₂H₄₀AgClN₄Se₂ [M - Cl]⁺ 627.0629; found 627.0674. **2D ¹H DOSY NMR** (CDCl₃, 500 MHz): diffusion coefficient = 1.05 x 10⁻⁹ m² s⁻¹ (MW = 378 g mol⁻¹). Trace amounts of another complex were found with a diffusion coefficient = 8.511 x 10⁻¹⁰ m² s⁻¹ (MW = 579 g mol⁻¹, which most likely correspond to a [AgCl(L)₂] structure; however, the signal was too weak to analyse any further).

[AgCl(9)]. A vial was charged with **9** (66.6 mg, 0.21 mmol), silver chloride (61.2 mg, 0.42 mmol, 2.0 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature overnight,

then filtered through a microfilter, and evaporated to yield a white solid. The solid was washed with pentane (2 x 5 mL) and dried under high vacuum to yield a white powder. Yield: 76 mg, 78%. **¹H NMR** (CDCl₃, 500 MHz): δ_H 6.96 (s, 2H, N(CH)₂N), 4.88 (tt, 2H, *J* = 11.9, 3.8 Hz, N-CH), 2.20 – 2.13 (m, 4H, CH₂), 1.91 – 1.85 (m, 4H, CH₂), 1.79 – 1.73 (m, 2H, CH₂), 1.57 – 1.36 (m, 8H, CH₂), 1.26 – 1.14 (m, 2H, CH₂). **¹³C{¹H}-APT NMR** (CDCl₃, 101 MHz): δ_C 148.8 (C-Se), 116.8 (N(CH)₂N), 58.6 (N-CH), 32.9 (CH₂), 25.6 (CH₂), 25.4 (CH₂). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} -82.7. **HRMS** *m/z* calcd. for C₃₀H₄₈AgClN₄Se₂ [M - Cl]⁺ 731.1255; found 731.1303. **2D ¹H DOSY NMR** (CDCl₃, 500 MHz): diffusion coefficient = 8.71 x 10⁻¹⁰ m² s⁻¹ (MW = 551 g mol⁻¹).

[AgCl(10)]. A vial was charged with **10** (51.3 mg, 0.107 mmol), silver chloride (30.7 mg, 0.21 mmol, 2.0 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature overnight, then filtered through a microfilter, and evaporated to yield a white solid. The solid was washed with pentane (2 x 5 mL) and dried under high vacuum to yield a white powder. Yield: 52.7 mg, 79%. **¹H NMR** (CDCl₃, 500 MHz): δ_H 6.93 (s, 2H, N(CH)₂N), 5.27 (p, 2H, *J* = 7.0 Hz, N-CH), 1.98 – 1.90 (m, 4H, CH₂), 1.73 – 1.57 (m, 10H, CH₂), 1.48 – 1.28 (m, 30H, CH₂). **¹³C{¹H} NMR** (CDCl₃, 101 MHz): δ_C 150.9 (C-Se), 117.3 (N(CH)₂N), 56.1 (N-CH), 30.3 (CH₂), 23.9 (CH₂), 23.8 (CH₂), 23.7 (CH₂), 23.5 (CH₂), 21.8 (CH₂). **⁷⁷Se NMR** (CDCl₃, 76 MHz): δ_{Se} -66.3. **HRMS** *m/z* calcd. for C₅₄H₉₇AgClN₄Se₂ [M - Cl]⁺ 1067.5011; found 1067.5030. **2D ¹H DOSY NMR** (CDCl₃, 500 MHz): diffusion coefficient = 7.94 x 10⁻¹⁰ m² s⁻¹ (MW = 670 g mol⁻¹).

[AgCl(12)]. A vial was charged with **12** (73.5 mg, 0.107 mmol), silver chloride (30.7 mg, 0.21 mmol, 2.0 equiv.), and chloroform (2 mL). The reaction was stirred at room temperature overnight, then filtered through a microfilter, and evaporated to yield a white solid. The solid was washed with diethyl ether (2 x 5 mL) and dried under high vacuum to yield a white powder. Yield: 82.6 mg, 93%. The compound is a mixture of two rotamers with overlapping signals, as has been observed previously for other IPaul complexes;²³ these can be partially resolved by ¹H NMR, but not by ¹³C{¹H} NMR. **Major rotamer: ¹H NMR** (CDCl₃, 500 MHz): δ_H 7.35 – 7.06 (m, 18H, Ar CH), 6.97 – 6.93 (m, 4H, Ar CH), 6.79 (s, 2H, Ar CH), 6.15 (s, 2H, N(CH)₂N), 5.42 (s, 2H, CHPh₂), 2.32 (s, 6H, CH₃), 2.05 (s, 6H, CH₃). **Minor rotamer: ¹H NMR** (CDCl₃, 500 MHz): δ_H 7.31 – 7.12 (m, 18H, Ar CH), 6.89 – 6.87 (m, 4H, Ar CH), 6.69 (s, 2H, Ar CH), 5.86 (s, 2H, N(CH)₂N), 5.38 (s, 2H, CHPh₂), 2.32 (s, 6H, CH₃), 2.14 (s, 6H, CH₃). **Mixture of rotamers: ¹³C{¹H} NMR** (CDCl₃, 101 MHz): δ_C 154.9 (C-Se, determined by HSQC), 143.0 (Ar C), 142.7 (Ar C), 142.5 (Ar C), 142.5 (Ar C), 141.4 (Ar C), 141.1 (Ar C), 140.5 (Ar C), 135.4 (Ar C), 135.6 (Ar C), 133.4 (Ar C), 131.1 (Ar CH), 130.9 (Ar CH), 130.0 (Ar CH), 129.9 (Ar CH), 129.8 (Ar CH), 129.5 (Ar CH), 129.5 (Ar CH), 128.5 (Ar CH), 128.5 (Ar CH), 128.4 (Ar CH), 126.8 (Ar CH), 126.7 (Ar CH), 121.4 (N(CH)₂N), 121.2 (N(CH)₂N), 52.1 (CHPh₂), 51.9 (CHPh₂), 29.8 (CH₃), 21.8 (CH₃), 18.7 (CH₃), 18.5 (CH₃). **HRMS** *m/z* calcd. for C₉₀H₈₀AgClN₄Se₂ [M - Cl]⁺ 1483.3759; found 1483.3574. **2D ¹H DOSY NMR** (CDCl₃, 500 MHz): diffusion coefficient = 6.60 x 10⁻¹⁰ m² s⁻¹ (MW = 998 g mol⁻¹).

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Raw data underpinning this study (NMR FIDs) can be downloaded from the Strathclyde PURE data repository at the following URL: [http://dx.doi.org/\[DOI to follow\]](http://dx.doi.org/[DOI to follow])

§ 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/entries/1837514-1837524>.

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