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Exploring the Coordination of Cyclic Selenoureas to Gold(I)

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Supporting Information

ABSTRACT: NHC-derived selenoureas, which are useful for the quantification of NHC electronic properties, are deployed as ligands for Au(I). Surprisingly, while some compounds led to the expected [AuCl(SeUr)] species, selenoureas derived from more π -accepting NHCs unexpectedly furnished crystals of the corresponding [Au(SeUr)₂][AuCl₂] species, in which ligand rearrangement had occurred.

■ INTRODUCTION

The synthesis and exploration of new motifs in organometallic chemistry is of importance to the discovery of new, useful complexes for catalysis, medicines, and materials. Gold complexes have been used for a number of applications, particularly in homogeneous catalysis¹⁻³ but increasingly as anticancer agents⁴ and as luminescent materials.⁵ We report herein the synthesis of a number of new Au¹ complexes bearing selenourea ligands. Selenium-based ligands have been used with a variety of metal centers. Selenoureas (SeUr) in particular have been used as ligands for species including iridium photocatalysts,⁶ iridium and rhodium polymerization catalysts,⁷ precursors to zinc selenides,8 and copper complexes of biological relevance.^{9–11} The latter examples are particularly interesting, as different coordination geometries could be obtained: a 1:1 mixture of SeUr: [CuX] (X = Cl, Br, I) led to tetrameric $[Cu_4X_2(\mu-X)_2(\mu-SeUr)_4]$ complexes, while a 2:1 ratio allowed the isolation of trigonal-planar $[CuX(SeUr)_2]$ species.¹⁰ In gold chemistry,¹² a few examples of [AuCl-(SeUr)₂] complexes are known,^{13,14} as well as cationic [AuL(SeUr)₂] complexes.^{15–18}

We recently prepared a range of N-heterocyclic carbene (NHC)-derived selenoureas, in order to quantify the π -backbonding ability of NHCs via ⁷⁷Se{¹H} NMR spectroscopy, according to the method of Ganter.¹⁹ We therefore sought to prepare a range of complexes bearing these species as ligands and probe the changes in NMR spectra and solid-state structure on coordination to gold(I).

RESULTS AND DISCUSSION

Synthesis of Cyclic Selenoureas and Their Gold(I) Complexes. Several known compounds (1a-g) were deployed: [Se(IPr)] (1a) and [Se(SIPr)] (1c) were first reported by Ganter et al.,¹⁹ while [Se(IPr^{OMe})] (1b), [Se(SIPr^{OMe})] (1d), [Se(IPr*)] (1e), and [Se(IPr*^{OMe})] (1f) were disclosed recently.²⁰ [Se(IⁱPr^{Me})] (1g) has been reported previously.²¹ Three additional selenoureas were prepared, either by reaction of the free carbene with elemental selenium



([Se(IPr^{Cl})] (1h)) or by deprotonation of the corresponding imidazolium salt in the presence of elemental selenium ([Se(IMes)] (1i), [Se(SIMes)] (1j)). These compounds cover a range of 1,3-diarylimidazol-2-ylidenes, as well as an example of a 1,3-dialkylimidazol-2-ylidene. The Tolman electronic parameters (TEP)²² of all the corresponding NHCs are known,^{20,23} and the δ_{Se} chemical shift is proposed to allow the relative back-bonding abilities of each NHC to be quantified; the values reported here extend the range of values previously reported by Ganter and co-workers using this method (Figure 1).¹⁹ Further studies into the nature of the bonding in these compounds, and how it relates to the selenium NMR data, are currently underway in our research group; the typically very bulky *N*-aryl substituents may mean that chemical shift anisotropy has a significant effect here.

New complexes of these selenourea species with gold were prepared by reaction of $[AuCl(SMe_2)]$ with 1 equiv of the selenourea compound in THF at room temperature (Scheme 1). Unfortunately, complex **2g** decomposed upon workup: during removal of the solvent, a gold mirror formed on the inside of the vial. This suggests an important role for bulky *N* substituents, which may serve to stabilize the gold complex and prevent agglomeration. For the other examples, filtration and removal of the solvent furnished the desired complexes in quantitative yield. These new species were characterized by a number of methods (see the Experimental Section), including ¹H, ¹³C{¹H}, and ⁷⁷Se{¹H} NMR spectroscopic analyses and elemental analysis. These analyses were all consistent with the monomeric gold chloride structure.

Solid-State Characterization of Gold(I) Complexes. Single crystals of **2a**,**c**-**f**,**i**,**j** were prepared by slow diffusion of hexane into a saturated solution of the complex in DCM. X-ray analysis of these crystals revealed the expected linear two-coordinate [AuCl(SeUr)] structure for complexes **2a**,**e**,**f**,**i**,**j** (Figure 2) but led surprisingly to [Au(SeUr)₂][AuCl₂]

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Article 1c 1d 1h 1j 1e 1f 1a 1b 1i 1g 113 87 83 35 181 177 174 nd nd nd 190 185 174 110 106 104 90 87 27 -18 1g 200 150 100 50 0 -50 δ_{Se} (ppm) π -accepting ability C /Pr Ph Pł 1a X = CH, R = H 1c X = CH₂, R = H 1e R = Me 1h 1i X = CH 1f R = OMe 1j X = CH_2

1b X = CH, R = OMe **1d** X = CH_2 , R = OMe

Figure 1. Selenourea compounds used in this study and their relative π -accepting properties quantified using δ_{Se} in acetone (red) or CDCl₃ (blue). The known range reaches 800 ppm for highly π accepting NHCs.¹





complexes for 2c,d, which bear more π -accepting saturated NHC derivatives (Figure 3). This result was explored further by growing new crystals for analysis using strictly oxygen and water free solvents, in order to rule out the possibility of decomposition during crystallization or of water interfering with this process. In each case, crystals appeared to grow as a single cluster and a single morphology; analysis of multiple crystals from selected samples furnished the same results. However, when the crystals were redissolved in deuterated solvents, the NMR spectra obtained were the same as the initial NMR spectra. When 1 equiv of [AuCl(SMe₂)] was exposed to 0.5 equiv each of 1c,d, the resulting mixture comprised a 1:1 mixture of the products obtained separately, yet a 1:2:1 mixture of products would be anticipated if $[L_2Au][AuCl_2]$ species were formed in solution. This suggests either that the $[Au(SeUr)_2]$ -[AuCl₂] form is present as an impurity which crystallizes preferentially or that interconversion between the two forms is quite facile.

Key bond lengths and angles are recorded in Table 1. Notably, the Au-C_{ipso} distances (the distance between the gold center and the aryl ring of the selenourea) is within the sum of the van der Waals radii of the two atoms (ca. 3.36 Å), suggesting an interaction. In some complexes (e.g., 2f), Se-H distances of just under 3.10 Å are observed. However, H atoms were located using the riding model; thus, there is some uncertainty in their location. In the monomeric complexes, the Se-Au-Cl angle deviates from 180° by ca. 5-10°. C-Se-Au angles are all in the range of ca. 103-107°. There is no evidence of aurophilic interactions in these crystal structures, presumably due to the steric bulk of the NHC-derived selenourea compounds.

A search of the Cambridge Structure Database reveals a limited number of examples of solid-state structures of [AuX(SeUr)] complexes. Aroz et al. reported the dinuclear complex $[{Au(C_6F_5)}_2Mbis]$ (Mbis = 3,3'-methylenebis(1methyl-1,3-dihydro-2H-imidazole-2-selenone), based on the



Figure 2. X-ray crystal structures of complexes 2a,e,f,i,j with thermal ellipsoids at the 50% probability level. Most H atoms are excluded for clarity.

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Figure 3. X-ray crystal structures of complexes 2c,d with thermal ellipsoids drawn at the 50% probability level. Most H atoms are excluded for clarity.

Table 1. Key Bond Lengths (Å) and Angles (deg) in Selenourea-Au(I) Species 2

	Au-Se	Se-C	Au-C _{ipso}	C–Se–Au	Se-Au-Cl
$2a^{a,b}$	2.361	1.867	3.093	103.40	175.46
$2c^{c}$	2.398	1.871	3.142	105.59	
$2d^{c}$	2.379	1.862	3.144	106.61	
$2e^{a}$	2.353	1.865	3.191	104.38	174.47
$2f^a$	2.354	1.870	3.247	106.94	170.93
$2i^a$	2.360	1.870	3.184	105.82	174.07
2j ^{<i>a</i>}	2.360	1.868	3.085	105.38	173.32
^a Takes	the form	[L-Au-Cl]	. ^b Average	from two	independent
molecules. ^{<i>c</i>} Takes the form [L-Au-L][AuCl ₂].					

coordination of two $[Au(C_6F_5)]$ units to two methylene-linked cyclic selenoureas, which is quite different from the arrangements reported here.¹³ Fettouhi et al. and Bhabak and Mugesh have each crystallized a cationic complex of the form $[Au(PMe_3)(SeUr)]_2[Cl]_2$ (SeUr = selenourea (3a), 1-methyl-1,3-dihydro-2H-imidazole-2-selenone (3b)) which displayed aurophilic interactions (with Au-Au distances of 3.04 and 3.10 Å, respectively).^{24,25} In both of these complexes, more acute C-Se-Au angles are observed (97.85, 100.34, 96.78, and 101.15°, respectively) with similar slight bending of the angle around the gold center (Se-Au-C angle of 177.49°; Se-Au-P angles of 175.06, 172.41, and 175.98°). Notably, these two examples feature much smaller ligands in comparison to the bis(aryl)-substituted examples considered here. The coordination behavior of these new selenourea compounds (2) is interesting, particularly given that each of the two motifs is obtained under identical reaction and crystallization conditions.

Solution-State Characterization of Gold(I) Complexes. While solid-state characterization methods suggested different structures for gold(I) chloride complexes of different



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selenoureas, we were intrigued about their structure in solution; the two isomers are difficult to differentiate using standard 1D experiments and 2D correlation techniques. We therefore turned to diffusion-based NMR experiments to elucidate the molecular weight of the complexes in solution (Figure 4).



Figure 4. Overlay of 2D 1 H-DOSY spectra recorded for 2a (red) and 2c (blue).

These experiments revealed very similar diffusion coefficients in chloroform-*d* solution for **2a**,**c** (ca. $(7.5 \pm 0.1) \times 10^{-10}$ and $(7.6 \pm 0.1) \times 10^{-10}$ m² s⁻¹, respectively). Using the correlation proposed by Morris and co-workers,²⁶ the molecular weights of these species can be estimated at 748 and 728, respectively, versus 700 and 702 for the monomeric [AuCl(SeUr)] complexes. The [Au(SeUr)₂]⁺ fragments would be expected to have diffusion coefficients of 6.24×10^{-10} and 6.23×10^{-10} m² s⁻¹. These species therefore adopt a monomeric structure in solution.

The presence of the ⁷⁷Se nuclide allows the electronic environment of the selenium atom, and how this changes on coordination to gold(I), to be probed.²⁷ Coordination to the gold(I) chloride center led to a systematic decrease in the δ_{Se} value of typically 20–30% (Figure 5), suggestive of a less deshielded environment. The ³¹P NMR chemical shift of phosphines is known to systematically *increase* upon binding to the AuCl fragment.¹⁷ A plausible explanation is that, when the selenoureas bind to the gold(I) center, less electron density is available to donate into the aromatic system.

Most interestingly, the propensity of the ligand to form $[Au(SeUr)_2][AuCl_2]$ -type complexes instead of [AuCl(SeUr)] species appears to be related to the δ_{Se} chemical shift on the ⁷⁷Se{¹H} NMR spectrum, although the limited number of examples here makes it difficult to propose general trends.

Selenoureas with higher δ_{Se} values (suggesting that they are derived from more π accepting imidazol-2-ylidenes) appear to lead to the bis-selenourea motif. This may be due to the less electron rich selenium centers (as shown by higher δ_{Se}) binding more strongly to a cationic gold(I) fragment than to neutral gold(I): i.e., the former ought to be more Lewis acidic than the latter.



Figure 5. Plot of δ_{se} for cyclic selenoureas bound to gold(I) versus δ_{se} for the unbound cyclic selenourea; annotations refer to the NHC from which the cyclic selenourea was derived, while the dashed line has a slope of unity and an intercept of zero.

CONCLUSIONS

In conclusion, we have explored the coordination chemistry of a series of NHC-derived selenourea compounds with gold(I). New complexes were characterized by NMR spectroscopy and elemental analysis. X-ray crystal diffraction studies revealed two distinct geometries: selenoureas based on more π accepting NHC ligands led to [Au(SeUr)₂][AuCl₂] species, while others led to the expected [AuCl(SeUr)] motif. However, the complexes take the form [AuCl(SeUr)] in the solution state, as confirmed by ¹H DOSY NMR studies of **2a**,**c**, yet mass spectroscopy studies suggested that **2a**,**c** both form [Au-(SeUr)₂]⁺ ions in the spectrometer.²⁸ Further work to generate new derivatives of these complexes and explore the catalytic activity of selenourea–gold(I) complexes is currently underway in our laboratories.

EXPERIMENTAL SECTION

Reactions were performed on the bench, under ambient conditions, unless otherwise stated. Selenium was obtained from Strem and used as supplied. Dry THF was obtained from an MBraun solvent purification system. Other solvents and reagents were used as supplied. ¹H, ¹³C{¹H}, and ⁷⁷Se{¹H} spectra were recorded on Bruker Avance 400 and 500 MHz spectrometers with either BBFO or QNP probes. Chemical shifts for ¹H and ¹³C{¹H} NMR spectra are reported in ppm relative to SiMe₄; chemical shifts for ⁷⁷Se{¹H} NMR spectra are reported in ppm relative to SeMe₂ and are externally referenced to PhSeSePh (δ_{Se} 463 ppm). Coupling constants are in hertz. Signals on the ¹³C{¹H} and ⁷⁷Se{¹H} NMR spectra were singlets unless otherwise stated. Elemental analyses were performed by the London Metropolitan University Elemental Analysis Service. Results are reported as an average of two analyses. Accurate mass spectroscopic analyses were carried out by the EPSRC National Mass Spectrometry Service Centre, Swansea, U.K., using a ThermoFisher LTQ Orbitrap XL instrument. The synthesis and characterization of [Se(IPr)] (1a), $[Se(IPr^{OMe})]$ (1b), [Se(SIPr)] (1c), $[Se(SIPr^{OMe})]$ (1d), $[Se(IPr^*)]$ (1e), $[Se(IPr^{*OMe})]$ (1f), and $[Se(I^{P}r^{Me})]$ (1g) have been reported previously.^{19–21} IMes·HCl, SIMes·HBF₄ and IPr^{Cl} were prepared according to the published procedures.^{29,30} Caution! Care should be taken when handling highly toxic elemental selenium. Special measures must also be taken for its disposal.

[Se(IPr^{CI})] (1h). In the glovebox, a solution of IPr^{CI} (154.0 mg, 0.337 mmol) in THF (5 mL) was prepared. Outside of the glovebox, the solution was transferred under argon via cannula into an ovendried flask containing selenium (75.6 mg, 0.957 mmol, 2.8 equiv). The reaction mixture was stirred overnight. The THF was removed in vacuo, the residue was dissolved in DCM (5 mL), and this solution

was passed through a pad of Celite, which was then washed with further DCM (5 mL). The DCM was removed in vacuo, and the residue was washed with pentane (3 × 2 mL) and dried under high vacuum to yield the title compound as a white powder (137.7 mg, 0.257 mmol, 76%). ¹H NMR (CDCl₃, 500 MHz): δ 7.54 (t, ³J_{HH} = 7.8, 2H), 7.34 (d, ³J_{HH} = 7.8, 4H), 2.63 (sept., ³J_{HH} = 6.8, 4H), 1.35 (d, ³J_{HH} = 6.8, 12H), 1.26 (d, ³J_{HH} = 6.8, 12H). ¹³C{¹H} NMR (CDCl₃, 95 MHz): δ 173.6. ¹H NMR (CDCl₃, 24.97. ⁷⁷Se{¹H} NMR (CDCl₃, 95 MHz): δ 173.6. ¹H NMR (acetone-d₆, 400 MHz): δ 7.56 (t, ³J_{HH} = 7.7, 2H), 7.41 (d, ³J_{HH} = 7.7, 4H), 2.69 (sept., ³J_{HH} = 6.9, 4H), 1.33 (d, ³J_{HH} = 6.9, 12H), 1.25 (d, ³J_{HH} = 6.9, 12H). ¹⁷Se{¹H} NMR (acetone-d₆, 76 MHz): δ 174.0 Anal. Calcd for C₂₇H₃₄N₂Cl₂Se: C, 60.45; H, 6.39; N, 5.22. Found: C, 60.45; H, 6.29; N, 5.30.

[Se(IMes)] (1i). IMes·HCl (1.005 g, 2.95 mmol) and KO^tBu (368.9 mg, 3.29 mmol, 1.1 equiv) were suspended in dry THF (40 mL), in an oven-dried flask, under argon. Selenium was added (769.4 mg, 9.74 mmol, 3.3 equiv). The reaction mixture was stirred overnight at room temperature. The THF was removed in vacuo, the residue was dissolved in DCM (20 mL), and this solution was passed through a pad of Celite, which was then washed with further DCM (5 mL). The DCM was removed in vacuo, and the residue was washed with pentane $(3 \times 10 \text{ mL})$ and dried under high vacuum to yield the title compound as a pale red powder (916.8 mg, 2.39 mmol, 81%). ¹H NMR (CDCl₃, 500 MHz): δ 7.02 (s, 4H), 6.97 (s, 2H), 2.35 (s, 6H), 2.13 (s, 12H). $^{13}C{^{1}H}$ NMR (CDCl₃, 125 MHz): δ 157.6, 139.5, 135.5, 134.3, 129.4, 120.3, 21.3, 18.1. ⁷⁷Se{¹H} NMR (CDCl₃, 95 MHz): δ 26.7. ¹H NMR (acetone-d₆, 500 MHz): δ 7.31 (s, 2H), 7.01 (s, 4H), 2.32 (s, 6H), 2.09 (s, 12H). ⁷⁷Se{¹H} NMR (acetone- d_{6} , 95 MHz): δ 34.6. Anal. Calcd for C₂₁H₂₄N₂Se: C, 65.79; H, 6.31; N, 7.31. Found: C, 65.65; H, 6.37; N, 7.32.

[Se(SIMes)] (1j). SIMes·HBF₄ (1.198 g, 3.04 mmol) and KO^tBu (370.3 mg, 3.30 mmol, 1.1 equiv) were suspended in dry THF (40 mL), in an oven-dried flask, under argon. Selenium was then added (739.9 mg, 9.37 mmol, 3.1 equiv). The reaction mixture was stirred overnight at room temperature. The THF was removed in vacuo, the residue was dissolved in DCM (20 mL), and this solution was passed through a pad of Celite, which was then washed with further DCM (5 mL). The DCM was removed in vacuo, and the residue was washed with pentane $(3 \times 10 \text{ mL})$ and dried under high vacuum to yield the title compound as a white powder (1.004 g, 2.60 mmol, 86%). ¹H NMR (CDCl₃, 500 MHz): δ 6.98 (s, 4H), 4.00 (s, 4H), 2.32 (s, 12H), 2.31 (s, 6H). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 180.1, 138.6, 136.4, 135.0, 129.6, 48.8, 21.3, 18.0. ⁷⁷Se{¹H} NMR (CDCl₃, 95 MHz): δ 109.7. ¹H NMR (acetone- d_{6} , 500 MHz): δ 6.94 (s, 4H), 4.08 (s, 4H), 2.29 (s, 12H), 2.27 (s, 6H). ⁷⁷Se{¹H} NMR (acetone-d₆, 95 MHz): δ 113.1. Anal. Calcd for C₂₁H₂₆N₂Se: C, 65.44; H, 6.80; N, 7.27. Found: C, 65.35; H, 6.93; N, 7.16.

General Procedure for the Synthesis of [AuCl(Se(NHC))]Complexes. In air, a vial was charged with [Se(NHC)] (1 equiv), $[AuCl(SMe_2)]$ (1 equiv), THF (0.15 M), and a stirring bar. The mixture was stirred at room temperature for 2 h. The product typically precipitated from the solution. It could be redissolved by adding DCM, after which the solution was passed through a microfilter. The solution was concentrated. Hexane was added, the resulting precipitate was broken into fine particles, and the solvent was removed in vacuo.

[AuCl(Se(IPr))] (2a). The product was a pale solid (74.8 mg, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 7.63 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 7.7 Hz, 4H), 7.21 (s, 2H), 2.42 (hept, J = 6.9 Hz, 4H), 1.37 (d, J = 6.9 Hz, 12H), 1.18 (d, J = 6.9 Hz, 12H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 151.2, 145.6, 132.8, 131.9, 125.3, 123.8, 29.3, 24.8, 23.5. ⁷⁷Se{¹H} NMR (95 MHz, CDCl₃): δ 69.0. Anal. Calcd for C₂₇H₃₆AuClN₂Se: C, 46.33; H, 5.18; N, 4.00. Found: C, 46.19; H, 5.28; N, 4.16.

[AuCl(Se(Pr^{OMe}))] (2b). The product was a pale solid (41.1 mg, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 7.16 (s, 2H), 6.88 (s, 4H), 3.93 (s, 6H), 2.46 (hept, J = 6.8, 4H), 1.39 (d, J = 6.8, 12H), 1.19 (d, J = 6.8, 12H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 162.2, 152.0, 147.0, 125.8, 124.0, 110.8, 55.8, 29.4, 24.7, 23.4. ⁷⁷Se{¹H} NMR (95

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MHz, CDCl₃): δ 67.9. Anal. Calcd for C₂₉H₄₀AuClN₂O₂Se: C, 45.83; H, 5.30; N, 3.69. Found: C, 45.76; H, 5.45; N, 3.57.

[*AuCl(Se(SIPr))*] (*2c*). The product was a pale solid (74.9 mg, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 7.56 (t, *J* = 7.4, 2H), 7.32 (d, *J* = 7.4, 4H), 4.15 (s, 4H), 2.90 (hept, *J* = 7.3, 4H), 1.45 (d, *J* = 7.3, 12H), 1.32 (d, *J* = 7.3, 12H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 177.4, 146.5, 133.2, 131.1, 125.5, 52.7, 29.4, 25.2, 24.5. ⁷⁷Se{¹H} NMR (95 MHz, CDCl₃): δ 125.8. Anal. Calcd for C₂₇H₃₈AuClN₂Se: C, 46.20; H, 5.46; N, 3.99. Found: C, 45.98; H, 5.53; N, 4.07.

[AuCl(Se(SIPr^{OMe}))] (**2d**). The product was a pale solid (81.1 mg, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 6.81 (s, 4H), 4.10 (s, 4H), 3.89 (s, 6H), 2.84 (hept, J = 6.9, 4H), 1.43 (d, J = 6.9 Hz, 12H), 1.30 (d, J = 6.9 Hz, 12H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 178.1, 161.6, 147.9, 126.2, 111.1, 55.7, 52.7, 29.6, 25.2, 24.5. ⁷⁷Se{¹H} NMR (95 MHz, CDCl₃): δ 124.3. Anal. Calcd for C₂₉H₄₂AuClN₂O₂Se: C, 45.71; H, 5.56; N, 3.68. Found: C, 46.04; H, 5.59; N, 3.85.

[AuCl(Se(IPr*))] (2e). The product was a pale solid (46.8 mg, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 7.33–7.24 (m, 20H), 7.17–7.12 (m, 12H), 6.98 (s, 4H), 6.85–6.81 (m, 8H), 5.46 (s, 2H), 5.20 (s, 4H), 2.35 (s, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 149.1, 142.8, 142.0, 141.9, 140.9, 131.9, 131.3, 130.1, 129.3, 128.7, 128.5, 127.2, 126.9, 123.3, 52.0, 22.2. ⁷⁷Se{¹H} NMR (95 MHz, CDCl₃): δ 73.0. MS (ESI-Orbitrap): calcd for C₆₉H₅₆AuN₂⁷⁴Se ([M – Cl]⁺), 1183.3328; found, 1183.3335.

Cl]⁺), 1183.3328; found, 1183.3335. [AuCl(Se(IPr*^{OMe}))] (2f). The product was a pale solid (41.4 mg, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 7.28–7.18 (m, 20H), 7.11–7.06 (m, 12H), 6.81–6.77 (m, 8H), 6.62 (s, 4H), 5.34 (s, 2H), 5.14 (s, 4H), 3.61 (s, 6H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 161.4, 142.8, 142.5, 141.9, 130.1, 129.2, 128.7, 128.5, 127.3, 127.2, 127.0, 123.5, 116.2, 55.6, 52.2. ⁷⁷Se{¹H} NMR (95 MHz, CDCl₃): δ 72.0. MS (ESI-Orbitrap): calcd for C₆₉H₅₆AuN₂⁷⁴Se ([M – Cl]⁺), 1215.3226; found, 1215.3227.

[AuCl(Se(IPr^{CI}))] (2h). The product was a pale solid (43.9 mg, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 7.70 (t, J = 7.9, 2H), 7.41 (d, J = 7.9, 4H), 2.42 (hept, J = 6.8, 4H), 1.40 (d, J = 6.8, 12H), 1.25 (d, J = 6.8, 12H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 151.1, 146.1, 132.7, 129.8, 125.7, 119.6, 29.7, 24.2, 24.1. ⁷⁷Se{¹H} NMR (95 MHz, CDCl₃): δ 136.3. Anal. Calcd for C₂₇H₃₄AuCl₃N₂Se: C, 42.18; H, 4.46; N, 3.64. Found: C, 42.08; H, 4.54; N, 3.53.

[AuCl(Se(IMes))] (2i). The product was a pale solid (83.0 mg, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 7.16 (s, 2H), 7.09 (s, 4H), 2.41 (s, 6H), 2.10 (s, 12H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 146.8, 141.5, 134.8, 132.7, 130.2, 122.9, 21.5, 18.0. ⁷⁷Se{¹H} NMR (95 MHz, CDCl₃): δ 22.5. Anal. Calcd for C₂₁H₂₄AuClN₂Se: C, 40.96; H, 3.93; N, 4.55. Found: C, 41.17; H, 3.82; N, 4.48.

[AuCl(Se(SIMes))] (2j). The product was a pale solid (82.4 mg, quantitative). ¹H NMR (500 MHz, CDCl₃): δ 7.04 (s, 4H), 4.11 (s, 4H), 2.37 (6H), 2.29 (s, 12H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 173.7, 140.7, 135.7, 133.1, 130.5, 50.1, 21.4, 17.8. ⁷⁷Se{¹H} NMR (95 MHz, CDCl₃): δ 81.9. Anal. Calcd for C₂₁H₂₆AuClN₂Se: C, 40.82; H, 4.42; N, 4.53. Found: C, 40.69; H, 4.44; N, 4.47.

ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving NMR spectra for all new compounds, details of DOSY NMR experiments, mass spectra for **2a**,**c**, and crystallographic data for complexes **2a**,**c**-**f**,**i**,**j**. This material is available free of charge via the Internet at http:// pubs.acs.org. CCDC files 994254–994260 also contain crystallographic data for complexes **2a**,**c**-**f**,**i**,**j**.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

IMes, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; $I^{i}Pr^{Me}$, 1,3-diisopropylimidazol-2-ylidene; IPr, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; IPr^{Cl}, 1,3-bis(2,6-diisopropylphenyl)-4,5-dichloroimidazol-2-ylidene; IPr^{OMe}, 1,3-bis(2,6-diisopropyl-4-methoxyphenyl)imidazol-2-ylidene; IPr*, 1,3-bis(2,6-diphenylmethyl-4-methylphenyl)imidazol-2-ylidene; IPr*^{OMe}, 1,3-bis(2,6-diphenylmethyl-4-methoxyphenyl)-imidazol-2-ylidene; SIPr, 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene; SIPr, 1,3-bis(2,6-diisopropylphenylphenyl)-4,5-dihydroimidazol-2-ylidene; SIPr, 1,3-bis(2,6-diisopropylphenylphenylphenylphenylphenylphenylphenylphenylphenylphenylphenylp

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(27) A reviewer pointed out that the steric bulk in the proximity of the selenium atom may lead to chemical shift anisotropy; further studies are underway in our laboratories to examine bonding in these selenoureas and will be reported in due course.

(28) Mass spectroscopic studies were also carried out, using MALDI and ESI techniques, but these suggested that 2a,c both adopted a $[Au(SeUr)_2][AuCl_2]$ arrangement. We believe that ionization of these complexes in the mass spectrometer may perturb their arrangement. See the Supporting Information for data.

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