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Dinuclear gold(I) dithio- and diselenophosph(in)ate complexes forming mononuclear gold(III) oxidative addition complexes and reversible chemical reductive elimination products†

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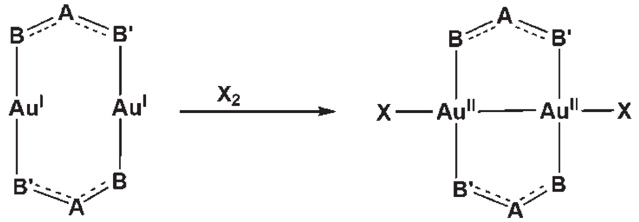
Dinuclear gold(I) dithio- and diselenophosph(in)ate complexes were prepared to serve as precursors for subsequent oxidative addition (OA) chemistry following reaction with mild oxidant iodine, I_2. The new OA products circumvented the formation of the expected dinuclear Au(II) complexes, but instead formed novel chelating mononuclear square-planar gold(III) products of the type $[AuI_2\{E_2PR_2\}]$ (R = $(CH_2)_2Ph$; E = S, **2**; E = Se, **3**) and $[AuI_2\{Se_2P(OR)_2\}]$ (R = Et, **4**; ^{i}Pr, **5**) directly. We further demonstrate that this process is chemically reversible as all the Au(III) complexes undergo chemical reductive elimination to the starting dinuclear Au(I) complexes in the presence of SnI_2 as determined by ^{119}Sn and ^{31}P NMR. The complexes (**2–5**) were all prepared from the reaction between I_2 and the corresponding dinuclear gold(I) precursor material. All new complexes were characterized by ^{1}H, ^{31}P, ^{77}Se (for E = Se) NMR, infrared spectroscopy, elemental analysis and single crystal X-ray diffraction.

Introduction

Oxidative addition (OA) is an important reaction class as it allows the formation of new metal–ligand bonds by cleavage of a bond in an organic or main-group reagent. The reagents can typically vary from low to high polarity. Furthermore, OA reactions lead to an increase of both the oxidation state and coordination number of the metal centre(s) involved.[1] As such, homogeneous catalytic cycles frequently contain an OA (and its reverse, reductive elimination) reaction, currently applied to a number of large industrial processes.[2] Homogeneous gold catalysts in particular have witnessed tremendous development during the past decade.[3] In gold chemistry, OA reactions of dinuclear gold(I) ylide complexes of the type $[Au(CH_2)_2PPh_2]_2$ (**A**) (Schmidbaur ylide) are the best known and by far the most intensely studied, see Scheme 1.[4]



Scheme 1 Classic dinuclear gold(II) OA products with a formal Au(II)–Au(II) bond obtained from small molecules adding across a variety of gold(I) metallacycles. A = P, B = B′ = CH_2 (**A**); A = P, B = S, B′ = CH_2 (**B**); A = CH, B = B′ = NR (**C**); X = Cl, Br, I, and other small molecules.

The OA event can be achieved if the gold centers are in close proximity; hence dinuclearity is an essential consideration to stabilize the d^9 system with the formation of a formal Au(II)–Au(II) bond upon oxidation.[5] Hence, factors related to the extent of the Au–Au bonding interaction, the electronic structure of each metal atom, and the nature of the ligand must be considered.[6]

Numerous reports have shown that small molecules such as X_2 (X = Cl, Br, I), CH_3I, CH_3NO_2, SO_2, $SOCl_2$, H_2S, $(PhCOO)_2$ and S_8 can successfully add across the two Au centres of the metallacycle, forming dinuclear Au(II) complexes.[4,5,7]

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The development of the methylenethiophosphane ligand in complexes of the type $[Au(CH_2)(S)PPh_2]_2$ (**B**) shows the same reactivity trends as (**A**).[8] Fackler and co-workers also made inroads with the amidinate ligand in complexes of the type $[Au(NRCHNR)]_2$ (R = bulky) (**C**), now well established.[9] These systems all contain C–P–C (**A**), C–P–S (**B**) and N–C–N (**C**) bridging monoanionic ligands.

In continuing the studies of (**A**), M. Laguna and co-workers examined the reactions of $[Au(Cl)(CH_2)_2PPh_2]_2$ with various alkynes in an attempt to form digold(II) acetylide complexes, but instead formed the first dinuclear gold(III) alkyne complex.[4e] The study further demonstrated that although dinuclear gold(II) complexes can afford heterovalent gold(I)/gold(III) complexes by disproportionation,[4f] the inverse reaction, that is, formation of digold(II) complexes by comproportionation of gold(I)/gold(III) complexes, can also be achieved.

The less studied bridging S–C–S case involves the $[Au_2\{S_2CC(CN)_2\}]^{2-}$ complex which does add X_2 (halide or other small molecule) but importantly, the negative charge of the resulting Au(II) complex appears to greatly improve stability[10] because for the related S–C–S bridging *neutral* dithiocarbamate complexes of the type $[AuS_2CNR_2]_2$, an OA reaction had been suggested, but was found to be too unstable to isolate at room temperature.[11] Recently, the addition of the elusive F_2 across type (**C**) had been achieved.[12] In all the standard cases for **A**, **B** and **C** outlined above, the important observation is that *the dinuclear unit remains intact* and is wholly isolable and stable after the OA event. Even in cases where isolated dinuclear Au(II) complexes are subjected to further oxidation to Au(III) species, *the dinuclear unit still remains intact*.[5]

The present study focused on the E–P–E (E = S, Se) bridging ligands as a seemingly innocent extension of the above, but its OA reactions consistently revealed a complete departure from the above reported observations. Gold(I) analogues with bridging S–P–S ligands have been reported extensively,[13] and the reversible addition of Cl_2 to the heteroleptic complex $[Au_2\{(CH_2)_2PMe_2\}\{S_2PPh_2\}]$ has been demonstrated.[14] The complex $[Au(S_2P(OH)Ph)_2]Cl$, reported in 1988, was the first structurally characterized mononuclear gold(III) complex with a S–P–S chelating ligand;[15] to date it has no Se counterpart, and its mechanism of formation remains unclear. Changing to the heavier Se analogue, dinuclear gold(I) complexes with Se-donor ligands are studied considerably less.[16] Although the Liu group has studied diselenophosphate complexes and clusters for a number of years,[17] the first dinuclear gold(I) complexes with Se–P–Se bridging ligands, $[Au\{Se_2P(OR)_2\}]_2$ (R = Et, ^{i}Pr), was described.[18] Recently, one of us communicated an example of a structurally characterized gold(III) complex with a S–P–S chelate as well as an oxidative bromination product related to complexes **2–5** reported here, but for the corresponding dithiophosphonate ligand.[19] The present study cements the view with several examples that OA reactions for E–P–E bridging ligands across gold(I) centers do not lead to readily isolable dinuclear gold(II) complexes, but instead show a different and unexpected reactivity pathway.

Experimental

Materials and measurements

All chemicals were purchased from commercial sources and used as received. Solvents were purified following standard protocols.[20] All of the reactions were performed in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. The starting $[AuCl(THT)]$[18a] and dinuclear $[AuSe_2PR_2]_2$ (R = OEt, O^{i}Pr, CH_2CH_2Ph) complexes were prepared according to the reported methods.[18b,c] The ligand $[NH_4][S_2P(CH_2CH_2Ph)_2]$ was prepared according to the literature methods.[18d] The elemental analyses were done using a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded on a Bruker Advance DPX300 FT-NMR spectrometer, which operates at 300 MHz while recording ^1H, 121.49 MHz while recording ^{31}P, and 57.24 MHz while recording ^{77}Se nuclei. The $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR are referenced externally against 85% H_3PO_4 (δ = 0 ppm) and PhSeSePh (δ = 463 ppm), respectively. The chemical shift (δ) and coupling constant (J) are reported in parts per million and hertz, respectively. The NMR spectra were recorded at ambient temperature unless noted otherwise. IR spectra were recorded on a JASCO FT-IR 401 spectrometer at 25 °C using CsI plates. Melting points were measured using a Fargo MP-2D melting point apparatus.

Safety note

Selenium and its derivatives are toxic! These materials should be handled with caution.

Synthesis

$[Au\{S_2P(CH_2CH_2Ph)_2\}]_2$, 1. A solution of $NH_4[S_2P(CH_2CH_2Ph)_2]$ (0.201 g, 0.619 mmol) and [AuCl(tht)] (0.198 g, 0.619 mmol) were mixed in 20 mL of THF. The solution was stirred at −50 °C for 1 h under nitrogen. The solvent was evaporated under vacuum to obtain $[Au_2\{S_2P(CH_2CH_2Ph)_2\}_2]$ as a yellow powder. The NH_4Cl byproduct was removed by filtration, the product extracted into CH_2Cl_2 and the solvent subsequently removed under reduced pressure. Yield: 0.284 g (91%). Anal. Calcd for $C_{32}H_{36}Au_2P_2S_4$: C, 38.25; H, 3.61. Found: C, 38.11; H, 3.34. mp: 155 °C (dec). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.59 (m, 8H, CH_2Ph), 3.12 (m, 8H, PCH_2), 7.28 (m, 20H, Ph). ^{31}P NMR (121.49 MHz, $CDCl_3$, δ, ppm): 77.7. Anal. Calcd for $C_{32}H_{36}Au_2P_2S_4$: C, 38.25; H, 3.61. Found: C, 38.11; H, 3.34.

$[AuI_2\{S_2P(CH_2CH_2Ph)_2\}]$, 2. A mixture of $[Au_2\{S_2P(CH_2CH_2Ph)\}_2]$ **1** (0.100 g, 0.099 mmol) and I_2 (0.050 g, 0.198 mmol) was stirred in 20 mL of THF at −50 °C under a nitrogen atmosphere for 1 h. The purple solution obtained was filtered and dried under vacuum. The residue was washed with de-ionized water and again dried under vacuum to obtain $[AuI_2\{S_2P(CH_2CH_2Ph)_2\}]$ as a purple powder. Yield: 0.132 g (88%). Anal. Calcd for $C_{16}H_{18}AuI_2PS_2$: C, 25.41; H, 2.40. Found: C, 25.30; H, 2.23. mp: 133 °C (dec). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.30 (m, 8H, CH_2Ph), 3.07 (m, 8H, PCH_2), 7.20 (m, 20H, Ph). ^{31}P NMR (121.49 MHz, $CDCl_3$, δ, ppm): 97.4. Anal. Calcd for $C_{16}H_{18}AuI_2PS_2$: C, 25.41; H, 2.40. Found: C, 25.30; H, 2.23.

Reductive elimination of [$AuI_2\{S_2P(CH_2CH_2Ph)_2\}$], 2 by SnI_2. The reaction of [$AuI_2\{S_2P(CH_2CH_2Ph)_2\}$] **2** (0.147 g, 0.194 mmol) and SnI_2 (0.038 g, 0.101 mmol) was stirred in 20 mL of $CHCl_3$ at −50 °C under a nitrogen atmosphere. The purple solution rapidly turned red, and stirring of the resulting red solution was continued for 1 h. The reaction mixture was filtered and a dark-red precipitate was collected by filtration, washed with water and dried under vacuum to obtain SnI_4 as a dark-red powder. Yield: 0.058 g (95%). ^{119}Sn NMR (111.92 MHz, THF, δ, ppm): −1781.5. The filtrate, on the other hand, was evaporated to dryness under a vacuum to obtain a dark-yellow solid. The solid was washed with deionized water, then subjected to column chromatography (Al_2O_3) by using THF as an eluent to afford yellow solution. This was dried under vacuum to obtain **1** as a yellow powder. Yield: 0.074 g (76%). ^{31}P NMR (121.49 MHz, $CDCl_3$, δ, ppm): 77.7.

[$AuI_2\{Se_2P(CH_2CH_2Ph)_2\}$], 3. Compound **3** was synthesized in a fashion similar to **4** by utilizing K[$Se_2P\{(CH_2)_2Ph\}_2$] (0.041 g, 0.09 3 mmol). Yield: 0.061 g (76.7%). Anal. Calcd for $C_{16}H_{18}AuI_2PSe_2\cdot0.9C_4H_8O$: C, 25.73; H, 2.78. Found: C, 26.04; H, 2.36. mp: 138 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.62 (m, 4H, CH_2P), 3.12 (m, 4H, CH_2Ph), 7.28 (m, 10H, Ph), $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ, ppm): 42.9 ($J_{P\text{–}Se}$ = 377 Hz). ^{77}Se NMR (57.24 MHz, $CDCl_3$, δ, ppm): 25.28 (d, $J_{P\text{–}Se}$ = 377.3 Hz). IR [CsI, ν(Au–Se)]: 222 cm^{-1}.

[$AuI_2\{Se_2P(OEt)_2\}$], 4. Stirring of $NH_4[Se_2P(OEt)_2]$ (0.028 g, 0.094 mmol) and [AuCl(tht)] (0.030 g, 0.094 mmol) in THF (30 mL) at −50 °C under a nitrogen atmosphere for 3 h yielded a yellow solution of $[Au\{Se_2P(OEt)_2\}]_2$ and NH_4Cl. Iodine, I_2 (0.025 g, 0.098 mmol) was added and stirring continued for 30 min. After evaporation, the residue was extracted by CH_2Cl_2 (20 mL) and dried under vacuum to obtain a black purple powder. The resulting black purple powder was recrystallized from $CHCl_3$ at −20 °C. Yield: 0.059 g (86.7%). Anal. Calcd for $C_4H_{10}AuI_2O_2PSe_2\cdot4H_2O$: C, 5.99; H, 2.26. Found: C, 5.59; H, 2.04. mp: 185 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.51 (t, $^3J_{HH}$ = 7.1 Hz, 6H, OCH_2CH_3), 4.36 (m, 4H, OCH_2CH_3), $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ, ppm): 53.55 ($J_{P\text{–}Se}$ = 519.5 Hz); ^{77}Se NMR (57.24 MHz, $CDCl_3$, δ, ppm): 345.9 (d, $J_{P\text{–}Se}$ = 519.8 Hz). IR [CsI, ν(Au–Se)]: 222 cm^{-1}.

[$AuI_2\{Se_2P(O^iPr)_2\}$], 5. Compound **5** was synthesized in a similar fashion as **4** above by utilizing $NH_4[Se_2P(O^iPr)_2]$. Yield: 0.048 g (81.4%). Anal. Calcd for $C_6H_{14}AuI_2O_2PSe_2\cdot0.3C_4H_8O$: C, 11.09; H, 2.12. Found: C, 11.21; H, 2.49. mp: 172 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.47 (d, $^3J_{HH}$ = 6.3 Hz, 12H, $OCH(CH_3)_2$), 4.95 (m, 2H, $OCH(CH_3)_2$), $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ, ppm): 45.95 ($J_{P\text{–}Se}$ = 511.4 Hz); ^{77}Se NMR (57.24 MHz, $CDCl_3$, δ, ppm): 376.32 (d, $J_{P\text{–}Se}$ = 511.6 Hz) IR [CsI, ν(Au–Se)]: 222 cm^{-1}.

X-ray structure determination

Crystals were mounted on glass fibers with epoxy resin, and all geometric and intensity data were collected on a Bruker APEXII CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). Data reduction was carried out using the SAINT-Plus software.[21] An empirical absorption correction was applied using the SADABS program.[22] Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package,[23] incorporated in the *SHELXTL*/PC version 5.10.[24] Crystal data and selected bond lengths and angles for **1–5** are summarized in Tables 1–4.

Results and discussion

Synthesis

In this study, we focused on I_2 because as an oxidant it seems to reveal quite different reactivity trends in gold chemistry

Table 1 Crystallographic data for complexes **1–5**

	1	2	3	4	5
Formula	$C_{32}H_{36}Au_2P_2S_4$	$C_{16}H_{18}AuI_2PS_2$	$C_{16}H_{18}Au\ I_2PSe_2$	$C_4H_{10}AuI_2O_2PSe_2$	$C_{12}H_{28}Au_2I_4O_4P_2Se_4$
M_r	1004.72	756.16	849.96	729.78	1515.66
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a (Å)	9.6496(2)	13.013(3)	9.4588(8)	8.827(2)	8.7465(11)
b (Å)	12.8257(2)	9.3266(19)	11.8888(10)	8.851(3)	8.7967(11)
c (Å)	14.1389(3)	18.341(4)	18.7731(18)	18.150(5)	21.903(3)
α (°)	79.90°	90°	90.00	90.00	90.353(3)
β (°)	85.08°	107.03(3)°	102.103(4)	101.497(7)	100.611(3)
γ (°)	74.07°	90°	90.00	90.00	90.214(3)
V	1655.28(6)	2128.4(9)	2064.2(3)	1389.4(7)	1656.4(4)
Z	2	4	4	4	2
ρ_{calcd} (g cm^{-3})	2.016	2.360	2.735	3.489	3.039
μ (mm^{-1})	9.224	10.079	13.72	20.36	17.08
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)
Reflections collected	8034	7198	4143	2442	6381
Independent reflections [R_{int}]	6807 [R_{int} = 0.0336]	1879 [R_{int} = 0.0344]	3652 [R_{int} = 0.070]	1343 [R_{int} = 0.075]	4654 [R_{int} = 0.039]
Final R indices [$I > 2\sigma(I)$]^{a,b}	0.0243, 0.0514	0.0241. 0.0530	0.0424, 0.1168	0.0447 , 0.1033	0.0519 , 0.1383
R Indices (all data)	0.0334, 0.0545	0.0316, 0.0574	0.0489, 0.1207	0.1149, 0.1393	0.0768 , 0.1559
GooF	1.033	1.141	1.150	1.013	1.041
Largest diff. peak and hole (e Å^{-1})	1.118 and −0.677	0.752 and −1.580	2.809 and −3.148	1.430 and −1.749	1.765 and −1.875

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2 Selected bond distances (Å) and angles (°) for **1** and **2** with e.s.d.s. in parentheses

Complex **1**			
Au(1)–Au(1A)	3.2668(2)	P(1)–S(1)	2.023(1)
Au(1)–S(1)	2.292(1)	Au(1)–Au(2)	3.4558(2)
S(3)–Au(2)–S(4)	174.41		
Complex **2**			
Au(1)–I(1)	2.5997(7)		
Au(1)–S(1)	2.356(2)	S(1)–P(1)	2.051(2)
S(1)–P(1)–S(1A)	100.8(1)	I(1)–Au(1)–S(1A)	175.44(4)

Table 3 Selected bond distances (Å) and angles (°) for complexes **3–4** with e.s.d.s. in parentheses

Complex **3**			
Au–I	2.6288(6)–2.6412(6)	Se–P	2.192(2)–2.201(2)
Au–Se	2.4483(8)–2.4523(8)	I–Au–I	94.65(2)
Se–Au–Se	84.99(3)	Se–P–Se	97.82(8)
Complex **4**			
Au–I	2.6063(18)–2.6069(16)	Se–P	2.165(5)–2.169(6)
Au–Se	2.449(2)–2.455(2)	I–Au–I	94.92(5)
Se–Au–Se	86.04(7)	Se–P–Se	101.0(2)

Table 4 Selected bond distances (Å) and angles (°) for complexes **5** with e.s.d.s. in parentheses

Au–I	2.6017(13)–2.6097(14)	Se–P	2.171(5)–2.181(4)
Au–Se	2.4326(18)–2.4604(18)	I–Au–I	94.28(4)–94.75(5)
Se–Au–Se	85.85(6)–85.91(5)	Se–P–Se	99.96(17)–100.06(16)

when compared to Cl_2 and Br_2. This is demonstrated by the following three examples: (i) the addition of I_2 to iodogold(I) compounds is more strongly ligand-dependent when compared to Cl_2 and Br_2, suggesting that a crucial threshold in oxidation potential is operative and that both electronic and steric effects control the outcome of the reaction,[25] (ii) elemental gold powder undergoes oxidative dissolution with thioamide–I_2 adducts, where the S-donor to I_2 interaction is believed to play an important charge-separation role in explaining the dissolution mechanism,[26] (iii) the complex $[Au(CH_2)(S)PPh_2]_2$ (**B**), mentioned above, shows interesting OA properties with I_2, forming both a homovalent Au(II)–Au(II) and a heterovalent Au(I)–Au(III) dinuclear complex, isolated separately through a simple change in solvent polarity.[8] These processes are unique to the Au–I system.

A summary of the synthesis methodology used is outlined in Scheme 2. Complex **1** serves as an example for the preparation of other precursors to obtain complexes **2–5** and was obtained from the reaction between a solution of $NH_4[S_2P(CH_2CH_2Ph)_2]$ and [AuCl(tht)] (molar ratio 1 : 1) in 20 mL of THF. The mixture was stirred at −50 °C for 1 h under nitrogen. The solvent was evaporated under vacuum. The material was extracted into dichloromethane and filtered over anhydrous magnesium sulfate to remove NH_4Cl. The solvent of the filtrate was removed under reduced pressure, allowing complex **1** to be isolated as a yellow powder. At room temperature, the Au(III) complexes slowly decompose in solution: small amounts of **3–5** yield Au(0) metal and oxidized ligand (see below) before OA takes place; this problem is circumvented by performing the reaction at −50 °C.

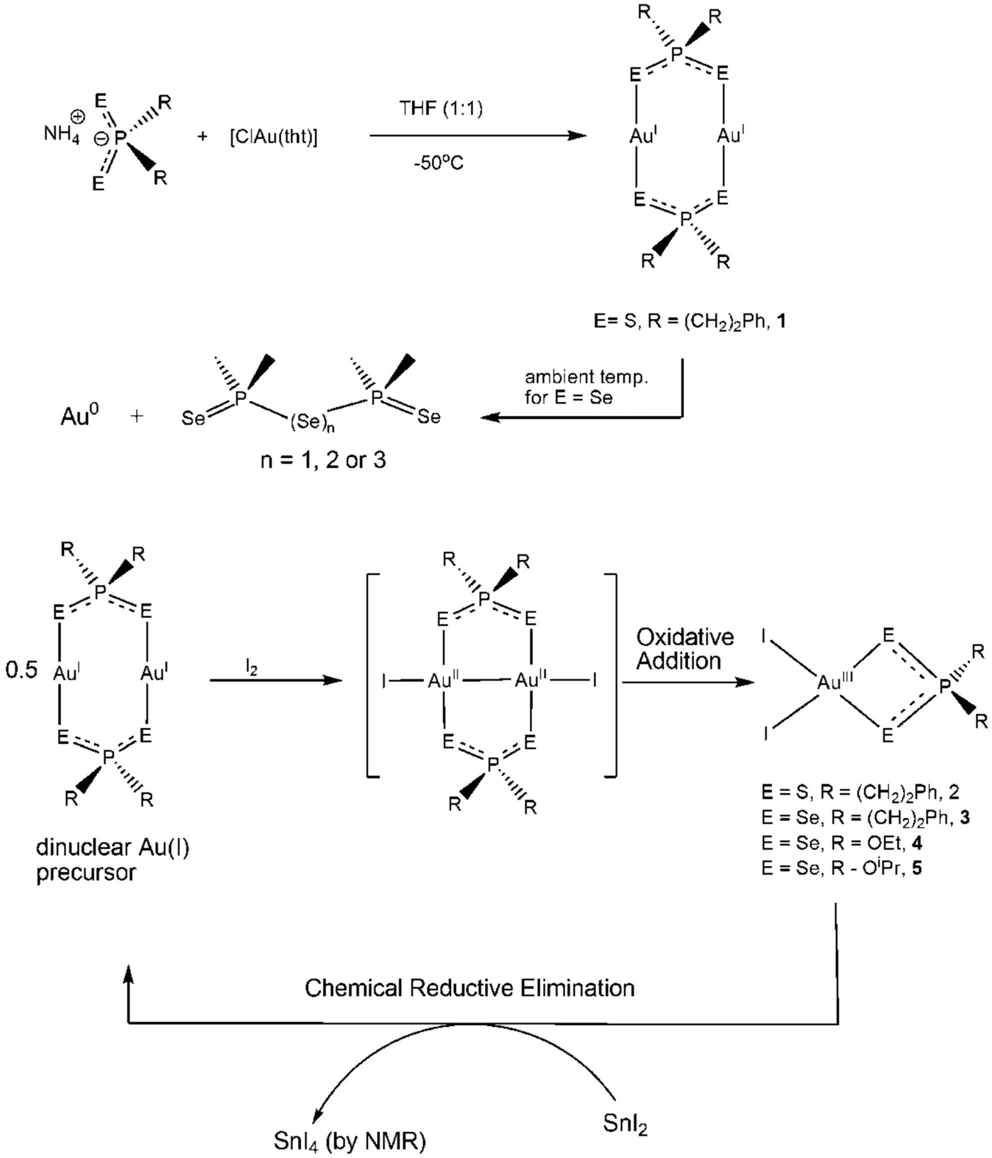
Complexes **2–5** were all prepared *in situ*, once the dinuclear gold(I) species formed in solution (tested by TLC), solid iodine was added (molar ratio 1 : 1 with respect to ammonium salt) and stirred for an additional 30 minutes. Complexes **1–5** were all isolated in high >75% yield.

NMR and IR spectroscopy

The complexes **1–5** were characterized by solution ^1H and ^{31}P NMR. A key question is whether any sign of an OA Au(II)–Au(II) complex could be observed. The OA reaction was monitored by ^{31}P NMR at −50 °C where only the starting dinuclear gold(I) precursor material and a Au(III) product was detected, see the next section. Warming the solution up to room temperature, another product was identified as the oxidized form of the ligand which is a thermosensitive compound, see Scheme 2. We propose that the oxidation is due to either the temperature effect or the slight excess of I_2 used. In our hands, no trace of Au(II) species was ever detected by NMR, let alone isolated. It should further be pointed out that the number of non-stoichiometric Se linkages between the P atoms of the oxidized ligand is dependent on the nature of the R group which was independently identified, as follows: $(RO)_2P(Se)–Se_n–(Se)P(OR)$ [n = 1 for R = CH_2CH_2Ph; n = 2 for R = ^iPr; n = 3 for R = Et].[27] The dinuclear Au(I) complex **1** showed a singlet peak at 77.7 ppm, the remaining mononuclear Au(III) complexes showed singlet peaks resonating at 97.4 (**2**), 42.9 (**3**), 53.55 (**4**) and 45.95 (**5**) ppm, respectively. Complex **2** was clearly shifted more downfield, presumably due to the dithio moiety *vs.* the diseleno moieties on **3–5**. The ^{77}Se NMR for **3–5** showed a far larger variation. The ^{77}Se NMR showed doublet peaks due to $J_{P–Se}$ coupling resonating at 25.28 ppm for the diselenophosphinate **3**, but significantly more downfield at 345.9 and 376.32 ppm for the diselenophosphates **4** and **5**, respectively. IR spectra of compounds **3–5** were recorded and displayed a ν(Au–Se) stretching vibration peak at 222 cm^{-1} for both **4** and **5**, respectively, a slight bathochromic shift, ~20 cm^{-1}, to their precursors.[18]

Proof of reversible chemical reductive elimination

The present study makes the substantial claim that the OA Au(III) products (**2–5**) are chemically reversible through a reductive elimination reaction with SnI_2 and we demonstrate that the original Au(I) starting material not only reforms, but the fate of the reductant has also been established. The reductive elimination of halogens from a metal centre is a process of interest and usually examined in the context of catalysis and sustainable energy. RE has unfavourable thermodynamics, and is typically driven by a trapping mechanism due to the fast kinetics of the OA reaction of halogens. A number of Au(III) thiolate complexes have been shown to undergo reversible reductive elimination–oxidative addition processes in solution



Scheme 2 Summary of synthesis methodology used and products formed in the present study.

via thermal and photochemical pathways.[28] A thermally triggered reductive elimination of bromine from Au(III) as a path to Au(I)-based coordination polymers was also achieved.[29] Thus, we reacted complex **2** with SnI_2 (molar ratio 2 : 1) in CH_3Cl at −50 °C under a nitrogen atmosphere and monitored the progress of the reaction over one hour by ^{31}P NMR, see Fig. 1.

The purple coloured solution turned red rapidly and yielded a precipitate. The reaction mixture was filtered and the deep-red precipitate was removed by filtration and confirmed to be SnI_4 whose ^{119}Sn NMR shift is at −1781.5 ppm,[30] in a yield of 95%.

The SnI_4 species confirms the fate of the SnI_2 reductant as the sole oxidized product. The filtrate was subsequently evaporated to dryness under a vacuum to obtain a dark-yellow solid. Following work-up, the yellow powder was isolated in a yield of 76%, and ^{31}P NMR at 77.7 ppm confirmed complex **1**. Cases of RE reactions from Au–Se systems are rare. More than 40 years ago, van der Linden and Nijssen reported on a series of gold(III) diselenocarbamates of the type $[Au\{Se_2CNEt_2\}_2]Br$ and $[AuBr_2\{Se_2CNEt_2\}]$.[31] The former was demonstrated to undergo reversible one-electron reduction while the latter did not isolate from the OA reaction of Au(I), unlike the case in the present study.

X-ray crystal structures

Complexes **1–5** were all characterized by single-crystal X-ray crystallography. Complex **1** is the only dinuclear complex, shown in Fig. 2. Complex **1** crystallized in the triclinic space group $P\bar{1}$. Selected bond lengths and angles are listed in Table 2 and a perspective view of **1** is shown in Fig. 2. X-ray analysis reveals that complex **1** consists of the commonly

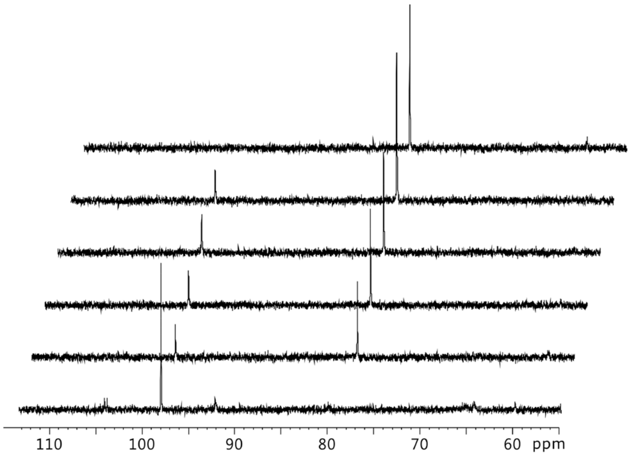


Fig. 1 The reaction between **2** and SnI_2 monitored by ^{31}P NMR spectroscopy at 0, 5, 10, 15, 30 and 60 min increments. At T = 0 min (bottom), only the Au(III) complex **2** is observed, whilst after 60 min (top), only the precursor complex **1** is observed.

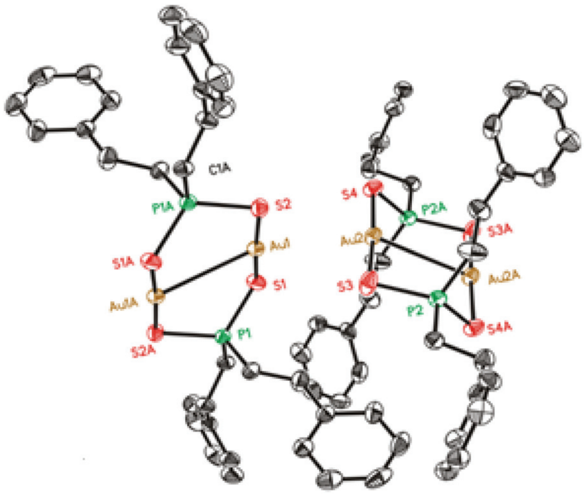


Fig. 2 Thermal ellipsoid drawing (30% probability) of **1**. Hydrogen atoms are omitted for clarity.

observed 8-membered gold(I) metallacycle in an elongated chair conformation. The complex shows an intramolecular Au···Au interaction at a distance of 3.2668(2) Å, as well as an intermolecular Au···Au interaction at a distance of 3.4558(2) Å. The gold centres are slightly distorted from linearity as shown by the S–Au–S bond angle of 174.4°. Complex **2** crystallized in the monoclinic space group *C*2/*c*. Selected bond lengths and angles are listed in Table 2 and a perspective view of **2** is shown in Fig. 3. X-ray analysis reveals that complex **2**, similar to **3–5**, consists of a 4-coordinate square planar geometry around the gold(III) center.

Complex **2** contains a chelating S–P–S ligand and two *cis* iodo ligands. Complexes **3–5** are the seleno analogues of the study and are structurally very similar. Complex **3** crystallized in the monoclinic space group $P2_1/n$. Selected bond lengths and angles are listed in Table 3 and a perspective view of **3** is shown in Fig. 4. Complex **3** showed the Au–I and Se–P bond lengths at 2.62 and 2.19 Å, respectively, while the Au–Se bond length is at 2.43 Å. The bond angles for I–Au–I, Se–Au–Se, and Se–P–Se are at 94.6, 84.9 and 97.8°, respectively. Complex **3** also revealed some intermolecular I···(Se and Se···(Se interactions at 3.779 and 3.511 Å, respectively, to form a 1D chain ((Fig. 5). Surprisingly these weak interactions do not exist in compounds 4 and 5.

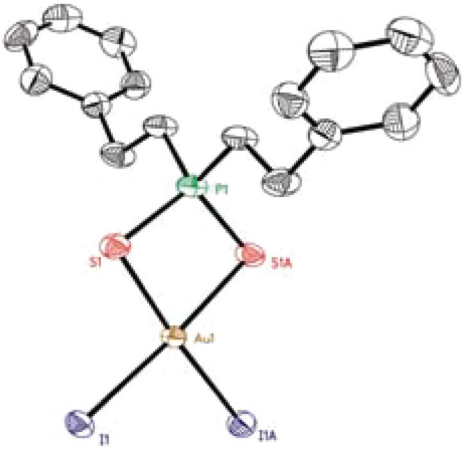


Fig. 3 Thermal ellipsoid drawing (30% probability) of **2**. Hydrogen atoms are omitted for clarity.

Complex **4** crystallizes in the monoclinic system in the space group $P2_1/c$, shown in Fig. 6. Complex **4** is clearly mononuclear with a slightly distorted square-planar geometry about the Au atom and has Au–I, Au–Se and Se–P bond lengths of 2.60, 2.44 and 2.16 Å, respectively. Significant bond angles include I–Au–I, Se–Au–Se, and Se–P–Se at 94.9, 86.0 and 101.0°, respectively, in all respects slightly larger than for **3**.

Complex **5** crystallizes in the triclinic system in space group $P\bar{1}$, as shown in Fig. 7. Complex **5** is virtually identical to **4** in terms of bond angles and lengths.

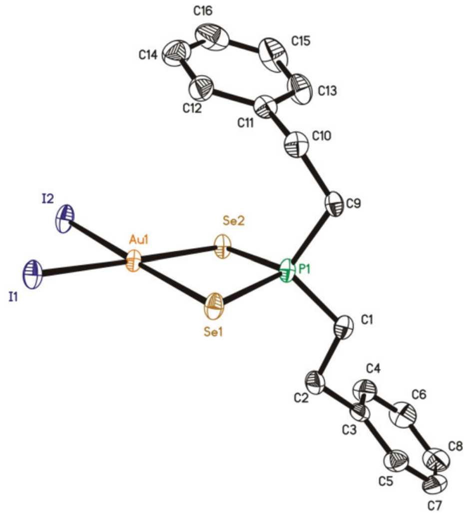


Fig. 4 Thermal ellipsoid drawing (30% probability) of **3**. Hydrogen atoms are omitted for clarity.

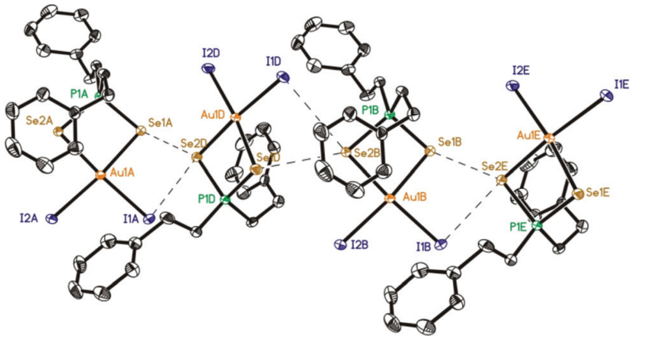


Fig. 5 Portion of crystal packing structure of complex **3** showing Se⋯(Se and Se⋯(I interactions.

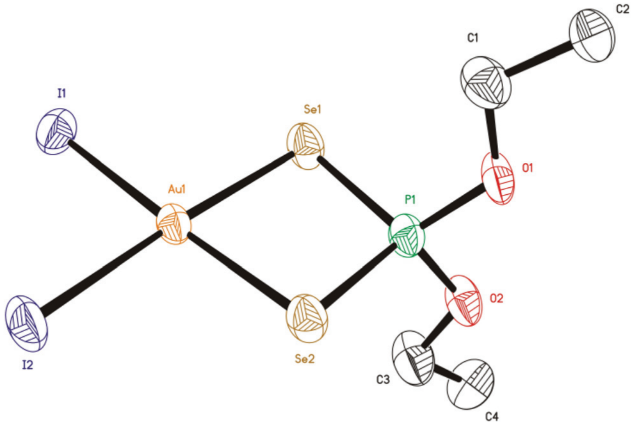


Fig. 6 Thermal ellipsoid drawing (30% probability) of **4**. Hydrogen atoms are omitted for clarity.

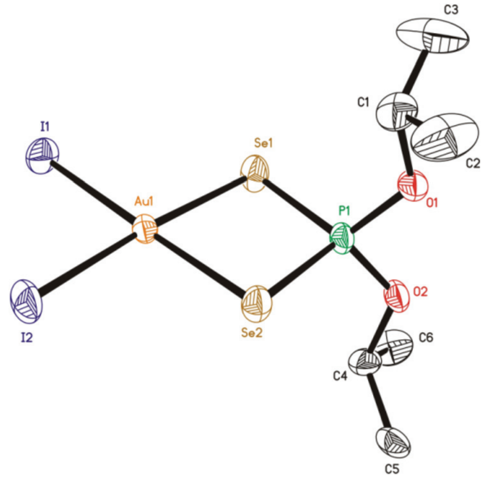


Fig. 7 Thermal ellipsoid drawing (30% probability) of **5**. Hydrogen atoms are omitted for clarity.

Conclusions

We report the first examples of dinuclear gold(I) complexes with a neutral Au_2E_4 (E = S, Se) manifold to induce any kind of OA reaction with iodine and forming a mononuclear gold(III) product. A novel series of complexes containing for the first time both a Se–P–Se chelating and iodo ligands across a Au(III) center are reported. The importance of these OA reactions is that they departed entirely from any related dinuclear gold(I) chemistry that has gone before through a simple change to E–P–E bridging ligands.

This result strongly favours the idea that the OA event is driven by the *electronic properties of the ligand* since there is no Au–Au bond or interaction to support stability in the final Au(III) product. The dinuclear units ruptured under mild conditions into stable and well defined Au(III) complexes in high yield. We further demonstrate that the process is reversible, and chemical (as opposed to thermal or photochemical) reductive elimination could be achieved using the reductant SnI_2.

We anticipate that more surprising results will continue in this system until such a time that OA pathways across dinuclear gold(I) centers can be given a sound and predictable theoretical footing.

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